

# Greener & Sustainable Methods For Removal of Heavy Metal Ions From Waste Water: Review

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## Abstract

The toxicity of heavy metals present in the ecosystem poses a great threat to all living organisms. The exposure of heavy metals into the natural environment may be due to natural or anthropogenic activities. The treatment of heavy metals is of special concern due to their high mobility in natural water ecosystems, bio-accumulating tendency and toxicity. In recent years, various methods for heavy metal removal from wastewater have been studied extensively. Biosorption is one of them. It is a greener & sustainable process for waste water treatment. Biosorption is a rapid phenomenon of passive metal sequestration by the biomass/adsorbents. Biosorption utilizes various certain natural materials of biological origin, including plant biomass agriculture waste etc.

**Keywords:** Agriculture waste, Biosorption, Heavy metals, Plant-biomass, Sustainable, Waste water

### Introduction

Heavy metal contamination has increased beyond the recommended limits in the ecosystems and is harmful to all life forms due to their long-term effect on health. Preservation of the environment has become increasingly important due to the urgent ecological problems brought about by industrialization and urbanization. Lakes and rivers are particularly vulnerable to this sort of contamination as a result of the discharge of large quantities of effluents from industries and municipalities. Metals that are released into the ecosystems tend to persist indefinitely, accumulating in living tissues throughout the food chain and hence pose a serious threat not only to the environment but also public health. The term "heavy metals" refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration.

The awareness about toxicity of heavy metal is rapidly growing around the world and have led to concerns about the treatment and removal of heavy metals from effluents to permissible limits before discharging into natural streams and rivers. Toxicity due to presence of heavy metals in water is therefore of prime academic and regulatory concern. Industrial waste constitutes the major source of various kinds of metal pollution in natural water . There are at least 20 metals which cannot be degraded or destroyed; they may undergo chemical or microbial transformations, resulting in the huge impact on the environment and public health Out of these twenty, eleven metals lead (Pb), chromium (Cr), mercury (Hg), uranium (U), selenium (Se), zinc (Zn), arsenic (As), cadmium (Cd), cobalt (Co), copper (Cu), nickel (Ni) classified as toxic, are emitted into environment in quantities that pose risks to human health summarized in Table 1.

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Heavy Metal	Main Sources	Permissible limit by WHO (mg/l)	Features/Harmful Effects
Arsenic	Hydrothermal activity, ore deposits, coal combustion, Smelting, mining, rock sedimentation, pesticides, insecticides, ceramics, tanning & textile.	0.01	Stomach pain, vomiting, diarrhea, impaired nerve function, Bronchitis, dermatitis, bone marrow depression, hemolysis, cancers of the bladder, skin, and lungs.
Cadmium	Mining, refining, plastics, batteries, pigments, welding, electroplating, smelting, alloy manufacturing, pesticides, nuclear plants	0.003	Renal dysfunction, lung disease, damage to respiratory system, carcinogenic, bone lesions, hypertension, weight loss "Itai-Itai" disease in Japan due to cadmium toxicity is well known.
Chromium	Steel fabrication, canning industry, leather tanning, paints & pigments, textile, dyeing, electroplating, wood preservatives	0.05	Cr(VI) is more toxic than Cr(III). Cr (III) is essential trace element needed for glucose metabolism in humans, plants and animals. carcinogenic, cause skin irritation, lung carcinoma, headache, nausea, diarrhea, vomiting
Cobalt	Colorants in glass, ceramics, and paints, as catalysts, and as paint driers.	0.002	Vomiting, diarrhea, bleeding, coma, and even death.
Copper	Wire drawing, paint manuf., printed circuit board manuf., polishing, electronics plating, wood preservatives,	1.5	Does essential work in animal metabolism. dizziness, diarrhea, vomiting, reproductive & developmental toxicity, neuro-toxicity, cramps, convulsions, liver damage
Mercury	Paper industry, batteries, pesticides, mining, paint & metallurgical process	0.001	Damage to nervous system, impairment of pulmonary and kidney function, chest pain, corrosive to skin, eyes, muscles, dermatitis The classic example of mercury poisoning is Minamata Bay.
Nickel	Paint, electroplating, mineral processing, enameling	0.02	Serious lung and kidney problems, gastrointestinal distress, pulmonary fibrosis and skin dermatitis, carcinogen.
Lead	Automobile, mining, paint, pesticides, smoking, electroplating, pigments, batteries,	0.01	Damage to central nervous system, liver, kidney, gastrointestinal and reproductive system, mental retardation in children, Anemia, insomnia, headache, dizziness, irritability, weakness of muscles, hallucination.
Selenium	Anthropogenic sources, such as surface mining, coal-fired power plants, and irrigated agriculture.	0.05	Discoloration of the skin, pathological deformation and loss of nails, loss of hair, excessive tooth decay and discoloration, lack of mental alertness, and listlessness.

**Table 1: Main sources, permissible limit, harmful effects of most common Heavy metals**

**Different techniques used for the heavy metal ion removal**

There are various methods which are being used to remove toxic heavy metal ions from waste water. The different techniques available currently for heavy metal removal are compiled in Table 2. Among various methods of treatment for low concentrations of metal ions in wastewater, the adsorption/biosorption process is most recommended and an efficient way to treat industrial waste effluents.

Technique	Operations	Advantage	Disadvantages
Chemical Precipitation	Metal ions get precipitated by adding suitable anion	Simple, cost effective, most of the metals can be removed	Generation of high water content sludge, disposal problems, ineffective in removal of metal ions in low conc.
Chemical coagulation	By addition of suitable coagulants	Sludge setting, dewatering,	High cost, large consumption of chemicals
Ion exchange	Cations or anions are exchanged by synthetic organic ion exchange resin	High regeneration of materials, metal selective	Expensive, non selective, sensitive to pH, cannot handle conc metal solution
Electro chemical methods (electrodialysis)	Electro-deposition using insoluble anodes, use of electrical current	Metal selective, no chemical consumption, pure metals obtained	High capital cost, high running cost, pH & density of solution
Membrane process and ultra-filtration (Reverse Osmosis)	Semi permeable membrane are used at a pressure greater than the osmotic pressure of the solution	Less solid waste produced, less consumption of chemicals, high efficiency	High initial & running cost, low flow rates, removal % decreases with the presence of other metals
Solvent extraction	Compounds are separated based on their relative solubilities. Involves use of a solvent - a fluid that has the ability to dissolve another substance.	low energy consumption, large production capacity, fast action, easy continuous operation and ease of automation.	High cost, technical skills required.
Adsorption	Solid adsorbent binds heavy metal ions by	High efficiency, most of the metals can be removed	high cost of adsorbent
Biosorption	Natural biological materials binds metal ions	High efficiency	Relatively slower process and the regeneration of the biosorbent is tedious.

**Table 2: Common techniques used for waste water treatment**

**Biosorption**

“Biosorption is a biological physico-chemical process in which a biological material, such as plant biomass or microorganisms, is used to absorb or adsorb a target species, such as metal ions.” [1]. Biosorption can be defined as the “ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake”. Biosorption is a complex process driven by several factors. Mechanisms involved in the biosorption process include chemisorption, complexation, adsorption-complexation on surface and pores, ion exchange, micro-precipitation, heavy metal hydroxide condensation onto the biosurface, and surface adsorption. Biosorption is a property of both living and dead organisms (and their components), and has been exploited as a promising biotechnology because of its simplicity [2]. In this process binding and concentration of adsorbate from aqueous solutions by certain types of inactive and dead microbial biomass takes place.

Biosorption can be of two types metabolism dependent and metabolism independent[3]. The uptake of metal ions through cell wall or cell membrane depends on the cell's metabolism. Such type of metabolism generally takes place in living cells and depends on the reaction of metal ions with an active defense system of the various microorganisms. In metabolism independent biosorption mechanism, metal uptake takes place through physical adsorption, ion exchange and chemical sorption. Cell walls of microbial biomass, mainly composed of polysaccharides, proteins and lipids have different functional groups for interactions with metal ions such as aldehydic, ketonic, amide, carboxyl, sulphate, phosphate and amino groups. This type of biosorption is usually rapid than metabolism dependent mechanisms and can be reversible.

Biosorption is a greener & sustainable process for waste water treatment. It is an environmentally friendly technique which utilizes natural products or waste agricultural material, hence following the basic principles of green chemistry as formulated by Paul Anastas: “Prevention of waste/by-products, Maximum incorporation of the reactants (starting materials and reagents) into the final product, Prevention or minimization of hazardous products and Designing of safer chemicals”. Additionally for any sustainable process cost is a very important factor. Biosorption is an affordable process and reduces the use of expensive chemicals or instruments/apparatus. Metals can also be recovered by desorption.

**Biosorbents**

Most of the biosorbents are waste materials of animal and plants present already in abundance. The biosorbents, unlike mono functional ion exchange resins, contain a variety of functional sites including carboxyl, imidazole, sulphhydryl, amino, phosphate, sulfate, thioether, phenol, carbonyl, amide and hydroxyl moieties [4]. The main characteristics of biosorbents are high adsorption capacity, easily & abundantly available, cheap, with the possibility of desorption for metal recovery. The metal uptake by biosorbent is measured by the parameter  $q_e$ , it is the amount of metal accumulated per gram of biosorbent. The mechanism of biosorption is effected by different factors i.e. pH of metallic solutions, amount of biosorbent, temperature and concentration of metallic solutions. The optimized conditions i.e. lower metal ion concentration, higher acidic pH, higher dosage of biosorbent and moderate temperature have been observed for the biosorption process occurring for the removal of heavy metals from waste waters in a large scale[5]. Biosorptive processes using nonliving biomass is more applicable than living microorganism as the later requires rather complicated procedures. Selection of biosorbent from an extremely large number of readily available and inexpensive biomaterials is the most important issue. Yet there are no limits to explore new low cost easily available biosorbents, they can be divided in different categories depending on the source Table 3.

Category	Examples
Algae	Micro , macro , brown & red seaweed
Bacteria	Gram positive & negative, cyanobacteria
Fungi	Molds, mushrooms, yeast
Chitosan-based adsorbents	natural adsorptive polymer
Mineral adsorbents	zeolite, silica, and clay
Industrial wastes	Fermentation waste, food/beverage waste
Agriculture waste	Fruit /vegetable waste, rice straw, wheat bran, soyabean hulls, peels, husk,shell,fiber
Natural materials	Plant materials, sawdust, tree barks, roots,seeds, weeds

**Table 3: Different categories of biosorbents used**

The current review emphasizes mainly on Natural materials (nonliving biomass). The biosorbent capability for removing a target pollutant can be derived through simple chemical and/or physical method(s). Although simple cutting and/or grinding of dried biomass yields stable biosorbent particles.

#### **Mechanism of Biosorption**

Biosorbents have complex structures suggesting that there could be many possible ways to remove various heavy metal ions. Presence of many chemical/functional groups facilitates attraction and sequestering metal ions. There are different common functional groups present in biosorbents like amide, amine, carbonyl, carboxyl, hydroxyl, imine, imidazole, sulfonate, sulfhydryl, thioether, phenolic, phosphate, and phosphodiester[6]. However, the presence of some functional groups does not guarantee successful biosorption of pollutants, as there could be some steric, conformational, or other barriers also present. "Biosorption of a certain pollutant by a certain biomass depends on various factors, including the number of reactive sites in the biosorbent, accessibility of the sites, availability of the sites, affinities between the sites and the particular pollutant of interest. Biosorption is a fast and reversible reaction of the heavy metals with biomass and occurs primarily due to the 'affinity' between the adsorbent and adsorbate. Biomass exhibits this property as an ion exchange of biological origin. The mechanisms of biosorption are generally based on **physicochemical** interactions between metal ions and the functional groups present, such as electrostatic interactions, ion exchange, and adsorption by physical forces, precipitation, entrapment in inner spaces and metal ion chelation or complexation. The biosorption process involves a solid phase (sorbent or biosorbent) and a liquid phase (solvent, normally water) containing dissolved species to be sorbed (sorbate, metal ion). "Due to higher affinity of the sorbent for the sorbate species, the latter is attracted and bound with different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution". Metal uptake by non-living cells is mainly in passive mode which takes place immediately, the first stage is thought to be physical adsorption or ion exchange at the cell surface, reaching the adsorption equilibrium within 30-40 min [7]. Passive mode is independent of energy, mainly through chemical functional groups of the material, comprising the cell and particularly cell wall, hence making the process quite cost effective.

**Factors Affecting Biosorption**

The mechanism of metal biosorption is a complicated process. Heavy metal uptake can involve different types of biosorption processes that will be affected by various physical and chemical factors, and these factors will determine the overall biosorption performance of a given biosorbent, (i.e. its uptake rate, its specificity for the target, and the quantity of target removed). For this reason, the first step of almost all research has been to examine the individual and/or cooperative effect(s) of various factors on biosorption. In the case of batch biosorption processes for removing ionic metals, the important factors include solution pH, temperature, initial pollutant concentration, biosorbent dosage, biosorbent size, agitation speed, and also the coexistence of other pollutants.

Of these factors, the pH appears to be the most important regulator of the adsorption process. The pH affects the solution chemistry of the pollutants themselves, the activity of functional groups in the biosorbents, and the competition with coexisting ions in solution. In general, as solution pH increases, the biosorptive removal of cationic metals is enhanced, while that of anionic metals is reduced. In some cases, a higher pH will cause precipitation of cationic metals, making neutral conditions essential in this case. Temperature seems to affect biosorption to a lesser extent within the range from 20 to 35°C. Biosorptive removal of most adsorptive pollutants is endothermic, thus higher temperature usually enhances biosorptive removal of the adsorbate through increases in its surface activity and kinetic energy. However, higher temperature can also cause physical damage to the biosorbent; thus, room temperature is usually desirable for the biosorption processes. Unlike controlled laboratory conditions, industrial effluents contain various pollutants including the target, one of interest. These factors influence biosorptive removal of a target pollutant by competing with the adsorbate for binding sites, by changing its activity, or by forming complexes with it. The effects of other process factors on the biosorptive removal of adsorptive pollutants are briefly summarized in Table 4

**Table 4: Factors affecting biosorption of heavy metals by Batch mode process**

Factor	Role of the factor	Effect on biosorption of Heavy metals
Particle size		Higher surface area in batch process increases the % adsorption
Solution pH	Most important factor, effects the solution chemistry, activity of functional groups present in the biosorbent, competition with the coexisting ions in solution	Biosorption of cationic metals increases with increase of pH a higher pH will cause precipitation of cationic metals, but reduces for anionic metals.
Temperature	Usually endothermic process	Usually enhances the removal till a certain temp by increasing surface activity & kinetic energy of the adsorbate, higher temperatures may damage physical structure of the biosorbent.
Biosorbent dose	More active sites would be available for the adsorption	Increases removal efficiency
Metal ion concentration	Fractional adsorption depends on this	Increases up to a limit and then decreases
Agitation speed	Minimize the mass transfer resistance	Amount of metal absorbed increases with increase in agitation speed. It is expected to facilitate convective transport of metal ions to sorbent surface. But it may damage the structure of biosorbent.

**Equilibrium Isotherms** The biosorption process involves a solid phase (sorbent) and a liquid phase (solvent, normally water) containing the dissolved species to be adsorbed (adsorbate). Quantification of adsorbate-adsorbent interactions is fundamental for the evaluation of potential implementation strategies. To compare pollutant uptake capacities of different types of biosorbents, adsorption phenomena can be expressed as batch equilibrium isotherm curves.

The equilibrium models are extensively used to investigate the amount of metal ions adsorbed by biomass. The distribution of metal ions between solution and biomass is a measure of position of equilibrium and can be expressed by different isotherms shown in table 5. Among these, the Langmuir and Freundlich models have been most commonly used, with a high rate of success. There are no critical reasons to use more complex models if the two parameter models can fit the experimental data reasonably well .

Single Component	Langmuir	$q = \frac{q_m b C_e}{1 + b C_e}$	Monolayer sorption
	Freundlich	$q = K C_e^{1/n}$	Simple expression
	Temkin	$q = \frac{RT}{b} \ln(a C_e)$	Considering temperature
	Dubinnin Radush-kevich	$q = q_D \exp[-B_D \{RT \ln(1 + \frac{1}{C_e})\}^2]$	Considering temperature
	Langmuir-Freundlich	$q = \frac{q_m b C_e^{1/n}}{1 + b C_e^{1/n}}$	Combination
	Redlich-Peterson	$q = \frac{a C_e}{1 + b C_e^n}$	Approaches Freundlich at higher conc.
	Sips	$q = \frac{a C_e^n}{1 + b C_e^n}$	Complicated
	Radke-Prausnitz	$q = \frac{a r C_e^n}{a + r C_e^{n-1}}$	Complicated
	Khan	$q = \frac{q_m b C_e}{(1 + b C_e)^n}$	Complicated
	Toth	$q = \frac{q_m b C_e}{\{(1 + b C_e)^{1/n}\}^n}$	Complicated
Brannauer	$q = \frac{q_m B C_e}{(C_s - C_e) \{1 + (B - 1)(C_e / C_s)\}}$	Multilayer sorption	

Multi Component	Langmuir	$q_i = \frac{q_{mi} b_i C_i}{1 + \sum_{i=1}^N (b_i C_i)}$	Competitive
	Langmuir-Freundlich	$q_i = \frac{q_{mi} b_i C_i^{1/mi}}{1 + \sum_{i=1}^N (b_i C_i^{1/mi})}$	Competitive
	Redlich-peterson	$q_i = \frac{a_i C_i}{1 + \sum_{i=1}^N (b_i C_i^{ni})}$	Competitive

Table 5: Different models used Equilibrium isotherm

**Kinetics**

To achieve the proper design of adsorption we need to also study the kinetics. Batch kinetic modeling is necessary to describe the response of the biosorption system to changes caused by variations in the experimental conditions and the properties of biosorbents, as well as, the parametric sensitivity of the model to process parameters.

The model results can be affected by biosorbent size, initial pollutant concentration, the maximum uptake capacity of biosorbent, mass transfer coefficients, and solute diffusivity. Thus, kinetics studies give detailed information on adsorbate uptake rates and on rate-controlling steps such as external mass transfer, intraparticle mass transfer, and biosorptive reaction(s). Intra-particle diffusion has often been shown to be an important factor in determining the attainment of equilibrium in immobilized biosorbents. Table 6 shows representative kinetic models for a biosorptive reaction. Derivation of these equations as well as their physical meaning has been summarized in the literature. In most cases, both pseudo-first- and second-order kinetic equations have been commonly employed in parallel, and one was often claimed to be better than the other, according to marginal differences in the correlation coefficient. In general, the pseudo-second-order equation has been successfully applied to the biosorption of metal ions, from aqueous solutions.

Expressions	Equation form	Remarks
Second-order rate equation	$\frac{1}{C_t} = kt + \frac{1}{C_0}$	Early applied second-order rate equation in solid/liquid system
Lagergren equation(pseudo first order model)	$q_t = q_e (1 - e^{-kt})$	Based on adsorption capacity
Elovich equation	$q = \left(\frac{2.3}{\alpha}\right) \log(t + t_0) - \left(\frac{2.3}{\alpha}\right) \log t_0$	Chemisorption
Webber-Morris equation	$q_t = kt^{1/2} + C$	Intra-diffusion
Ho equation(pseudo second order model)	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	Based on adsorption capacity
General rate equation	$-\frac{d\lambda_1}{dt} = k\lambda_1^n$	Non-fixed reaction order

Table 6: Different models used for Kinetic Study



some of the biosorbents used for successful removal of heavy metals is given in the table below.

Metal removed	Material used	pH	Adsorption capacity mg/g	References
Ni(II)	Caesalpinia bonducella Seed Powder	5	188.7	8
Cu(II)	Papaya seed	6	212.7	9
Cd(II)	Polyalthia longifolia Seeds (litchi)	6	20.74	10
As(V)	Pine leaves	4	3.27	11
Cd(II)	Loquat leaves	6	29.24	12
Cd(ii) Cu(II) Ni (II)	Moringa oleifera leaves	5,6,6	171.37, 167.90, 163.88	13
Pb(II), Zn(II)	Tea leaves (exhausted)	1-6	120.8, 79.76	14
Cr(III), Cu(II)	Rice husk	5-6	630, 22.5	15
Hg(II)	Coconut fiber (modified)	2-10	166.67	16
Cu(II), Pb(II), Zn(II)	Groundnut	3-5	85%, 98%, 98%	17
Cu(II)	Portulaca	6	85.47	18
Ni(II), Cr (IV)	Rice husk		100%, 98%	19
Ni(II), Cr(VI) ,Pb(II)	Brassica Campestris		98%, 91%, 49%	20
Ni(II)	Barbadensis Miller leaves powder	1-10	60.02	21

**Table 8: Natural materials based biosorbents used in different studies**

#### Aim of the study

This paper is to review the different materials used for heavy metals biosorption. It focuses on factors such as pH, temperature, adsorbent dose, etc that significantly affect the biosorption capacities.

#### Conclusion

The area of biosorption can be of academic as well as industrial importance for mass adoption of this as a cheaper sustainable green process; if the other industrial and domestic wastes are utilized with the naturally occurring materials. Some waste products from industrial, agricultural activities and some natural materials also can be sourced as potentially economical alternative for removing harmful heavy metal ions from water. Research in this field is now focusing on experimenting with various materials and processes related to biosorption.

#### References

- Gadd, G. M. (2009). *Biosorption: Critical review of scientific rationale, environmental importance and significance for pollution treatment*. *Journal of Chemical Technology & Biotechnology*, 84(1), 13–28. doi:10.1002/jctb.1999
- Bilal M, Shah JA, Ashfaq T, Gardazi SMH, Tahir AA, Pervez A, Haroon H, Mahmood Q. 2013 *Waste biomass adsorbents for copper removal from industrial wastewater—A review*. *Journal of Hazardous Materials*. <http://dx.doi.org/10.1016/j.jhazmat.2013.07.071>.
- Ahalya N, Ramchandra TV and Kanamadi RD. *Biosorption of heavy metals*. *Research J of Chemistry and Environ*. 2003; 7: 4.
- Wang J, Chen C. *Biosorbents for heavy metals removal and their future*. *Biotechnol Adv*. 2009; 27: 195–226.
- Kuyucak N and Volesky B. *Biosorption for recovery of metals from industrial solutions*. *Biotechnol Lett*. 2008; 10: 137-142.

6. Chakresh Kumar Jain & Davendra Singh Malik<sup>2</sup> & Anuj Kumar Yadav Applicability of plant based biosorbents in the removal of heavy metals: a review *Environ. Process.* (2016) 3:495–523 DOI 10.1007/s40710-016-0143-5
7. Ali Ali Redha Removal of heavy metals from aqueous media by biosorption *ARAB JOURNAL OF BASIC AND APPLIED SCIENCES* 2020, VOL. 27, NO. 1, 183–193 <https://doi.org/10.1080/25765299.2020.1756177>
8. Gutha Y, Munagapati VS, Alla SR, Abburi K (2011) Biosorptive removal of Ni(II) from aqueous solution by *Caesalpinia bonducella* Seed Powder. *Sep Sci Technol* 46:2291–2297
9. Hadi NBA, Rohaiza NAB, Sien WC (2011) Removal of Cu(II) from water by adsorption on papaya seed. *Asian Trans on Eng* 1(5):49–55
10. Rao RAK, Rehman F, Kashifuddin M (2012) Removal of Cr(VI) from electroplating wastewater using fruit peel of litchi (*Litchi chinensis*). *Desalin Water Treat* 49:136–146
11. Shafique U, Ijaz A, SalmanM, ZumanWu, Jamil NR, Javid A (2012) Removal of arsenic from water using pine leaves. *J Taiwan Inst Chem Eng* 43:256–263
12. Al-Dujaili AH, Awwad AM, Salem NM (2012) Biosorption of cadmium (II) onto loquat leaves (*Eriobotrya japonica*) and their ash from aqueous solution, equilibrium, kinetics, and thermodynamic studies. *International Journal of Industrial Chemistry* 3:22
13. Reddy DHK, Seshaiyah K, Reddy AVR, Lee SM (2012) Optimization of Cd(II), Cu(II) and Ni(II) biosorption by chemically modified *Moringa oleifera* leaves powder. *Carbohydr Polym* 88:1077–1086
14. Shrestha B, Homagai PL, Pokhrel MR, Ghimire KN (2012) Exhausted tea leaves- a low cost adsorbent for the removal of lead(II) and zinc(II) ions for their aqueous solution. *J Nepal Chem Soc* 30:123–129
15. Sobhan Ardakani S, Parvizi Mosaed H, Olyaie E (2013) Heavy metals removal from wastewaters using organic solid waste—rice husk. *Environ Sci Pollut R* 20:5265–5271
16. Johari K, Saman N, Song ST, Heng JYY, Mat H (2014) Study of Hg(II) Removal From Aqueous Solution Using Lignocellulosic Coconut Fiber Biosorbents: Equilibrium and Kinetic Evaluation. *Chem Eng Commun* 201: 1198–1220
17. Janya Suthiwong S, Phiri SM, Kijjanapanich P, Rene ER, Esposito G, Lens PN. Copper, lead and zinc removal from metal-contaminated wastewater by adsorption onto agricultural wastes. *Environ Technol.* 2015; 36:3071-83.
18. Abha Dubey & Anuradha Mishra A Novel Plant-Based Biosorbent for Removal of Copper (II) from Aqueous Solutions: Biosorption of Copper (II) by Dried Plant Biomass *J. Renew. Mater.*, Vol. 5, No. 1, 2017( 54-61)
19. Waheed Tariq, Muhammad Saifullah, Tanveer Anjum, Madiha Javed, Nafeesa Tayyab, Imran Shoukat REMOVAL OF HEAVY METALS FROM CHEMICAL INDUSTRIAL WASTEWATER USING AGRO BASED BIO-SORBENTS *Acta Chemica Malaysia (ACMY)*2 (2) (2018) 09-14
20. Rabia Baby Shaikh, Bullo Saifullah and Fawad ur Rehman Greener Method for the Removal of Toxic Metal Ions from the Wastewater by Application of Agricultural Waste as an Adsorbent *Water* 2018, 10, 1316; doi:10.3390/w10101316
21. Shweta Gupta & Arinjay Kumar Removal of nickel (II) from aqueous solution by biosorption on *A. barbadensis* Miller waste leaves powder *Applied Water Science* volume 9, Article number: 96 (2019)