

Adsorption of the Heavy Metal Ions onto Bio sorbents: A review

Ahmed M. Abu-Dief^{1,*} and Mallak Megalea Zikry²

¹Chemistry Department, Faculty of Science, Sohag University, 82534 Sohag, Egypt.

²Medicinal and Aromatic Plants Researches Department, Horticulture Research Institute (HRI), Agri. Res. Center (ARC), Giza, Egypt.

Received: 2 Jul. 2018, Revised: 18 Aug. 2018, Accepted: 23 Aug. 2018.

Published online: 1 Sep. 2018.

Abstract: Heavy metal pollution possess a great potential threat to the environment and has its own damaging effects to plants, animals and ultimately to human health, because of its release into the environment and water bodies results in a variety of illnesses related with the risk of dermal damage, respiratory problems and several kinds of cancer. The removal of heavy metals from aqueous solutions by using biomass to reduce the problem of limited and scarce water resources which is considered the most important obstacles at all that prevent the continued implementation of plans State's expansion, maximize benefit from the available water resources and reduce the growing gap between available water resources and the required water needs to maintain international water security and the health of the human. Thus, our study is to investigate the ability of natural bio sorbents for removing heavy metal aqueous solution.

Keywords: heavy metal, bio sorption, removal efficiency, aqueous solution, natural bio sorbents.

1 Introduction

Toxic heavy metals release into the environment such water bodies causes food contamination and so food safety for the human consumption is a serious worldwide public issue [1]. There is evidence that heavy metals present in the environment, even in low concentration, are responsible for producing a variety of illnesses related with the risk of dermal damage, respiratory problems and several kinds of cancer. [2] Owing to longer residence time and ability to form non-biodegradable compounds and its toxic effects, removal of heavy metal from contaminated sites is given priority to restore ecosystem functions and stability [3]. So treatment of waste water as an additional resource to reduce the problem of limited and scarce water resources by the addition of this resource to maximize benefit from the available water resources and reduce the growing gap between available water resources and the required water needs. Heavy metals can be removed from aqueous solutions by several non-effective methods such as ion exchange, chemical precipitation, adsorption and membrane separation [4]. Many studies were conducted to develop an effective, available and environmental-friendly methods for removal of heavy metals by using biosorbents, as microbial biomass, waste materials generated due to agricultural by-products such as: sugar cane bagasse fly ash and peat [5], rice husks and straws [6], soya bean, saw dust,

walnut and seeds hull, corn cobs and banana peels [7]. The feasibility of heavy metals ions removal from aqueous solution onto natural biosorbents such rice straw, rice bran, rice husk, hyacinthroots, neem leaves has been investigated [8]. Thus, our study aim to convert agricultural waste to useful, economic value biosorbents for the removal of heavy metal from aqueous solution which would be useful to the environment and to maximize benefit from waste water. As the cheaper biosorbent materials increasing the economic value of this plant under different initial metal ions concentration, pH, contact time, dosage, concentration and temperature.

2 Heavy Metal

The use of natural materials for heavy metals removal is becoming a concern in all countries. Heavy metals have been excessively released into the environment due to rapid industrialization and have created a major global concern. Heavy metal ions have great effects on all forms of life [9]. Heavy metals are presented in nature and industrial waste water, so the presence of heavy metals in surface and ground water pose a contamination problem. Large number of industries can produce and discharge wastes containing different heavy metals into the environment. The main source of heavy metal pollution are metal plating, mining, smelting, battery manufacturing, tanneries, petroleum refining and pigment manufacture. The term "heavy metal" is entirely applied to a group of metals (and metal-like elements) with density greater than 5 g/cm³, atomic number above 20 and is toxic or poisonous at low

* Corresponding author E-mail: ahmed_benzoic@yahoo.com

concentrations [10].

The main elements that considered as a heavy metals are chromium (Cr), manganese (Mn), cobalt (Co), copper (Cu), zinc (Zn), molybdenum (Mo), mercury (Hg), nickel (Ni), tin (Sn), lead (Pb), cadmium (Cd), antimony (Sb), etc. Three kinds of heavy metals are of concern, including toxic metals (such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn, etc.), precious metals (such as Pd, Pt, Ag, Au, Ru etc.) and radionuclides such as U, Th, Ra, Am, etc [11].

2.1 Chromium

There are two stable oxidation states of chromium found in the environment, Cr (III) and Cr (VI) which have contrasting toxicities, mobility and bioavailability. While Cr (III) is relatively innocuous and immobile, Cr (VI) moves readily through soils and aquatic environments and is a strong oxidizing agent capable of being absorbed through the skin. Trivalent chromium, Cr (III), is an essential element required for normal carbohydrate and lipid metabolism.

2.2 Lead

Lead is a heavy metal poison which forms complexes with Oxo-groups in enzymes to affect virtually all steps in the process of hemoglobin synthesis and porphyria metabolism [12]. Toxic levels of lead in human have been associated with encephalopathy, seizures and mental retardation [13].

2.3 Copper

Copper, one of the most widely used heavy metal, is mainly employed in, electrical, electroplating industries, and in larger amounts is extremely toxic to living organisms. The presence of copper (II) ions causes serious toxicological concerns, it is usually known to deposit in brain, skin, liver, pancreas and myocardium [14]. Copper usually occurs in nature as oxides and sulphides. Copper is an essential substance to human life. Copper is found in a variety of enzymes and is used for biological electron transport. Inhalation of copper produces symptoms similar to those of silicosis and allergic contact dermatitis. Copper normally occurs in drinking water from copper pipes, as well as from additives designed to control algal growth. Common oxidation states of copper include the less stable copper (I) state, Cu^+ , and the more stable copper (II) Cu^{2+} [15]. Environmental contamination due to copper is caused by mining, printed circuits, metallurgical, fiber production, pipe corrosion and metal plating industries [16] the other major industries discharging copper in their effluents are paper and pulp, petroleum refining and wood preserving. Agricultural sources such as fertilizers, fungicidal sprays and animal wastes also lead to water pollution due to copper. Copper may be found as a contaminant in food, especially shell fish, liver, mushrooms, nuts and chocolates.

Any packaging container using copper material may contaminate the product such as food, water and drink [17]. In some instances, exposure to copper has resulted in jaundice and enlarged liver. It is suspected to be responsible for one form of metal fume fever [18]. Containing is linked to an increase in lung cancer among exposed workers [19].

2.4 Cadmium

The most severe form of Cd toxicity in humans is "itai-itai", a disease characterized by excruciating pain in the bone [20, 21]. Other health implications of Cd in humans include kidney dysfunction, hepatic damage and hypertension [22]. However, it has been suggested that overall nutritional status (rather than mere Cd content of food) is a more critical factor in determining Cd exposure.

Emission, effluents and solid discharge from industries, vehicle exhaust and metals from smelting and mining, use of insecticides/pesticides, disposal of industrial and municipal wastes in agriculture, and excessive use of fertilizers are the most sources of contamination to water by heavy metals [23, 24, 25]. They cannot be destroyed biologically but are only transformed from one oxidation state or organic complex to another. Therefore, heavy metal pollution possess a great potential threat to the environment and human health, because of its release into the environment and water bodies results in food contamination and so food safety for human consumption is a serious worldwide public issue and is widely addressed, the entry of heavy metals in aquatic ecosystems is linked to the generation of various by products or wastes from metal refineries, battery and paint industries and mining of natural deposits [26, 27].

3 Adsorbents

Any material that has adsorptive properties, if adsorbent of a material that is not synthetically produced and has adsorptive properties in terms of chemical species of inorganic and organic origins the material is called natural adsorbent and can be used for the removal of heavy metals, such materials are Agricultural by product. Also biological materials (algae, fungi, microbial cultures, and aquatic plants) have been used as bio adsorbent in several studies [28]. Also many researchers studied the ability of natural bio sorbents to remove Cd^{2+} ions from aqueous solution. Bio sorption of cadmium ions by an agricultural waste product. Adsorbent materials derived from low-cost agricultural wastes can be used for the effective removal and recovery of heavy metal ions from wastewater streams. Intense research attention is now focused on cost effective, ecofriendly and easily available adsorbent particularly of biological origin natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive sorbents. However, the performance of a bio sorbent

depends on the characteristic properties of the biomass as well as the microenvironment of the target toxicant. The search for an appropriate and inexpensive biomass is a continuing process. The most effective and optimized utilization of a biomass demanded a detailed understanding of the binding mechanism [29, 30, 31]. The bio sorption process involves two phases as following: a solid phase (bio sorbent) and a liquid phase (solvent) which consist dissolved species to be sorbed (metal ions). There are numerous ways for the metal to be uptake by the cell due to the complex structure of microorganisms. Hence, the mechanism of bio sorption is a complicated process. Bio sorption mechanisms can be divided into two subdivisions by the dependence on the cells' metabolism, which are metabolism dependent and non-metabolism dependent. Bio sorption is considered to be a fast physical or chemical process. A significant number of bio sorption studies on the removal of heavy metal from aqueous solutions have been conducted worldwide. Nearly all of them have been directed towards optimizing bio sorption parameters to obtain the highest removal efficiency while the rest of them are concerned with the bio sorption mechanism. The bio sorption rate depends on the type of the process. According to literature, bio sorption can be divided into two main processes: adsorption of the ions on cell surface and bioaccumulation within the cell [32].

3.1 Advantages of Bio sorption Process

Overall, compared with the conventional heavy metal removal methods, the potential advantages of bio sorption process includes [33]:

- High selectivity in terms of removal and recovery of specific heavy metals.
- Ability to handle multiple heavy metals and mixed wastes.
- Use of naturally abundant renewable biomaterials that can be cheaply produced.
- Greatly improved recovery of bound heavy metals from the biomass.
- Operation over a wide range of physiochemical conditions including temperature, pH, and presence of other ions (including Ca (II) and Mg (II)).
- Greatly reduced volume of hazardous waste produced.
- High affinity, reducing residual metals to below 1 ppb in many cases.
- Relatively low capital investment and low operational cost.

3.2 Factors Effecting on Biosorption of Metals

Bio sorption depends on many factors that can effect on it. Some of these factors are related to the biomass and metal and the others are related to environmental conditions. The major factors that affect the bio sorption process are:

A- Characteristics of Biomass:

The nature of the biomass or derived product may be considered one of the important factors, including the nature of its application such as: freely-suspended cells, immobilized preparations, and living biofilms. Growth and nutrition on the biomass, and age can also influence bio sorption due to changes in cell size, wall composition, and extra cellular product formation.

B- Initial Metal Ion Concentration:

The initial concentration provides an important driving force to overcome all mass transfer resistance of metal between the aqueous and solid phases [42]. Increasing amount of metal adsorbed by the biomass will be increased with initial concentration of metals. Optimum percentage of metal removal can be taken at low initial metal concentration. Thus, the metal uptake increases with increase in initial concentration.

C- Temperature:

In contrast to bioaccumulation process, bio sorption efficiency remains unaffected within the range 20-35°C, although high temperatures, may increase bio sorption in some cases, but these high temperatures may cause permanent damage to microbial living cells and then decreasing metal uptake [34]. Adsorption reactions are generally exothermic and the adsorption increases with decreasing temperature. The maximum bio sorption capacity for Ni and Pb by *S. cerevisiae* was obtained at 25 °C and found to decrease as the temperature was increased to 40 °C [35].

D- Acidity:

pH seems to be the most important parameter in the bio sorption processes. Bio sorption is similar to an ion-exchange process, i.e. biomass can be considered as natural ion-exchange materials which mainly contain weakly acidic and basic groups. Therefore, pH of solution influences the nature of biomass binding sites and metal solubility; it affects the solution chemistry of the metals, the activity of the functional groups in the biomass and the competition of metallic ions. Competition between cations and protons for binding sites means that bio sorption of metals like Cu, Cd, Ni, Co and Zn is often reduced at low pH values [37, 38]. The metal uptake increases when pH increases from 3.0 to 5.0. Optimum value of pH is very important to get a

highest metal sorption, and this capacity will decrease with further increase in pH value.

E- The Surface Area to Volume Ratio:

It may be important for individual cells or particles, as well as the available surface area of immobilized biofilms. In addition, the biomass concentration may also affect bio sorption efficiency with a reduction in sorption per unit weight occurring with increasing biomass concentration [36].

F- Biomass Concentration:

Concentration of biomass in solution affects the specific uptake [39]. At a given equilibrium concentration, the biomass adsorbs more metal ions at low cell densities than at high densities [40]. So electrostatics interaction between the cells plays an important role in metal uptake. Lower biomass concentration, the specific uptake of metals is increased because an increase in bio sorbent concentration leads to interference between the bindings sites [41].

3.3 Thermodynamic and Kinetic Parameters for Bio sorption Process

The thermodynamic parameters, ΔH , ΔS , and ΔG , for the bio sorption process were calculated using the relationships (1) and (2).

$$\ln b = \Delta S^\circ/R - \Delta H^\circ/RT \quad (1)$$

Where, b (Langmuir constant related to energy). The plot of $\ln b$ versus $1/T$ yields a slope and intercept whose values correspond to $\Delta H/R$ and $\Delta S/R$, respectively. These values can then be used to compute ΔG by applying the Gibbs relationship:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2)$$

Calculation of metal uptake

The metal ions uptake at equilibrium was calculated by:

$$[q]_e = V(C_o - C_e)/W \quad (3)$$

where q_e in mg/g is metal ions absorption capacity, V in liters is the volume of the metal ions solution and W in gram is the amount of the bio sorbent, C_o and C_e in mg/L are initial and final (equilibrium) metal ion concentrations, respectively. The removal efficiency of the metal ions was also determined using:

$$R.E\% = ((C_o - C_e)/C_o) \times 100 \quad (4)$$

Where, $R.E\%$ is the percentage of metal ions removed.

Kinetics study analysis

The mechanism of the adsorption of Metal ions was tested using pseudo-first-order and pseudo-second-order kinetic models. Pseudo- first-order and pseudo-second order models are giving by Equations 5 and 6, respectively in a linear form.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

$$(t/q_t) = 1/(k_2 q_e^2) + (t/q_e) \quad (6)$$

Where, k_1 is the rate constant of pseudo, q_t is the metal ions solution uptake in mg/g at time t and q_e is the metal ions solution uptake in mg/g at equilibrium. A plot of $\ln(q_e - q_t)$ against t was made and q_e and k_1 values were obtained from the slope and intercept, respectively. k_2 is the rate constant of pseudo-second order. Plot of (t/q_t) against t gives $(1/k_2 q_e^2)$ as intercept from which k_2 can be obtained and $(1/q_e)$ as slope. Both models are tested for suitability using correlation coefficient, R^2 [30, 31].

4 Literature Survey on Removal of Heavy Metals by Bio sorbents

Vole sky (2001) et al., [43] revealed that the adsorption of metal ions from aqueous solution onto bio sorbent has been a subject of interest in chemistry, environmental sciences and other research area. It is maintained that heavy metal ligand adsorption onto biomass is a rather complex process affected by several factors. Mechanisms involved in the bio sorption process include chemisorption, complexation, adsorption-complexation on surface and pores, ion exchange, micro precipitation, heavy metal hydroxide condensation onto the bio surface, and surface adsorption.

Selatnia (2004) et al., [44] said that the most important parameters controlling heavy metal adsorption are metal ion type, metal concentration, pH of solution, bio sorbent dosage and contact time. The kinetics of heavy metals adsorption on bio sorbents is a significant factor in determining heavy metals retention in solid/solution environments, there is an observed relationship between the metal bio sorption and the magnitude of negative charge on the surface of the bio sorbent, which is related to the surface functional groups. Availability of negatively charged groups at the bio sorbent surface is necessary for the bio sorption of metals to proceed.

Ma (2004) et al., [45] indicated that the mechanism of bio sorption often involves chemical reaction between functional groups present on the bio sorbent surface and the metal ions. This involves, in most cases, formation of metal-organic complexes or cation exchange reactions due

to high cation exchange capacity of the bio sorbents.

Minamisawa (2004) et al., [46] investigated adsorption of Cd^{2+} and Pb^{2+} ions at pH 2- 6.7 onto the biomaterials chitosan, coffee, green tea, tea, yuzu, aloe, and Japanese coarse tea, and onto the inorganic adsorbents, activated carbon and zeolite. High adsorptive capabilities were observed for all of the biomaterials at pH 4 and 6.7. In the adsorption of Cd^{2+} ions, blend coffee, tea, green tea, and coarse tea have comparable loading capacities to activated carbon and zeolite. Although activated carbon, zeolite, and chitosan are utilized in a variety of fields such as wastewater treatment, chemical and metallurgical engineering, and analytical chemistry, these adsorbents are costly. On the other hand, processing of the test biomaterials was inexpensive, and all the biomaterials except for chitosan were able to adsorb large amounts of Cd^{2+} and Pb^{2+} ions after a convenient pretreatment of washing with water followed by drying. The high adsorption capability of the biomaterials prepared from plant materials is promising in the development of a novel, low-cost adsorbent. From these results, it is concluded that heavy metal removal using biomaterials would be an effective method for the economic treatment of wastewater. The proposed adsorption method was applied to the determination of amounts of Cd^{2+} and Pb^{2+} ions in water samples.

Park (2006) et al., [47] revealed that materials known as “natural adsorbents” have recently been successfully employed in metal adsorption processes. The term “natural adsorbent” is assigned to any material that is not synthetically produced and has adsorptive properties in terms of chemical species of inorganic and organic origins. Biosorption of heavy metals from aqueous solutions is a relatively new process that is proven very promising in the removal of contaminants from aqueous effluents.

Owoyokun, (2009) [48] showed that *Delonix regia* pod biosorbent proved to be a very effective biosorbent in the removal of MB dye from wastewaters depending on the

Results of the equilibrium, kinetic and thermodynamic studies of the bio sorption of MB dye solutions on *Delonix regia* (flamboyant tree) pod bio sorbent. Bio sorption of MB dye solutions was, to a large extent, dependent on initial concentration, bio sorbent dosage, pH and temperature. Bio sorption of MB dye solutions obeyed Langmuir and Freundlich isotherms. RL value from Langmuir and n from Freundlich isotherms shows that bio sorption of MB dye solutions on *Delonix regia* is favorable, thermodynamic studies confirmed that the bio sorption process was exothermic and spontaneous at room temperature and near room temperature. Kinetic studies carried out revealed that the kinetic data tended to fit well in second order kinetics, confirming the chemisorption of dye solutions on *Delonix regia*. **Ramakrishnan (2009) et al.**, [49] found out that flamboyant tree pod can sorb Hg^{2+} ions from water and adsorption process follows the pseudo-second kinetic model and the equilibrium data fitted well to both Freundlich and Redlich-Peterson isotherm model.

Chakravarty (2010) et al., [50] investigated the bio sorption of Metal ions on bael leaves (*Aegle marmelos*) for the removal of Metal ions from aqueous solution using different doses of adsorbent, initial pH, and contact time. The maximum Pb loading capacity of the bael leaves was at pH 5.1. SEM and FTIR studies indicated that the adsorption of Metal ions occurs inside the wall of the hollow tubes present in the bael leaves and carboxylic acid, thioester and sulphonamide groups are involved in the process. The sorption process was best described by pseudo second order kinetics. Among Freundlich and Langmuir isotherms, the latter had a better fit with the experimental data (cf. Fig1).

Jimoh (2012) et al., [51] showed that the metal adsorption for Cu^{2+} , Pb^{2+} and Co^{2+} ions onto *Delonix regia* is critically linked with pH, the role of hydrogen ion was investigated at different pH. The amount of metal ions

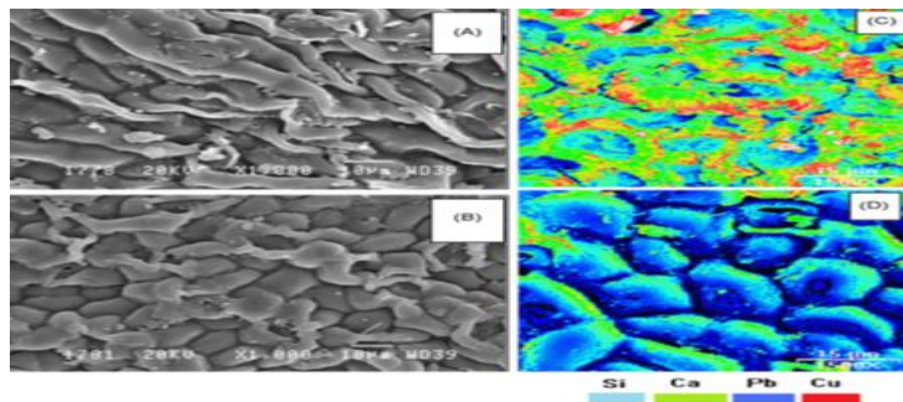


Fig. 1: SEM and metal mapping images of native bael leaves (A and C) and Pb(II) loaded bael leaves (B and D).

removed by the substrate at low pH of 1, 2, and 3 were low compared to pH of 4 and 5. This may be due to increase in competition between the hydrogen ion and the metal ions, because at this pH value, the concentration of hydrogen ion is high. As such hydrogen ions were being removed by the substrate, instead of the metal ions. It would be plausible to suggest that at lower pH value, the surface of the adsorbent is surrounded by hydroxonium ions (H_3O^+), thereby preventing the metal ions from approaching the binding sites of the sorbent. This means that at higher H^+ concentration, the bio sorbent surface becomes more positively charged such that the attraction between biomass and metal action is reduced. As the pH increases from 4 to 6, more negatively adsorption sites became available thus facilitates increase in amount of metal ions sorbed. Maximum occurred at pH 5. The plausible reason for the better adsorption observed at pH 5 and pH 6 may be attributed to the larger number of H^+ ions present, which in turn neutralize the negatively charged adsorbent surface, thereby reducing hindrance to the diffusion of organics at higher pH (cf. Fig.2).

Lim (2014) et al., [54] studied the ability of Calcareous skeletons in removing Cd^{2+} and Metal ions from aqueous solutions. The factors affecting adsorption were evaluated with respect to adsorbent size, contact time, adsorbent dosage, pH, and initial concentration to determine the optimum conditions for Cd^{2+} and Metal ions removal. The optimum dosage for removal of Cd^{2+} and Metal ions were 20 and 10 g/L, respectively. The pH of both metal solutions had shifted from acidic to alkali condition after equilibrating with the adsorbent. The adsorption capacity of CS appeared to be higher when the initial metal concentrations increased above 1 mg/L. This investigation has proved that CS has a great potential for removing metal contamination in acidic water.

Hossain (2015) et al., [2] studied that the shell dust of the

snail *L. luteola* (LSD), a waste biomaterial, as a low cost and environment friendly bio sorbent for cadmium removal from aqueous solution the maximum bio sorption capacity of LSD is 18.55 mg g^{-1} . The main functional group responsible for chelation are OH, C=O, C=C and C-C, as supported by FTIR analysis. The isotherm model follows Langmuir model ($R^2= 0.996$) better than Freundlich model ($R^2= 0.969$). The biosorption process conformed to the pseudo second order ($R^2= 0.999$) kinetics better than the pseudo first order ($R^2= 0.833$) kinetics.

Feizi (2015) et al., [24] indicated that the residues of sunflower, potato, canola, and walnut shell were used as sorbents to sorb heavy metals (Fe, Mn, Zn, Ni, Cu, and Cd) from aqueous solutions using batch experiments. The effect of pH and contact time was investigated. The plant residues showed considerable capacity for removal of Fe, Mn, Zn, Cu, and Cd from aqueous solution but Ni sorption by residues was negligible. Chemical activation of sorbents with NaOH enhanced Ni sorption. The sorption kinetic of heavy metals was described well by pseudo second order model, the sorption mechanisms such as electrostatic attraction and ion exchange as well as complexation seems to be the most occurring phenomena.

Shahanaz Begum (2015) et al., [55] indicated that the removal of heavy metals cadmium, chromium and lead from water has been taken up by batch adsorption techniques using *Mirabilis Jalapa* leaves powder as bio sorbent. Effect of pH, biomass dose and contact time highly affects the overall Cd^{2+} , Cr^{6+} and Pb^{2+} uptake of bio sorbent. The sorption was pH dependent and the percentage removal of Cd^{2+} , Cr^{6+} and Pb^{2+} was increased with increasing adsorbate solution pH. Maximum removal found to be at pH 6.0 for Cd^{2+} , 5.5 for Cr^{6+} and 4.5 for Pb^{2+} . The optimum time was observed to be 2 hours with optimum dosage 100 mg, results show that Freundlich isotherm models fit for the adsorption equilibrium data in the examined concentration

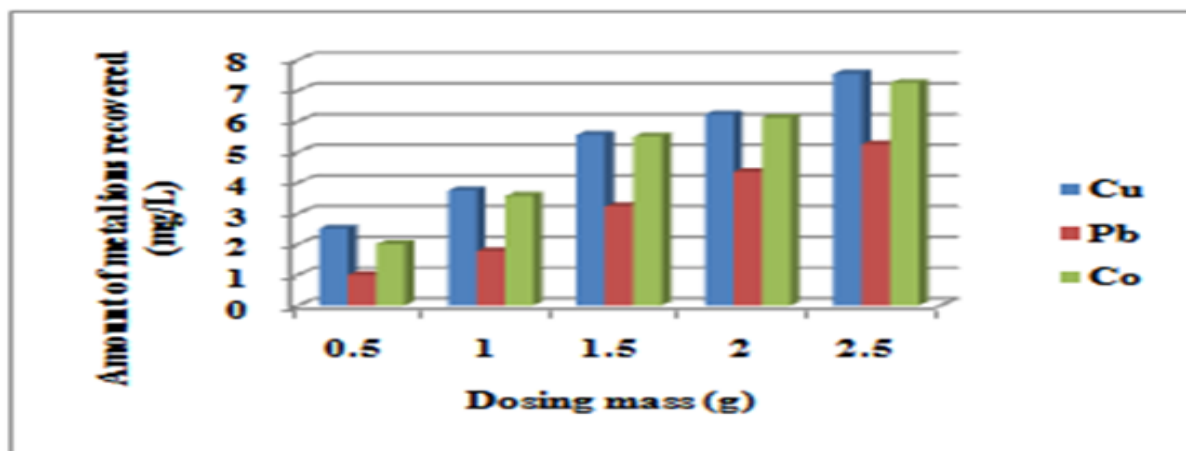


Fig.2: Effect of dosage on sorption of Co(II), Pb(II), and Cu(II) ions by *Delonix regia* flower.

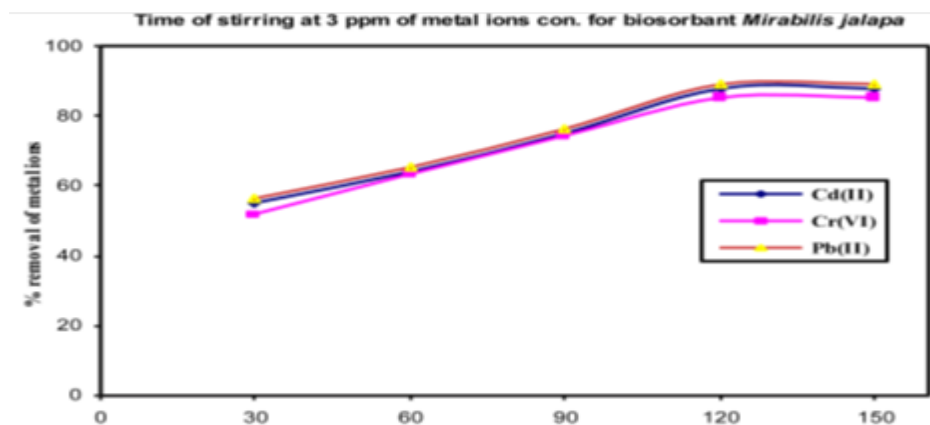


Fig.3: Adsorption of cadmium (II), chromium (VI) & lead (II) on biosorbent *Mirabilis jalapa* with various dosages.

range of (1 - 6 $\mu\text{g}/\text{mL}$). The selected *Mirabilis Jalapa* leaves powder was an effective, novel and eco-friendly bio sorbent for the removal of Cd^{2+} , Cr^{6+} and Pb^{2+} ions (cf. Fig.3).

Xu (2016) et al., [29] exhibited the recycling of agriculture wastes of ramie stalk as bio adsorbents for Cd^{2+} ions removal. Based on our experimental results, it is realized that Cd^{2+} adsorption to ramie stalk is highly pH sensitive, indicating the adsorption is driven by surface complexation reaction. The high adsorption capacity of ramie stalk toward Cd^{2+} ($q_m = 10.33 \text{ mg g}^{-1}$, $0.09 \text{ mol-Cd g}^{-1}$), which corresponds to around 21.95% of active adsorption sites available of ramie stalk, is believed to be closely related to its high cellulose and lignin content. The inhomogeneous surface of ramie stalk due to the high cellulose and lignin content also accounts for the observation that the adsorption kinetic is described well by the pseudo second order kinetic model. Results from thermodynamic studies suggest that the adsorption process is endothermic and spontaneous. All these properties demonstrate the potential of ramie stalk as a low cost bio adsorbent for the application of heavy metal removal.

Abdolali (2016) et al., [56] showed that bio sorbent namely multi-metal binding bio sorbent (MMBB) made from a combination of tea wastes, maple leaves and mandarin peels, was prepared to evaluate their bio sorptive potential for removal of Cd^{2+} , Cu^{2+} , Pb^{2+} , Zn^{2+} ions from multi-metal aqueous solutions. FTIR and SEM were conducted, before and after bio sorption, to explore the intensity and position of the available functional groups and changes in adsorbent surface morphology. Carboxylic, hydroxyl and amine groups were found to be the principal functional groups for the sorption of metals. Pseudo-first and pseudo second-order models represented the kinetic experimental data in different initial metal concentrations very well. Among two-parameter adsorption isotherm models, the Langmuir equation gave a better fit of the

equilibrium data. The calculated thermodynamic parameters indicated feasible, spontaneous and exothermic bio sorption process. Overall, this novel MMBB can effectively be utilized as an adsorbent to remove heavy metal ions from aqueous solutions.

Abdel-Rahman (2016b) et al., [31] studied The removing of toxic heavy metal from aqueous solution by agricultural bio sorbents by studying the effect of nano sized (Delonix regia) and chemically modified bio sorbent citric acid Delonix regia (CADR) for removing the Pb^{2+} ions. TEM, XRD and EDS, FT-IR, SEM methods were used for characterizing the bio sorbent (Delonix regia). The effect of contact time, pH, temperature, dosage of bio sorbent, and Pb^{2+} ion concentration on adsorption process were studied. The maximum bio sorption capacities (q_m) of Pb^{2+} by Delonix regia bio sorbent was 43.62 mg/g . The highest R.E was (93.5%) at pH 5. FT-IR method showed that the adsorption of metal ions occurs by functional groups on the surface of Delonix regia powder. The biosorption process was endothermic from thermodynamic parameters. The pseudo second-order model more fit ($R^2=0.999$) than the pseudo first-order model ($R^2 = 0.985$) from studying the kinetic parameters, The experimental data fit with Freundlich isotherm (R^2 close to 1). These results indicated that Delonix regia is available agricultural, low cost, environment friendly bio sorbent for removing the Pb^{2+} ions (cf. Fig.4).

4.1 Literature Survey on Removal of Heavy Metals by *Moringa Oleifera* and *Delonix Regia*

Montgomery, (2001) [57] observed that the active sites hypothesized to be responsible for the adsorptive capability of *Moringa oleifera* contain functional groups such as hydroxyl, carboxyl, amines, phenolic, methoxyl, hydroxyl-aliphatic groups. The plant is generally chemically composed of a large protein molecule with a molecular

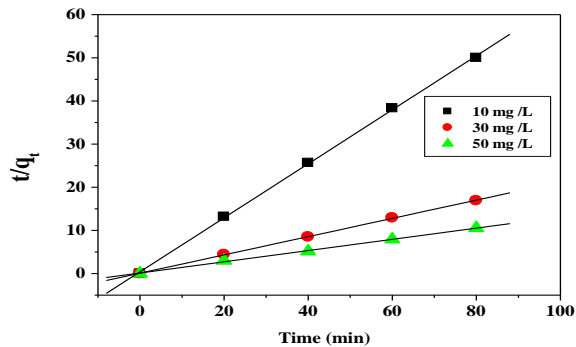


Fig.4: Pseudo-second order for sorption of Pb^{2+} ions by *Delonix regia* pod.

mass of 6.5 kDa. The protein occurs in large concentrations in the seeds, leaves, stem and bark. Further research, detailed indeed to answer specific chemistry questions on the adsorption behavior and nature (coagulation and flocculation properties) would be required to assign specific molecules to specific compositional function.

Reddy (2010a) et al. [58] investigated the removal efficiency of the bark of *Moringa oleifera* for Pb^{2+} from aqueous systems. It was revealed that the bark is endowed with hydroxyl and/or carboxyl functional groups as the Metal ions were observed to be chelated with these ions (cf. Fig. 5)

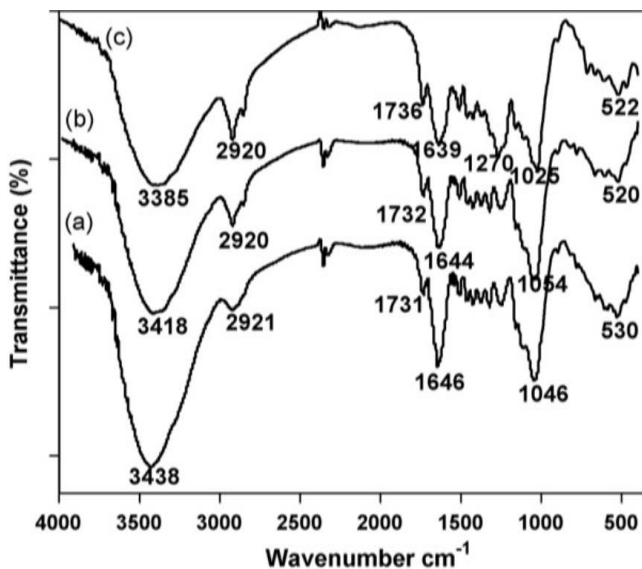


Fig.5: FTIR spectra of *Moringa oleifera*.

Meneghel (2013) et al. [59] indicated that the efficacy of using the byproduct of *Moringa oleifera* Lam. seeds as an adsorbent for removal of cadmium (Cd) from contaminated water. The effects of the adsorbent mass, solution pH, contact time, and temperature were evaluated. In the

preliminary studies, the mass of adsorbent (200–1200 mg) and pH conditions (5.0, 6.0, and 7.0) were varied. The time studies were performed at 20–180 min and the temperature studies at the range of 25–65 °C. The isotherms of adsorption were linearized according to Langmuir, Freundlich, and Dubinin–Radushkevich (D-R) models. The results showed better fit by the Freundlich and D-R models for Cd adsorption, describing a multilayer adsorption and, the maximum capacity of adsorption (q_m) obtained was 7.864 mg g⁻¹. Based on these results, it was concluded that the bio sorbent was effective in remediation of solutions containing Cd and thus the use of this alternative material is a viable option, since it has low cost and it is a byproduct which has not undergone previous treatment.

Meneghel (2014) et al. [60] studied the efficiency of *Moringa (Moringa oleifera* Lam.) seeds for removing lead ions Pb^{2+} from water was evaluated. Parameters such as solution pH, adsorbent mass, contact time between solution and adsorbent, isotherms, thermodynamic, kinetics, and desorption were evaluated. The maximum adsorption capacity of the biosorbent was found to be 12.24 mg g⁻¹, it has been concluded that *Moringa (Moringa oleifera* Lam.) seeds can be considered very effective and feasible for remediating Pb^{2+} contaminated solutions, since this material is itself an untreated and low-cost byproduct.

Ali (2015) et al., [4] used the *Moringa oleifera* leaves (bio sorbent) for Cd^{2+} ions removal from water as a natural alternative for synthetic sorbents. Synthetic water was used to find optimum conditions for water treatment using bio sorbent. The effect of biosorbent dosage and particle size, contact time, and pH effect were studied. Atomic Absorption Spectroscopy (AAS) was used to monitor the Cd^{2+} ions concentration before and after treatment with bio sorbent. Fourier Transform Infrared Spectroscopy (FTIR) was used to monitor bio sorbent structure changes before and after loading with Cd^{2+} ions. Many parameters were studied such as: dosage of bio sorbent (1–10 g/L), contact time (2–20 min), particle size, pH range, and Cd^{2+} ions concentrations. FTIR result showed changes in the finger print area of bio sorbent functional groups due to adsorption of Cd^{2+} ions. As a conclusion, *Moringa oleifera* leaves can be used as an effective, low cost, and environmentally friendly bio sorbent for the removal of Cd (II) from water.

Jimoh (2012) et al., [50] studied that the bio sorption process was pH, Contact time, dosage and metal ion concentration dependent. Contact time of adsorption was found to occur at 60 minutes for all three metal ions. Pseudo-First and Second order kinetic model can be used to describe the binding of Cu ions to *Delonix regia* flower. However, pseudo-first order can be used to describe the kinetics for the bio sorption of Pb and Co ions.

Removal of metal ions from their solutions in the presence of agricultural materials may be due to the adsorption on surface and pores, and also to complexation by these materials.

Ajisha (2015) et al., [61] showed that the pyrolyzed *Delonix regia* pod carbon for the removal of excess fluoride ions from the water that harm the human and the environment was studied. The adsorbent was characterized both physically and chemically. Surface chemistry characterization was done with pH-drift method. Batch adsorption studies were carried out for the effect of pH, dosage, contact time, initial fluoride concentration and temperature.

Equilibrium data were studied using Freundlich, Langmuir models, in which Freundlich isotherm was considered to be the best fit for the adsorbent. The sorption nature was studied using thermodynamic parameters which showed spontaneous, irreversible, stable and endothermic. The adsorption kinetics follows pseudo-second order.

Ali et al., (2016) [25] indicated that decrease in peanut hulls particle size increases the metal uptake. It is apparent that the greater accessibility to pores and a greater surface area are increased by decreasing the peanut hulls particle size. The number of diffusion paths is increased as a result of opened cracks and channels on the particle surface, and therefore the ability to penetrate the internal pore of peanut hulls structures is very high and the number of sorption sites for sorbent-solute interaction is increased, thereby resulting in increasing % Cu^{2+} ions removal from the solutions.

Kariuki et al., (2017) [62]. Studied that the potential of rogers mushroom (*Lepiota hystrix*) biomass in bio sorption of copper and lead from aqueous solutions. The efficiency of bio sorption was tested in batch experiments and the metal ion concentration analyzed using flame atomic absorption spectrometry. The analysis of FTIR spectrum reveals that the metal ions uptake by roger mushroom involves interaction of metal ion and hydroxyl, carboxyl and carbonyl groups of the biomass at optimum pH of 4.5–6.0 and sorbent mass of 1.5–2.1 g for Cu and Pb, respectively. Adsorption capacities were found to be 3.9 and 8.9 mg/g at a contact time of 25–40 min and initial metal ion concentration of 300–500 $\mu\text{g/g}$ for Pb and Cu, respectively. The biosorption process follows second order kinetics and fitted the Langmuir isotherm model. The result shows that rogers mushroom biomass has a good potential to be used in removal of metal ions and can be used up to three adsorption/desorption cycles without losing efficiency. Its use in real life situation can alleviate pollution and increase the quality of water for human consumption and sanitary purposes.

Aman et al., (2018) [63] used Rose flowers for the

extraction of essential oil or rose water. The vast majority of the leftover biomass is generally wasted. The aim of the present study was to analyse the rose flower biomass as a potential bio sorbent for metals chromium (III), mercury(II) and zinc(II), to remove them from industrial effluents. A number of variables were analysed, including untreated, acid-treated and base-treated biomass, biomass dosage, metal ion concentration, contact time, and pH. Increase in biomass dosage and metal ion concentration increased biosorption. The pH proved to be a very important factor and all the metals showed high adsorption at slightly acidic to moderately basic pH 6–10. They showed very low uptake at low pH. Contact time had little effect on the adsorption capacity of zinc, but was very crucial in the case of mercury. Base treatment favoured adsorption of mercury and zinc. The adsorption of Cr^{3+} , Hg^{2+} and Zn^{2+} on rose biomass can be explained by Langmuir and Freundlich isotherms equally well, and the adsorption process followed pseudo second order kinetics.

5 Adsorption of Heavy Metals by the Chemically Modified Bio sorbents

Treating biomass with a base like NaOH and a subsequent citric acid modification stabilizes the biomass due to insertion and crosslinking of carboxyl groups and thus increases its cation uptake ability [64].

Reddy (2010b) et al., [65] studied the *Moringa oleifera* leaves (MOL); an agro-waste material as a precursor to prepare a new biosorbent. The leaves were washed with base and citric acid, and obtained new chemically modified MOL bio sorbent (CAMOL) for sequestration of Metal ions from aqueous solution. The effect of experimental parameters such as pH, dose, initial concentration, contact time and temperature on the bio sorption was studied. The kinetic data were analyzed using three adsorption kinetic models: the pseudo-first and second-order kinetics and intra particle diffusion. The equilibrium data were analyzed using Langmuir, Freundlich, Dubinin–Radushkevick and Temkin isotherm models. The thermodynamic properties ΔG° , ΔH° and ΔS° showed that bio sorption of Metal ions onto CAMOL was spontaneous, endothermic and feasible in the temperature range of 293–313K. Investigations carried out proved that CAMOL is a bio sorbent with good potential for removal of lead from the aqueous medi (cf. Fig. 7).

Reddy (2012) et al., [66] indicated that action exchange bio sorbent was developed by chemically modifying the *Moringa oleifera* leaves powder by esterifying with NaOH followed by citric acid treatment. The modified bio sorbent was used for the removal of Cd^{2+} , Cu^{2+} and Ni^{2+} ions from aqueous solution. Different operational parameters such as the effect of pH, biomass dose, equilibrium time and temperature and initial metal ion concentrations were studied. Experimental data were analyzed by kinetic

parameters and found that bio sorption of three metal ions followed pseudo-second-order. Equilibrium data were analyzed using the Langmuir, Freundlich, isotherm models. The thermo dynamic properties, ΔG° , ΔH° and ΔS° showed that bio sorption of Cd^{2+} , Cu^{2+} and Ni^{2+} ions onto CAMOL were spontaneous, endothermic and feasible in the temperature range of 293-313K (cf. Fig. 6).

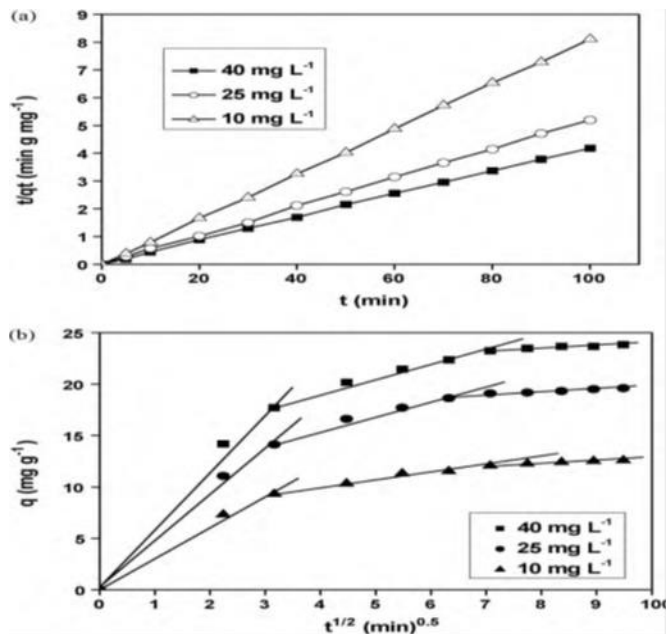


Fig.6: (a) Pseudo-second-order plots for the bio sorption of Pb(II) onto CAMOL. (b) Weber and Morris plots for the bio sorption of Pb(II) onto CAMOL.

Singha(2015) et al., [67] showed that the agricultural waste biomass has recently gained attention in the field of

Waste water remediation because of their abundance and renewable nature. In the present study, agricultural waste cellulosic biomass has been modified through succinylation

reaction and subsequently used as an adsorbent for the removal of Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} toxic metal ions from aqueous solution. The removal of metal ions from aqueous solution was investigated as a function of pH, contact time, temperature and metal ion concentration. Pseudo-second-order kinetic model was used to study adsorption kinetics for all metal ions. The thermodynamic parameters ΔH° and ΔG° values for metals ion adsorption on the succinylated okra biomass adsorbent showed the process to be spontaneous and exothermic in nature.

Salazar-Rabago (2016) et al.,[68] showed that the natural sawdust from white pine (*Pinusdurangensis*) was chemically modified by a hydro-thermal procedure using citric, malonic and tartaric acids. The adsorption capacity of modified sawdust towards Pb^{2+} ions was considerably enhanced due to the introduction of carboxylic groups on the surface of modified sawdust during the modification, and the adsorption capacity was almost linearly dependent on the concentration of carboxylic sites. The natural sawdust surface was acidic, and the MS surface became more acidic after the modification. At T 25 oC and pH 5, the maximum adsorption capacity of the optimal MS towards Pb^{2+} is high compared to natural sawdust and other modified sawdust reported previously. The adsorption capacity of modified sawdust was considerably reduced by decreasing the solution pH from 5 to 3 due to electrostatic interactions. The adsorption of Metal ions on the modified sawdust was mainly due to ion exchange at pH 3 and to both ion exchange and electrostatic attraction at pH 5.

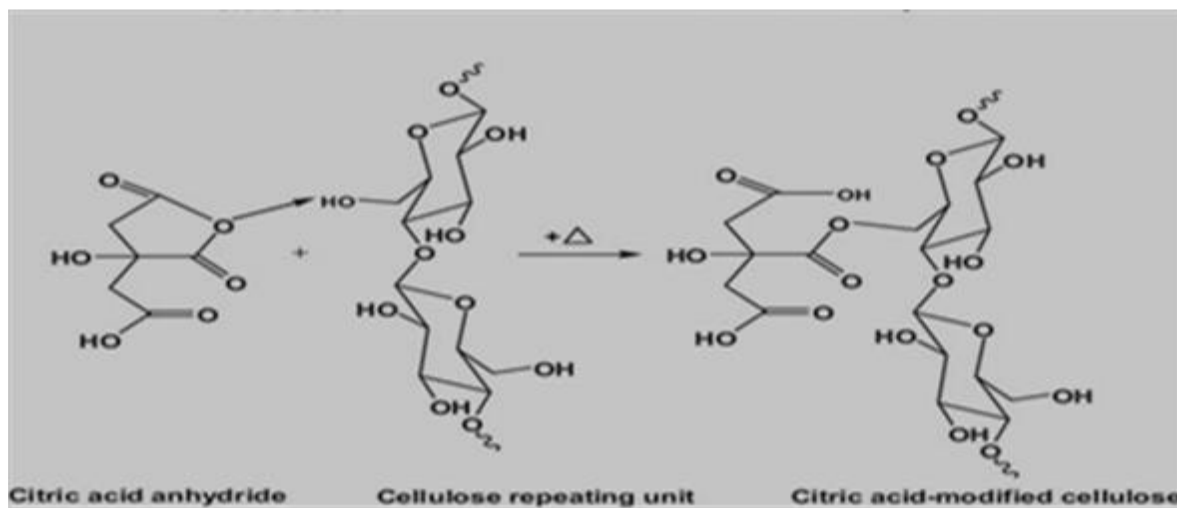


Fig.7: Proposed reaction between citric acid and the cellulose in MOL to produce citric acid-modified MOL.

List of abbreviations

C _e	Equilibrium concentration of the adsorbate (mg/L)
C _i	Initial concentration of the adsorbate (mg/L)
C _t	Equilibrium concentration of the adsorbate at time t (mg/L)
FTIR	Fourier transform infrared
DR	<i>Delonix regia</i>
CA	citric acid
CADR	<i>Delonix regia</i> treated with citric acid
Pb – DR	Lead - <i>Delonix regia</i> complex
Pb-CADR	Lead - <i>Delonix regia</i> treated with citric acid complex
MO	<i>Moringa oleifera</i>
Pb – M.O	Lead - <i>Moringa oleifera</i> complex
Pb-CAMO	Lead - <i>Moringa oleifera</i> treated with Citric acid complex
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
XRD	X–ray diffraction
EDAX	Energy disperse analysis X-ray
V (L)	Volume of solution used in the adsorption experiment in litre
w	Dry weight of adsorbent (g)
T	the absolute temperature (K)
R	the gas constants ($8.314 \times 10^{-3} \text{kJ mol}^{-1} \text{K}^{-1}$)

6 Conclusions

In the current contribution, the sources of heavy metal ions as a toxic materials as well as the reason why they need to be removed from our environment have reviewed. Conventional methods of removal are expensive; hence the search of using low cost, friendly ecosystem material must be needed. From the above literature study, it is observed that biosorption is the most economical and eco-friendly method for removal of heavy metal from domestic as well as industrial wastewater. It is being an alternative to conventional methods for the removal of toxic heavy metals from industrial effluents. It offers several advantages including cost effectiveness, high efficiency, minimization of chemical/biological sludge, and regeneration of biosorbent with possibility of metal recovery. The process of biosorption has many attractive features including removal of metals over quit broad range of pH and temperature, its rapid kinetics of adsorption and desorption and low capital and operation cost.

References

- [1] Pourgheysari, H.; Moazeni, M.; Ebrahimi, A. (2012) Heavy metal content in edible salts in Isfahan and estimation of their daily intake via salt consumption, *Int. J. Environ. Health. Eng.*, **1**, 8(2012).
- [2] Hossein F.; Ensiyeh T.; Afshin E.; Ali F.; Marzieh V. D.; Bijan B. (2013) effectiveness of *Moringa oleifera* powder in removal of heavy metals from aqueous solution., *F. Environ. B.J.*, **22**, 1516 - 1523(2013).
- [3] Asif H.; Satya R.; Gautam A. (2015) Biosorption of cadmium from aqueous solution by shell dust of the Freshwater snail *Lymnaea luteola*. *Environ. Technol. & Innovation.*, **4**, 82–91.
- [4] Ali, E. N.; Alfarra, S. R.; Yusoff, M. M.; Rahman, M. L., (2015) Environmentally Friendly Biosorbent from *Moringa oleifera* Leaves for Water Treatment. *Int. J. Environ. Sci. Dev.* **6**, 165 – 169(2015).
- [5] Gupta, V.K.; Ali, I. (2000) Utilization of bagasse fly ash (a sugar industry waste) for the removal of copper and zinc from wastewater. *Sep. Purif. Technol.*, **18**, 131-140(2000).

- [6] Han, X.; Liang, C.F.; Li, T.Q.; Wang, K.; Huang, H.G.; Yang, X.E. (2013) "Simultaneous removal of cadmium and sulfamethoxazole from aqueous solution by rice straw biochar." *J. Zhejiang Univ. Sci. B.*, **14**, 640 – 649(2013).
- [7] Memon, J.R.; Memon, S.Q.; Bhangar, M.I.; Memon, G.Z.; El-Turki, A.; Allen, G.C. (2008) "Characterization of banana peel by scanning electron microscopy and FT-IR spectroscopy and its use for cadmium removal," *Colloids Surf. B Biointerfaces*, **66**, 260 – 265(2008).
- [8] Singha, B.; Das, S.K. (2012) Removal of Pb(II) ions from aqueous solution and industrial effluent using natural biosorbents. *Environ. Sci. Pollut. Res.*, **19**, 2212–2226(2012).
- [9] J.C. Igwe and A.A. Abia, "Maiz Cob and Husk as Adsorbents for removal of Cd, Pb and Zn ions from wastewater," *The Physical Sci.*, **2**, 83-94(2003).
- [10] N Raut, G. Charif, Amal A-Saadi, Shinoona A-Aisri, and Abrar A Ajmi, "A Critical Review of Removal of Zinc from Wastewater," *Proceedings of the World Congress on Engineering, London, vol. I, July 4-6, 2012.*
- [11] J.L. Wang and C. Chen "Biosorption of heavy metals by *Saccharomyces cerevisiae*: a review," *Biotechnol Adv.*, **24**, 427-451(2006).
- [12] C.M.A. Ademorati, "Pollution by Heavy metals," *Environmental Chemistry and Toxicology, Foludex press Ibadan*, 171-172(1996).
- [13] K.Schuman, "The toxicological estimation of the heavy metal content (Cd, Hg, Pb) in food for infants and small children," *Z. Ernahrungswiss.*, **29**, 54-73(1990).
- [14] J.A. Davis, B. Volesky, and R.H.S.F. Vierra, "Sargassum seaweed as biosorbent for heavy metals," *Water Res.*, **34**(17), 427-4278(2000).
- [15] C.P. Yingh, "Biosorption of copper(II) and chromium(VI) onto activated sludge: isotherms and kinetic models," *M.Sc. Thesis, University Sains Malaysia, Malaysia, June 2007.*
- [16] D.C. Barrell, "Atomic Spectrophotometer Analysis of Heavy Metals Pollutants in Water," *Ann Arbor Science Publishers Inc., Ann Arbor, MI, 1975.*
- [17] H. Pendias and A. Kabata-Pendias, "Trace Metals in Soil and Plants," *CRC press, Boca Raton, FL*, 75-86(1992).
- [18] J.K. Wagoner and U. Soffiotti, "Occupational Carcinogenesis," *New York Academy of Science.*, 271(1976).
- [19] Y.B. Onundi, A.A. Mamun, M.F. Al Khatib, and Y.M. Ahmed, "Adsorption of copper, nickel and lead ions from synthetic semiconductor industrial wastewater by palm shell activated carbon," *Int. J. Environ. Sci. Tech. Autumn.*, **7**(4), 751-758(2010).
- [20] M. Kasuya, H. Teranishi, K. Aohima, T. Katoh, N. Horiguchi, Y. Morikawa, M. Nishijo, and K. Iwata, "Water pollution by cadmium and the onset of "itai-itai" disease," *Water Sci. Technol.*, **25**, 149-156(1992).
- [21] M. Yasuda, A. Miwa, and M. Kitagawa, "Morphometric Studies of renal lesions in "Itai-itai" disease: chronic cadmium nephropathy," *Nephron.*, **69**, 14 -19(1995).
- [22] C.D. Klaassen, "Heavy metals and Hardmen JG, Limbird LE, Gilman AG (eds). *Goodman and Gilman's: The pharmacological Basis of Therapeutics*," *McGraw Hill, New York.*, 1851-1875(2001).
- [23] Nriagu, J. O. and Pacyna, J., *Nature.*, **333**, 134 – 139 (1988).
- [24] Feizi, M. and Jalali, M., *J. Taiwan Institute of Chemical Engineers.*, **54**, 125–136 (2015).
- [25] Ali, R. M.; Hamad, H. A.; Hussein, M. M. and Malash, G. F., *Ecol. Eng.*, **91**, 317–332 (2016).
- [26] Zhuang, X.; Chen, J.; Shim, H. and Bai, Z., *Environ. Int.*, **33**, 406 – 413 (2007).
- [27] Sarma, H., *Journal of Environmental Science and Technology.*, **4**, 118 –138 (2011).
- [28] Pathomsiriwong, W. and Reanprayoon, P., *J. Environ. Sci. Technol.*, **5**, 332–342(2012).
- [29] Xu, S.; Gong, X. F.; Zou, H. L.; Liu, C. Y.; Chen, C. L. and Zeng X. X., *Water Sci. Technol.*, **73**, 396-404 (2016).
- [30] Abdel-Rahman, L. H., Abu-Dief, A. M., Abd-El Sayed, M. A. and Zikry, M. M., *J. Chem. Mater. Res.*, **8**(4), 8-22 (2016a).
- [31] Abdel-Rahman, L. H., Abu-Dief, Ahmed M., Abd-El Sayed, M. A. and Zikry, M. M. *Arch Chem Res.*, 1:1(2016b).
- [32] G.M. Gadd, "Heavy metal accumulation by bacteria and other microorganisms *Experientia*," **46**, 834-840(1990).
- [33] Z. Aksu, Y. Sag, and T. Kutsal, "The biosorption of copper by *C. vulgaris* and *Z. ramigera*," *Environ. Technol.*, **13**, 579-586(1992).
- [34] N. Goyal, S.C. Jain, and U.C. Banerjee, "Comparative studies on the microbial adsorption of heavy metals," *Adv. Environ. Res.*, **7**, 311-319(2003).
- [35] C. White, J.A. Sayer, and G.M. Gadd, "Microbial solubilization and immobilization of toxic metals: key biogeochemical processes for treatment of contamination," *FEMS Microbiol. Rev.*, **20**, 503-516(1997).
- [36] G.M. Gadd and C. White, "Copper uptake by *Penicillium ochro-chloron*: influence of pH on toxicity and demonstration of energy dependent copper influxing protoplasts," *J. Gen. Microbiol.*, **131**, 1875-1879(1985).
- [37] B. Greene and D.W. Darnall, "Microbial oxygenic photoautotrophs (cyanobacteria and algae) for metal-ion binding," *Microbial Mineral Recovery*, Ehrlich HL and Brierley CL, Ed., *McGraw-Hill, New York.*, 227- 302(1990).
- [38] X. Deng and P. Wang, "Isolation of marine bacteria highly resistant to mercury and their bioaccumulation process," *Bioresource Technology.*, **121**, 342-347(2012).
- [39] J.M. Modak and K.A. Natarajan, "Biosorption of metals using nonliving biomass-a review," *Miner. Metall. Proc.*, **12**, 189-196(1995).
- [40] R. Gourdon, S. Bhande, E. Rus, and S.S. Sofer, "Comparison of cadmium biosorption by gram positive and gram negative bacteria from activated sludge," *Biotechnology Letters.*, **12**, 839-842(1990).
- [41] Y. Nuhoglu and E. Malkoc, "Investigations of Nickel (II) Removal from Aqueous Solutions Using Tea Factory Waste," *J. Hazardous Materials.*, **127**, 120(2005).
- [42] A.L. Zouboulis, K.A. Matis, and I.C. Hancock, "Biosorption of metals from dilute aqueous solutions," *Sep. Purif. Met.*, **26**, 255- 295(1997).
- [43] Volesky, B., *Hydrometallurgy.*, **59**, 203-216 (2001).
- [44] Selatnia; Bakhti, M. Z.; Madani, A.; Kertous, L. and Mansouri, Y., *Hydrometallurgy.*, **75**, 11-24 (2004).
- [45] Ma, W. and Tobin, J.M., *Biochem. Eng. J.*, **18**, 33 - 40(2004).
- [46] Minamisawa, M.; Minamisawa, H.; Yoshida, S. and Takai, N., *J. Agric. Food Chem.*, **52**, 5606–5611 (2004).
- [47] Park, D.; Yun, Y. S.; Jo, J. H. and Park, J. M., *Ind. Eng. Chem. Res.*, **45**, 5059-5065 (2006).

- [48] Owoyokun, T. O., *Pacific J. Sci. Technol.*, **10**, 872-883 (2009).
- [49] Ramakrishnan, M. and Sulochana, N., *ActaChim.Slov.*, **56**, 282-287 (2009).
- [50] Chakravarty, S. , Mohanty, A. , Sudha, T.N. , Upadhyay, A.K. , Konar, J. , Sircar, J.K., Madhukar, A. , Gupta, K.K., *J. Hazard. Mater.*, **173**, 502-509(2010).
- [51] Jimoh, T. O.; Iyaka Y. A. and Nubaye M. M., *American. J. Chem.*, **2**, 165-170 (2012).
- [52] Liu, L.; Liu, J.; Li, H.; Zhang, H.; Liu, Jie and Zhang, H., *BioResources.*, **7**, 3555–3572 (2012).
- [53] Farhan, A. M.; Al-Dujaili, A. H. and Awwad, A. M., *Inter. J. Indust. Chem*, **4**, 1-8 (2013).
- [54] Lim, A. P.; Aris, A. Z. and Juahir, H., *Springer Science, Business Media Singapore chapter.*, **22**, 117-120 (2014).
- [55] Shahanaz Begum, S. A.; Tharakeswar, Y.; Kalyan, Y. and Ramakrishna Naidu, G., *J. Encapsulation and Adsorption Sci.*, **5**, 93-104 (2015).
- [56] Abdolali, A.; Ngo, H. H.; Guo, W.; Lu, S.; Chen, S. S.; Nguyen, N. C.; Zhang, X.; Wang, J; and Wu, Y, *Sci. Tot. Environ.*, **542**, 603–611 (2016).
- [57] Montgomery, D. C., *Design and Analysis of Experiments*, 5th ed., John Wiley and Sons, New York, (2001).
- [58] Reddy, D. H. K.; Seshaiiah, K.; Reddy, A. V. R.; Rao, M. M. and Wang, M. C., *J. Hazard. Mater.*, **174**, 831–838 (2010a).
- [59] Meneghel, A. P.; Goncalves A.C. Jr; Tarley, C. R.; Stangarlin, J.R., Rubio, F. and Nacke H., *Water Sci. Technol.*, **69**, 163-169 (2014).
- [60] Meneghel, A. P.; Goncalves A. C. Jr; Stangarlin, J. R.; Rubio, F. and Strey, L., *water, air and soil pollution*, **224**, 1383-1396 (2013).
- [61] Ajisha, M. A. T., and Rajagopal, K., *Int. J. Environ. Sci. Technol.*, **12**, 223–236(2015).
- [62] Zacharia Kariuki, Jackson Kiptoo, Douglas Onyancha, *Biosorption studies of lead and copper using rogers mushroom biomass ‘Lepiota hystrix’ South African Journal of Chemical Engineering*, 23, June 2017, 62-70.
- [63] Aroosa Aman, Dildar Ahmed, Naeem Asad, Rashid Masih & Hafiz Muhammad Abd ur Rahman, *Rose biomass as a potential biosorbent to remove chromium, mercury and zinc from contaminated waters, International Journal of environmental Studies*, **75**(5), 774(2018).
- [64] Zhu, B.; Fan, T. and Zhang, D., *J. Hazard. Mater.*, **153**, 300–308 (2008).
- [65] Reddy, D. H. K.; Harinath, Y.; Seshaiiah, K. and Reddy, A.V. R., *Chem. Eng. J.*, **162**, 626–634 (2010b).
- [66] Reddy, D. H. K., Seshaiiah, K., Reddy, A.V.R., Lee S.M., *Carbohydrate Polymers.*, **88**, 1077–1086 (2012).
- [67] Singha, A. S. and Guleria, A., *Engineering in Agriculture, Environment and Food.*, **8**, 52–60 (2015).
- [68] Salazar-Rabago, J. J. and Leyva-Ramos, R., *J. Environmental Management.*, **169**, 303- 312 (2016).