

# BIOSORPTION FOR METAL IONS REMOVAL FROM AQUEOUS SOLUTIONS: A REVIEW OF RECENT STUDIES

Nour T. Abdel-Ghani<sup>1</sup> and Ghadir A. El-Chaghaby<sup>2\*</sup>

<sup>1</sup> Chemistry Department, Faculty of Science, Cairo University, Egypt.

<sup>2\*</sup> RCFF, Agricultural Research Center, Giza, Egypt.

**Abstract-** *The presence of metal ions in aqueous solutions represents a major environmental problem. These inorganic species are persistent and non-biodegradable pollutants that should be eliminated from water. In the recent years biosorption have emerged as an economical and environmental friendly method for the decontamination of polluted water. The present work represents a review of the recently published literature discussing the use of non-modified biosorbents for the removal of metal ions from aqueous solution. In this review the main classes of biomass materials used as biosorbents are discussed along with the principle factors affecting the biosorption process such as: solution pH, biomass dose, metal ion concentration and contact time. The potential health and environmental hazards of metal ions in addition to the kinetic and isothermal models usually assessed to fit the biosorption experimental data were also reviewed.*

**Keywords** - Biosorption; biosorption capacity; isotherm; kinetics; metal ions; mechanism

## I. INTRODUCTION

The presence of inorganic pollutants such as metal ions in the ecosystem causes a major environmental problem. Toxic metal compounds coming to the earth's surface not only contaminate earth's water (seas, lakes, ponds and reservoirs), but can also contaminate underground water in trace amounts by leaking from the soil after rain and snow [1]. The numerous metals which are significantly toxic to human beings and ecological environments, include chromium (Cr), copper (Cu), lead (Pb), cadmium (Cd), mercury (Hg), zinc (Zn), manganese (Mn) and nickel (Ni), etc [2].

Metal ions are released into the environment from many sources. Arsenic is introduced in water through natural and anthropogenic sources: release from mineral ores, probably due to long term geochemical changes and from various industrial effluents like metallurgical industries, ceramic industries, dye and pesticides manufacturing industries and wood preservatives [3]. The major sources of antimony released into the environment through wastewater streams are such industries as lead-storage batteries, soldering, bearing and power transmission equipment, sheet and pipe metals, ammunition, flame retardants, ceramics, casting, pewter, enamels, and paints [4]. Wastewaters such as those generated during dyes and pigments production, film and photography, galvanometry, metal cleaning, plating and electroplating, leather and mining may contain undesirable amounts of chromium (VI) anions [5]. Cobalt, which is widely used in alloys (especially magnetic steels and stainless steels), electronics, porcelain and radioisotope therapy, is now

commonly found in contaminated water [6]. Manganese is released into the environment by industries such as those involved in the production of fertilizer, petrochemicals, electroplating, tanneries, metal processing, and mining [7]. Mercury can be found in wastewater discharged from chlor-alkali, paper and pulp, oil refinery, paint, fossil fuel burning, metallurgical processes, pharmaceutical and battery manufacturing [8]. Effluents from production of batteries, gasoline additives, pigments, alloys and sheets etc. contain often high concentrations of lead ions [9]. Mining and metallurgy of nickel, stainless steel, aircraft industries, nickel electroplating, battery and manufacturing, pigments and ceramic industries wastewaters contain high amounts of nickel ions [10]. Zinc can be found in wastewater from metallurgical processes, galvanizing plants, stabilizers, thermoplastics, pigment formation, alloys and battery manufacturing in addition to the discharges of municipal wastewater treatment plants [8].

Metal ions are reported as priority pollutants, due to their mobility in natural water ecosystems and due to their toxicity [11]. The problem associated with metal ions pollution is that they are not biodegradable and are highly persistent in the environment. Thus they can be accumulated in living tissues, causing various diseases and disorders [12]. Heavy metals toxicity can result in damage or reduced mental and central nervous function, lower energy levels and damage to blood composition, lungs, kidneys, liver and other vital organs [13]. The potential health hazards of some metal ions as given by the EPA [14] are summarized in Table1.

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In many countries, more strict legislations have been introduced to control water pollution. Various regulatory bodies have set the maximum prescribed limits for the discharge of toxic heavy metals in the aquatic systems [13]. The permissible limits for industrial effluents discharge set by the world health organization WHO [13] are 5-15(Zn), 0.05-1.5(Cu), 0.1(Cd), 0.1(Pb), 0.1-1 (Fe) and 0.05-0.5 (Mn).

It is thus a necessity to remove metal ions from wastewater before it can be discharged. In this respect, many physicochemical methods have been developed for the removal of metal ions from aqueous solutions including precipitation, evaporation, electro deposition, ion exchange, membrane separation, coagulation etc., [15]. However these methods have disadvantages such as secondary pollution, high cost, high energy input, large quantities of chemical reagents or poor treatment efficiency at low metal concentration [16]. It can be said that the conventional methods for metal ions removal from wastewater are limited by technical and economical barriers, especially when concentration of metals in the wastewater is low (<100 ppm) [17]. Therefore the search and development of an efficient and low-cost metal removal processes is of utmost importance.

In this endeavor, biosorption has emerged as an alternative and sustainable strategy for cleaning up water [18]. Biosorption uses inexpensive biomaterials to sequester environmental pollutants from aqueous solutions by a wide range of physicochemical mechanisms, including ion exchange, chelation, complexation, physical adsorption, and surface microprecipitation. The biomaterials used in this process are termed biosorbents [18].

**TABLE 1. LIST OF SOME METAL IONS AND THEIR HEALTH HAZARDS [14]**

Contaminant	Potential Health Effects from Long-Term Exposure Above the maximum contamination level
Antimony	Increase in blood cholesterol; decrease in blood sugar
Arsenic	Skin damage or problems with circulatory systems, and may have increased risk of getting cancer
Barium	Increase in blood pressure
Beryllium	Intestinal lesions
Cadmium	Kidney damage
Chromium (total)	Allergic dermatitis
Copper	Short term exposure: Gastrointestinal distress Long term exposure: Liver or kidney damage

Lead	Infants and children: Delays in physical or mental development; children could show slight deficits in attention span and learning abilities  Adults: Kidney problems; high blood pressure
Mercury (inorganic)	Kidney damage
Selenium	Hair or fingernail loss; numbness in fingers or toes; circulatory problems

Biosorption is a physical-chemical process, simply defined as the removal of substances from solution by biological material. This is a property of both living and dead organisms (and their components), and has been heralded as a promising biotechnology because of its simplicity, analogous operation to conventional ion-exchange technology, apparent efficiency and availability of biomass and waste bio-products [19]. Various waste biomaterials, micro-organisms, bacteria, fungi, yeast and algae have been reported for the removal of metal ions from aqueous solutions [20].

The present work was carried out to provide a review of the recent researches discussing the potential use of cost effective, natural and non-modified biosorbents for the removal of metal ions from aqueous solutions.

## 2. Origin of biosorbents

### 2.1. Biosorbents from agricultural wastes

Agricultural wastes represent a potential source for producing biosorbents as they have no prominent utilization [21]. Biosorbent production may be added value to the agro-wastes and eventually reduced the agro-wastes management problems over the world [21].

Agro-materials usually are composed of lignin and cellulose as major constituents and may also include other polar functional groups of lignin, which includes alcohols, aldehydes, ketones, carboxylic, phenolic and ether groups [21]. These groups have the ability to some extent to bind heavy metals by donation of an electron pair from these groups to form complexes with the metal ions in solution [11].

During the past few years, several research articles were published reporting the successful use of different kinds of agricultural wastes in the removal of metal ions from aqueous solution.

Munagapati et al. [22] reported the use of *Acacia leucocephala* bark powder as an effective, low cost, and environmental friendly biosorbent for the removal of Cu(II), Cd(II) and Pb(II) ions from aqueous solution with sorption capacities of 147.1, 167.7 and 185.2 mg/g; respectively. *Moringa oleifera* bark (MOB), an agricultural solid waste by-product has been developed into an effective and efficient biosorbent for the removal of Ni (II) from aqueous solutions with maximum biosorption capacity of 30.38mg/g [23]. Cork

waste biomass has been proved to be an efficient biomaterial useful for Cd(II) and Pb(II) removal from aqueous solutions [24]. The maximum uptake of Cu (II) and Cr (III) ions by peanut shells was found to be 25.39 mg/g and 27.86 mg/g; respectively [17].

Rice straw was shown to have a high Cd(II) removal potential to from large-scale effluent contaminated by heavy metals with a biosorption capacity of 13.9 mg/ g [16].

Alomá et al. [10] suggested that sugarcane bagasse waste can be used beneficially for nickel removal from aqueous solution with a maximum sorption capacity of 2 mg/g. Sunflower hulls were used for the biosorption of heavy metal ions Cu (II) from aqueous solutions [25] and showed a maximum sorptive capacity amounting to 57.14 mg/g. The garden grass (GG) was firstly used by Hossain et al. [21] to remove copper (II) from water as bioadsorbent and the maximum adsorption and desorption capacities were 58.34 and 319.03 mg/g, respectively.

Martins et al. [26] reported that Castor leaf powder can be applied immediately to remove Cd(II) and Pb(II) from contaminated water with adsorption capacities of 0.340 and 0.327 mmol/ g, respectively. Unmodified spent oil palm shell, a waste from palm oil industry, was effectively applied as a potential filter bed media for constructed wetland application and its monolayer adsorption capacities for Cu(II) and Pb(II) ions were 1.756 and 3.390 mg/g, respectively [27]. Antimony (III) was removed using green bean husk (GBH) as the adsorbent. The equilibrium adsorption capacity of GBH was found to be 20.14 mg/g [4]. The potential use of Ficus carica leaves (fig leaves) for the removal of cadmium (II) and lead(II) ions from aqueous solutions has been investigated and the maximum monolayer biosorption capacity was found to be 30.31 mg of Cd(II)/g of and 34.36 mg of Pb(II)/g [28]. The biosorption of copper(II), zinc(II), cadmium(II) and lead(II) from aqueous solutions by dead *Avena fatua* biomass and the effect of these metals on the growth of this wild oat were investigated. The maximum values for the adsorption of copper, zinc, cadmium and lead by *A. fatua* were determined to be 0.27, 0.25, 0.73 and 0.84 mmol g<sup>-1</sup>, respectively [29]. Recently fruit wastes have been reported to have relatively good uptake capabilities for metal ions removal. Fruit peels that are typically generated in large quantities by the fruit juice industry have received little scientific attention, in spite of their high quantity of pectin, which contains carboxylate groups [30]. The biosorption of lead, copper and cadmium using different cortex fruit wastes including banana (*Musa paradisiaca*), lemon (*Citrus limonum*) and orange (*Citrus sinensis*) peel has been evaluated [19]. The authors of that study found that banana peel was capable of adsorbing around 65 mg of Pb and Cd per gram but only 36 mg of Cu per gram. For lemon and orange peels, the best retention rate was for Pb (77.6 and 76.8 mg/g) then Cu (70.4 and 67.2 mg/g) and finally Cd (12 and 28.8 mg/g). The maximum biosorption capacity for lead (II) ions adsorption onto *Punica granatum* L. (*P. granatum* L.) peels was found to be 193.9 mg/g [31].

Bayo [32] demonstrated the effectiveness of native grapefruit biomass (NGB), a by-product of the food industry

to adsorb Cd(II) ions from aqueous solution and treated urban effluents in presence of Pb(II), Cu(II) and Ni(II) ions. The feasibility of adsorption of uranium(VI) from aqueous solution was studied and the peel exhibited a high U(VI) sorption capacity 270.71 mg/g [33]. A feasibility study was performed on Indian almond leaf biomass (*Terminalia catappa* L.) to remove palladium (Pd(II)) and platinum (Pt(IV)) ions from aqueous solution by biosorption. The maximum biosorption capacity of *T. catappa* L. biomass for Pd(II) and Pt(IV) ions were 41.86 and 22.50, respectively [34]. Torab-Mostaedi et al. [30] reported adsorption capacities of 42.09 and 46.13 mg/g for the biosorption of cadmium and nickel, respectively from aqueous solution onto grapefruit peel using batch technique.

The latest published research articles reporting the use of agricultural biosorbents for metal ions removal from aqueous solutions include the use of: buckwheat hulls for the removal of Hg(II) ions [35]; *Morus alba* L. pomace for Cd(II) removal ( $Q_{\max}=21.69$  mg/g) [36]; mango leave dust for Cr(VI) removal ( $Q_{\max}=250.23$  mg/g) [37]; water hyacinth for Cu(II) and Zn(II) removal ( $Q_{\max}=0.49$  and 2.66 mg/g, respectively) [38]; spent coffee ground for Cu(II) removal ( $Q_{\max}=0.214$  mmol/g) [39]; *Lathyrus sativus* husk for Cr(III) and Cr(VI) removal ( $Q_{\max}=24.6$  and 44.5 mg/g, respectively) [40]; Mosambi (*Citrus limetta*) peel dust for Cr(VI) removal ( $Q_{\max}=250$  mg/g) [41]; pinion shell for Cu(II) removal ( $Q_{\max}=4.29$  mg/g) [42].

## 2.2. Biosorbents from algae biomass

The term “algae” refers to a large and diverse assemblage of organisms that contain chlorophyll and carry out oxygenic photosynthesis [43].

Among biosorbent materials, algae have proved to be both economic and eco-friendly, as they are abundantly available, have regeneration and metal recovery potentiality, lesser volume of chemical and/or biological sludge to be disposed off, high efficiency in dilute effluents and high surface area to volume ratio [44]. They provide a cost effective solution for industrial wastewater management [44]. Generally speaking about the biosorption mechanism it can be said that the presence of biosorbents' cell wall as well as its chemistry are of greater importance. In this respect, the biosorption in algae has mainly been attributed to the cell wall properties where both electrostatic attraction and complexation can play a role [43]. Algal biomasses contain high content of carboxyl groups from mannuronic and guluronic acids on the cell wall polysaccharides [45].

According to Romera et al. [46] algae are divided into several evolutionary pathways completely independent: a “red pathway” with red algae (*Rhodophyta*), a “brown pathway” with brown algae (inter alia, *Chromophyta*) and a “green pathway” that includes green algae (*Chlorophyta*). The cell walls of brown algae generally contain three components: cellulose, alginic acid and sulphated polysaccharides. As a consequence, carboxyl and sulphate are the predominant active groups in this kind of algae [46]. Red algae also contain cellulose, but their interest in connection with biosorption lies in the presence of sulphated polysaccharides made of galactanes (agar and carragenates) [46]. Green algae are

mainly cellulose, and a high percentage of the cell wall proteins bonded to polysaccharides to form glycoproteins. These compounds contain several functional groups (amino, carboxyl, sulphate and hydroxyl) which could play an important role in the biosorption process [46].

Several authors were interested in studying the application of algal biomass for metal ions removal from contaminated water. Rathinam et al. [47] evaluated the biosorptive removal of cadmium by red macro alga *Hypnea valentiae* and observed a maximum removal of about 17 mg of cadmium per g of micro algae. Gupta et al. [48] reported a maximum capacity of 40.9 mg/g for the biosorption of nickel ions from aqueous solutions onto the biomass of *Oedogonium hatei*.

Four red macroalgal species of *Corallina mediterranea*, *Galaxaura oblongata*, *Jania rubens* and *Pterocladia capillacea* were examined by Ibrahim [45] to remove Co(II), Cd(II), Cr(III) and Pb(II) ions from aqueous solution with the maximum biosorption capacities ranging from 28.5 mg/g to 105.2 mg/g.

Lee and Chang conducted a study to evaluate the biosorption capacity from aqueous solutions of the green algae species, *Spirogyra* and *Cladophora*, for lead (Pb(II)) and copper (Cu(II)) [49]. The capacity of *Spirogyra* to adsorb Pb(II) and Cu(II) was 87.2 mg/g and 38.2 mg/g, respectively and the capacity of *Cladophora* to adsorb Pb(II) and Cu(II) was 45.4 mg/g and 13.7 mg/g, respectively. Arsenic (III) biosorption from aqueous solution by dead green algae (*Maugeotia genulflexa*) biomass was successfully achieved with a maximum biosorption capacity of 57.48 mg/g [3].

A comparative evaluation of bioaccumulation and biosorption of Cu (II) and Pb (II) ions by algal cells of *Chlamydomonas reinhardtii* was conducted by Flouty and Estephane [50] and the amount of Pb (II) and Cu (II) biosorbed by the algal biomass were 0.286 and 0.109 mg/g, respectively. The biosorption of trivalent chromium by protonated brown algae, *Pelvetia canaliculata*, was studied in batch system and the maximum chromium uptake was found to be 0.6 mmol/g [51].

The biosorption of Pb(II), Cd(II), and Co(II) from aqueous solution on green algae waste biomass from *Ulva lactuca* sp. was investigated and the maximum biosorption capacities were reported as 0.27, 0.26 and 0.19 mmol/g for Pb(II), Cd(II) and Co(II), respectively [52]. The biosorption of Cd(II) and Pb(II) from aqueous solution onto the biomass of the blue green alga *Anabaena sphaerica* was investigated by Abdel-Aty et al. [53] and the maximum biosorption capacities for Cd(II) and Pb(II) were found to be 111.1 and 121.95 mg/g, respectively.

González et al. [54] reported the usefulness of *Sargassum muticum* brown alga for the biosorption of hexavalent chromium from the aqueous solutions with maximum biosorption capacity equal to 196.1 mg/g. The maximum biosorption capacities for Co (II), Cr (III), Cd (II) and Pb (II) ions from water using dead algae biomass (*Scenedesmus quadricauda* Chodat) were found to be 32.8, 20.3, 63.9 and 123.0 mg/g, respectively [55]. In the same trend, the

maximum uptake of Cu(II) by dried green alga *Oscillatoria* sp. was 36.2 mg/g [56]. The maximum adsorption capacities for Co(II), Cr(II), Cd(II), and Pb(II) onto nonliving biomass (*Neochloris pseudoalveolaris*, Np) were found to be 20.1, 9.73, 51.4 and 96.2 mg/g, respectively [57].

More recent, *Sargassum filipendula* (a marine alga) was found to be an efficient biosorbent for copper and nickel with maximum capacities of 1.324 and 1.070 mmol/g, respectively [58]. The biosorption of cadmium(II) and lead(II) ions from aqueous solution was evaluated using the algae nonliving biomass (*Rivularia bulata*) and the maximum adsorption capacities for Cd(II) and Pb(II) were found to be 26.36 and 34.30 mg/g [59]. The maximum adsorption capacity of Cu(II) using a dried and untreated macro algae species (*Ulva lactuca*) was calculated as 38 mg/g [60]. The maximum uptake capacities of Cu (II) and Ni (II) ions using marine brown algae *Sargassum angustifolium* were 0.94 and 0.78 mmol/g dry alga, respectively [61].

From the former reviewed studies it can be noticed that the biosorption capability of the alga biosorbents depend somewhat on the type of the algal biomass used in the biosorption process. Several authors have reported that "brown algae" have higher metal ions biosorption capacity compared to red and green algae species. This was attributed according to Romera et al. [46] to the presence of alginates in the cell wall of brown algae which could be responsible for such behaviour by anchoring the metal to the biomass.

### 2.3. Biosorbents from bacterial biomass

As previously discussed, the cell wall structure plays an important role in the biosorption process. A variety of functional groups located on the bacterial cell wall are known to be included in metal biosorption. These include carboxyl, amine, hydroxyl, phosphate, and sulfhydryl groups. The mechanism of metal biosorption by bacterial biomass occurs through complexation, coordination, physical adsorption, chelation, ion exchange, inorganic precipitation and/or a combination of these processes [62]. The metabolism-independent process of metal binding to the cell walls of bacterial biomass and external surfaces is the main mechanism present in the case of non-living biomass; and involves an adsorption process, such as ionic and physicochemical adsorption [62].

Chatterjee et al. [63] found that the maximum adsorption capacities (mg/g) for the different metals by dead biomass of thermophilic bacteria *Geobacillus thermodenitrificans* were 79.9 mg/g for  $\text{Fe}^{+3} > 70.7 \text{ mg/g}$  for  $\text{Cr}^{+3} > 69.76 \text{ mg/g}$  for  $\text{Co}^{+2} > 50.0 \text{ mg/g}$  for  $\text{Cu}^{+2} > 48.26 \text{ mg/g}$  for  $\text{Zn}^{+2} > 42.9 \text{ mg/g}$  for  $\text{Cd}^{+2} > 37.86 \text{ mg/g}$  for  $\text{Ag}^{+} > 32.26 \text{ mg/g}$  for  $\text{Pb}^{+2}$ . The maximum adsorption capacities by *Pseudomonas aeruginosa* ASU 6a (Gram-negative) and *Bacillus cereus* AUMC B52 (Gram-positive) used as inexpensive biosorbents for Zn(II) were found to be 83.3 and 66.6 mg/g, respectively [62]. Also, the biosorption of Pb(II) ions from aqueous solutions using the bacteria *Rhodococcus opacus* was investigated and the maximum biosorption capacity obtained was 95.2 mg/g [64].

Abu Hassan et al. [7] showed that *Bacillus* sp. was a more effective biosorbent than activated sewage sludge for the removal of  $Mn^{2+}$  from aqueous solution with a maximum sorption capacity equal to 43.5 mg  $Mn^{2+}$ /g biomass. The potential use of *B. cereus* and *B. pumilus* as metal sorbents for the removal of  $Pb^{+2}$  was studied and the adsorption capacities of *B. cereus* and *B. pumilus* were found to be 22.1 mg/g and 28.06 mg/g, respectively [65]. The ability of *Trametes versicolor* biomass for biosorption of Cu(II) ions from aqueous solution was studied and its maximum biosorption capacity was found to be 140.9 mg/g [66]. The maximum adsorption of Co(II) and Mn(II) using the bacterial strain *Rhodococcus opacus* as biosorbent was found to be 13.4 mg/g and 6.91 mg/g for cobalt and manganese respectively [67].

Abd-Alla et al. [68] found the maximum adsorption capacities *Rhizobium* spp. a gram-negative soil bacteria for  $Cd^{2+}$  and  $Co^{2+}$  biosorption to be 135.3 and 167.5 mg/g, respectively. Puyen et al. [69] reported that *Micrococcus luteus* DE2008 exhibited a specific removal capacity of 408 mg/g for copper and 1965 mg/g for lead. Cadmium removal from aqueous solutions using a *Streptomyces lunalinharesii* strain was successfully achieved with maximum uptake of 24.8 mg  $g^{-1}$  [70]. The maximum Cu and Pb biosorption capacities on *B. thioparans* U3 were found to be 42.3 and 210.1 mg  $g^{-1}$ , respectively [71].

The sorption of four heavy metals, cadmium (Cd), chromium (Cr), mercury (Hg), and lead (Pb), on living and nonliving *Bacillus subtilis* B38 was investigated using batch experiments. The nonliving biomass generally showed greater or similar adsorptive capacities as compared with the living biomass, the bacterium had a stronger affinity to the cationic heavy metals than to the anionic one, and the equilibrium sorption amounts were 210.6, 332.3, and 420.9 mg/g for Cd(II), Hg(II), and Pb(II), respectively [72].

The biosorption properties of dead sulfate reducing bacteria (SRB) for the removal of Cu(II) and Fe(III) from aqueous solutions were studied. The maximum specific metal biosorption was 93.25 mg  $g^{-1}$  at pH 4.5 for Cu(II) and 88.29 mg  $g^{-1}$  at pH 3.5 for Fe(III) [73]. The ability of *Streptomyces lunalinharesii* to sorb copper and zinc from aqueous solutions was investigated through batch experiments and maximum capacities for Cu(II) and Zn(II) biosorption were found to be 11.53 and 13.64 mg/g, respectively [74].

It is interesting to note that some authors reported that the difference in biosorption capacities of the various bacterial biomasses depends on the nature of the bacteria. Gram-positive or Gram-negative bacteria have significant differences in their cell wall structure.

Joo et al. [61] found that *P. aeruginosa* ASU 6a (Gram-negative) have a higher metal biosorption capacity compared to *B. cereus* AUMC B52 (Gram-positive). The authors explained their finding by the fact that Gram-positive bacteria normally showing lower levels of surface complexation due to the heavily cross-linked peptido-glycan layer, while in Gram-negative bacteria, most of their lipo-polysaccharide (LPS), phospholipids, and proteins are exposed on the cell surface and are responsible for efficient metal binding capacity.

## 2.4. Biosorbents from fungal biomass

“Fungi” represent another group of microorganisms that have been efficiently used in the preparation of biosorbents for metal ions removal from contaminated waters. Fungi are easy to grow; produce high yields of biomass and at the same time can be manipulated genetically and morphologically [75].

The cell wall composition is the characteristic feature of the fungal species as it shows excellent metal-binding properties [76]. The major constituents of fungal cell wall are carbohydrates chitin (3-39%), chitosan (5-33%), polyuronide and polyphosphates (2-12%), lipids (2-7%) and proteins (0.5-2.5%) and there are marked variations in the wall composition between different fungal taxonomic groups [76].

The biosorptive capacity of dead fungal biomass has been studied extensively by several authors during the last few years. Velmurugan et al. [77] reported a maximum biosorption capacity of *Penicillium* sp. MRF-1 for Pb(II) to be 72.5 mg/g. Xiao et al. [78] studied the biosorption of cadmium by endophytic fungus (EF) *Microsphaeropsis* sp. LSE10 and their results showed that the maximum biosorption capacity was 247.5 mg/g. In the same way, the filamentous industrial fungus, *Rhizopus cohnii* (*R. cohnii*), was used as an efficient biosorbent for removing cadmium from wastewater and the biosorption experimental results showed that the maximum uptake of cadmium was 40.5 mg/g [79].

Bairagi et al. [80] demonstrated a viable option for the removal of lead from contaminated water with *Aspergillus versicolor* biomass (AVB). The maximum adsorption capacity of AVB has been found to be 45 mg Pb (II) per gram of the dry weight of the biomass. Similarly, Pang et al., [81] showed that *Penicillium citrinum* can effectively remove uranium from aqueous solutions with maximum capacity of 127.3 mg/g. The sorption of Cr(VI), Ni(II) and Zn(II) ions from synthetic solutions and electroplating effluent by immobilized *Trichoderma viride* biomass was studied and the fungal biomass recorded maximum biosorption capacities of 4.23, 7.41 and 6.27 mg/g for Cr(VI), Ni(II) and Zn(II); respectively [82]. Javaid et al. [76] explored the adsorption potential of *Pleurotus ostreatus* (a macro-fungus) to remove copper, nickel, zinc and chromium from water all together and achieved maximum biosorption capacities of 8.06, 20.40, 3.22 and 10.75 mg  $g^{-1}$  for Cu(II), Ni(II), Zn(II) and Cr(VI); respectively.

In the year 2012, the *Clitopilus scyphoides* (*Pleurotus mutilus*) fungal biomass residue displayed promising adsorption characteristics for cadmium recovery from contaminated water with maximum biosorption capacity equal to 200 mg/g [83]. Whereas a fungus, XJ-1, isolated from chicken manure compost that was phylogenetically related to *Penicillium chrysogenum* showed a maximum adsorption of 100.41 (mg/g dry biomass) for  $Cd^{2+}$  ions [84]. Duygu Ozsoy and van Leeuwen [85] found that it is possible to use dried *Rhizopus oligosporus* biomass to remove Ni (II) ions from their aqueous solutions with a capacity value of 116 mg/g.

Huang et al. [86] investigated the bio-sorption characteristics of  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Pb}^{2+}$  by the fruiting body of jelly fungus *Auricularia polytricha* and the biomass provided maximum biosorption capacities for of 63.3, 73.7, and 221 mg/g for Cd<sup>2+</sup>, Cu<sup>2+</sup>, and Pb<sup>2+</sup>, respectively.

Recently in 2013, Rani et al. [87] achieved maximum biosorption capacity of 26.1 mg/g for Ni (II) ions from aqueous solutions using *Aspergillus fischeri* fungi as a biosorbent. Meanwhile, Subbaiah and Yun [88] reported maximum capacity of 212.5 mg/g for Ni (II) biosorption from aqueous solution by the fungal mat of *Trametes versicolor* (rainbow) biomass. *Aspergillus fumigatus* was isolated from a gold mine tailings and its ability to remove metal ions from aqueous solutions was assessed. The maximum sorption capacity of the fungal biomass for As(III), As(V), Fe, Mn, Pb, and Zn were 11.2, 8.57, 94.33, 53.47, 43.66, and 70.4mg/g, respectively [89].

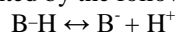
It has been confirmed by many authors that the effective biosorption of heavy metals by fungal biomass can be caused by different mechanisms including ion exchange, complexation, chelation, adsorption and microprecipitation [78]. Many works indicate that heavy metals ion exchange with  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from the biosorption sites of biomass as a key mechanism in metal biosorption processes [78,90].

### 3. Factors affecting metal ions biosorption

#### 3.1. Effect of pH

In the biosorption phenomenon, the pH value affects two aspects: metal ion solubility and biosorbent total charge, since protons can be adsorbed or released [46]. The acidity of the medium affects the competition ability of hydrogen ions with metal ions to active sites on the biosorption surface [48].

According to Romera et al. [46] the pH value of the medium affects the system's equilibrium state, can be represented by the following equations:



$$K_a = \frac{[\text{B}^-][\text{H}^+]}{[\text{B-H}]}$$

$$\text{p}K_a - \text{pH} = \log \left( \frac{[\text{B-H}]}{[\text{B}^-]} \right)$$

For pH values lower than pKa, equilibrium (1) shifts to the left, consuming protons and increasing pH until its value equals pKa. When the pH of the medium is higher than pKa, the opposite will happen [48].

It has been generally reported that in highly acidic medium (pH≈2) the removal of metal ions is almost negligible and it increases by increasing the solution pH up to a certain limit.

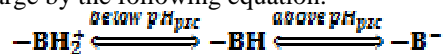
According to Feng et al.[91] the minimum biosorption at low pH is due to the fact that high concentration and high mobility of  $\text{H}^+$  ions, the hydrogen ions are preferentially adsorbed rather than the metal ions. At higher pH values, the lower number of  $\text{H}^+$  and greater number of ligands with negatives charges results in greater metal ions biosorption [91].

Regarding the role of pH in relation to the biosorbent surface, the different functional groups present on the

biosorbents structure should be discussed. As earlier mentioned the main functional groups usually found on a biosorbent surface include carboxyl, sulfhydryl, hydroxyl, and amino groups. Deprotonation of these functional groups occurs on increasing pH and these behave as negatively charged moieties which start attracting the positively charged metal ions [92]. On the other hand as the pH is lowered, the overall surface charges will become positive, which will inhibit the approach of positively charged metal cations [48].

The effect of pH on the biosorption process may also be explained in terms of pH of the point of zero charge, (pHpzc) at which the biosorbent surface is neutral. When the biomass is kept in a solution having pH less than pHpzc of biomass, the protonation of certain functional groups occur and the biomass behaves as a positively charged polymatrix [92]. An increase in pH above this point makes the functional groups on the biomass type deprotonate and act as negative species [92].

Farooq et al. [92] represented the effect of pH<sub>pzc</sub> considering that (-BH) represents the biomass type bearing zero charge by the following equation:



According to Ahmaruzzaman [13] at pH below the pH<sub>pzc</sub>, the predominant metal species ( $\text{M}^{2+}$  and  $\text{M}(\text{OH})^+$ ) are positively charged and therefore, the uptake of metals in the pH range below pH<sub>pzc</sub> is  $\text{H}^+ - \text{M}^{2+}$  (or  $\text{M}(\text{OH})^+$ ) exchange process. With an increase in pH above pH<sub>pzc</sub>, although the surface of the adsorbent is negatively charged, the adsorption still increases as long as the metal species are still positively charged or neutral. When both the surface charge of the adsorbent and metal species charge become negative, the adsorption will decrease significantly [13].

Another aspect that must be considered is the metal speciation in solution, which is also pH dependent [91].

**Figs.1** give representative examples for metal speciation diagrams (adopted from references [93] and [94]).

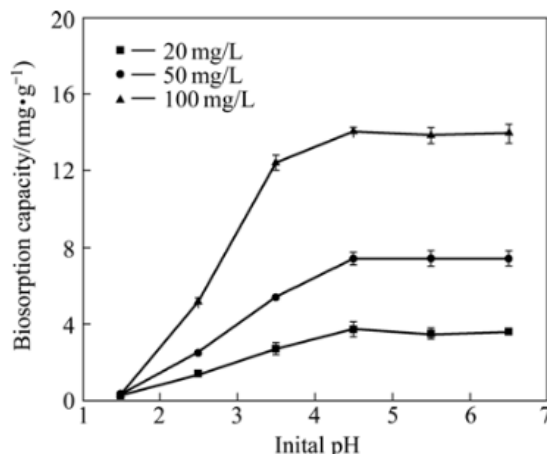
Reviewing the metal ions predominant species as function of the solution pH, the following information could be obtained:

- At pH < 3, Sb(III) exists as  $[\text{SbO}]^+$  and  $[\text{Sb}(\text{OH})_2]^+$  species, whereas  $\text{HSbO}_2$  and  $\text{Sb}(\text{OH})_3$  species predominate at the pH range of 3–10, while  $[\text{SbO}_2]^-$  species is predominant at pH > 10[4].
- Cu(II) exists as  $\text{Cu}^{2+}$  at pH 3 and above this pH other Cu(II) species like  $\text{Cu}(\text{OH})^+$  exist at pH 4-5 and  $\text{Cu}(\text{OH})_2$  is found at pH>6 [15].
- For chromium ions, at pH values lower than 3 the predominant species is  $\text{Cr}^{3+}$ , at pH close to 4 approximately the same proportion of  $\text{Cr}^{3+}$  and  $\text{Cr}(\text{OH})^{2+}$  exists, around pH=7 the chromium is mainly found precipitated as  $\text{Cr}(\text{OH})_3$  and finally at a basic pH the predominant species is  $\text{Cr}(\text{OH})_4^-$  [94].
- Free cadmium (II) and lead (II) ions are the predominant species formed in the pH between 3.5 and 5. At pH values higher than 8 for cadmium, or higher than 5 for lead, several hydroxyl low-soluble

species can be formed, i.e.  $\text{Cd}(\text{OH})_2$ ,  $\text{Cd}(\text{OH})_3^-$  or  $\text{Pb}(\text{OH})_2$  [95].

- In the pH range 2-3 Nickel is predominantly present as  $\text{Ni}^{2+}$  whereas at higher pH range (4.5-6) partial hydrolysis of the metal ions occur resulting in the formation of  $\text{Ni}(\text{OH})^+$  and  $\text{Ni}(\text{OH})_2$  [96].
- Se(IV) species in aqueous solution include selenious acid ( $\text{H}_2\text{SeO}_3$ ), biselenite ( $\text{HSeO}_3^-$ ) and selenite ( $\text{SeO}_3^{2-}$ ). Between pH 3.5 and 9.0 biselenite ion is the predominant ion in water. Above pH 9.0 selenite species dominate and as pH decreases below pH 3.5, selenious acid dominates [97].

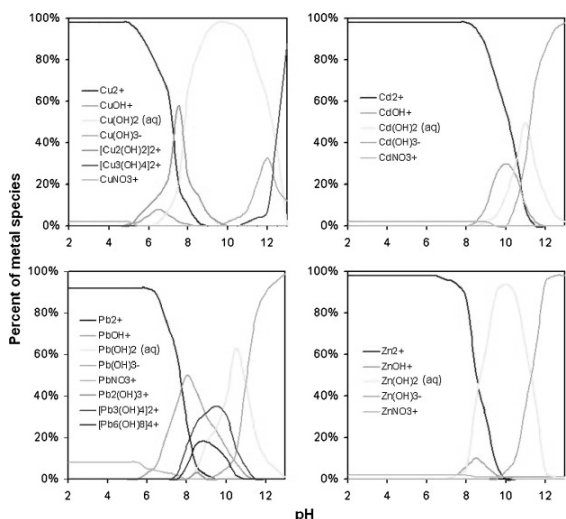
2.0 to 4.5 and then reached a plateau in the pH range of 4.5 to 6.5.



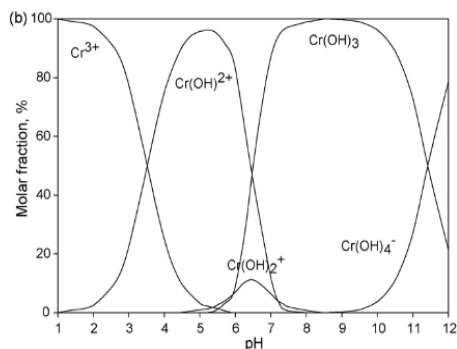
**Fig. 2a:** Effect of pH on Cd(II) biosorption capacity using biosorbent *R. cohnii* at different Cd(II) concentrations at contact time 12 h, dosage of 1 g/L and at 298 K (adopted from reference [79]).

Luo et al. [79] attributed that to the biosorption capacities of biosorbents which depend on the available binding sites provided by the functional groups existing on the surface of the biosorbents. Such sites were not available due to competition between  $\text{Cd}^{2+}$  and  $\text{H}^+$  ions at pH 2.0. With the acidity decreasing in the solution, the deprotonation of acid functional groups, such as carboxyl, phosphonate and phosphodiester, was strengthened and the attraction increased between negative charge on biomass and positive metal cations.

Reddy et al. [23] provided another explanation for the effect of solution pH on the biosorption of Ni(II) by *Moringa oleifera* bark (MOB). The authors observed that under highly acidic conditions (pH≈2.0) the amount of Ni(II) removal was very small, while the sorption had been increased with the increase in pH from 3.0 to 6.0 and then decreased in the range 7.0 and 8.0 (**Fig.2b**). They explained their results by considering the point of zero charge of MOB which they have determined to be  $4.2 \pm 0.67$  (PZC). Thus, at pH below (PZC), the surface of MOB would be positively charged due to protonation. This protonation effect was more pronounced at lower pH values due to the presence of higher concentration of  $\text{H}^+$  ions in the solution which resulted in more unfavorable Ni(II) biosorption. At the optimum pH value (pH 6.0) the surface of the MOB is negatively charged and favorable to the biosorption of Ni(II). Decreased biosorption at higher pH (pH>6) was due to the formation of soluble hydroxylated complexes of the metal ions and their competition with the active sites, and as a consequence, the retention had been decreased again.



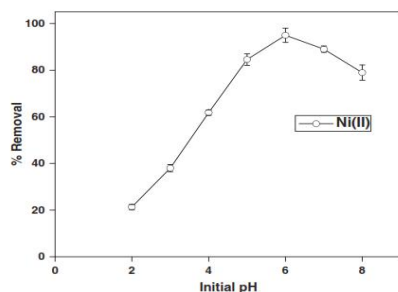
**Fig.1a:** Aqueous speciation of Cu, Cd, Pb and Zn as a function of pH in the single-element system (from reference [93]).



**Fig.1b:** Speciation diagram for Cr (III) at 25°C and 10 mg/L ion content (from reference[94])

Some examples of how the preceding information have been adopted by the authors working in the biosorption field to interpret their results are summarized as follows:

Luo et al. [79] studied the effect of initial solution pH on Cd (II) biosorption by the biomass of *Rhizopus cohnii* (*R. cohnii*) and stated that barely any biosorption was observed for a pH less than 2.0 (**Fig.2a**). The cadmium uptake of biosorbent *R. cohnii* increased with the pH increasing from



**Fig. 2b:** Effect of pH on the sorption of Ni(II) by MOB. Error bars represent  $\pm$ S.D (adopted from reference [23])

It is interesting to point out that the authors working with Cr(VI) biosorption indicated that the maximum chromium biosorption takes place at highly acidic pH values (pH=2) for various types of studied biomasses e.g. sawdust [5], pistachio hull waste biomass [99], Sargassum muticum brown alga [54], sugarcane baggasse biomass [100], *Rosa damascena* phytomass [101], etc.

The explanation of this behavior was given by considering the effect of initial solution pH in relation to the metal ion (chromium) species present in solution. According to González et al. [54] concerning Cr(VI) biosorption in the pH range 2.0-6.0,  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$  ions are in equilibrium [98]. At lower pH (pH < 2) values,  $\text{Cr}_3\text{O}_{10}^{2-}$  and  $\text{Cr}_4\text{O}_{10}^{3-}$  species are formed. The distribution of Cr(VI) and Cr(III) is strongly dependent on the pH of the solution, of the initial metal concentration and the dosage of the biosorbent. All the species of chromium in the solution were in their trivalent form at pH < 2 [102].

González et al. [54] further reported that the decrease in the biosorption with increase of pH may be due to the decrease in electrostatic force of attraction between the sorbent and sorbate ions. At lower pH ranges, due to the high electrostatic force of attraction, the percentage of Cr(VI) removal is high. At very low pH value, the surface of sorbent would also be surrounded by the hydronium ions which enhance the interaction of Cr(VI) with binding sites of the biosorbents by greater attractive forces. A sharp decrease in biosorption above pH 4 may be due to occupation of the biosorption sites by anionic species like  $\text{HCrO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{CrO}_4^{2-}$ , which retards the approach of such ions further toward the sorbent surface [103].

### 3.2. Effect of initial metal ion concentration

The initial concentration of metal ions in the solution plays a key role as a driving force to overcome the mass transfer resistance between the aqueous and solid phases [104].

It is generally agreed that the biosorption capacity increases as the initial metal ion concentration in the solution increases, whereas the metal removal percentage (also called removal efficiency) decreases by increasing the metal ion initial concentration.

As a rule, increasing the initial metal concentration results in an increase in the biosorption capacity because it provides a driving force to overcome mass transfer resistance between the biosorbent and biosorption medium [44].

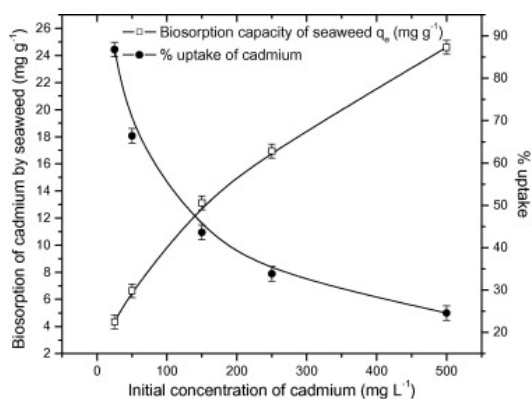
The removal efficiency of the ions by the biosorbent initially increases with increasing the initial ion concentration. At lower ions concentration in the solution, the ions would interact with the binding sites and thus facilitated almost 100% adsorption whereas at higher concentrations, more ions are left un-adsorbed in the solution due to the saturation of the binding sites [105].

Rathinam et al. [47] studied the effect of different initial cadmium concentrations of 25, 50, 150, 250, 500  $\text{mg L}^{-1}$  on its removal using *H. valentiae* biomass. The percentage (%) removal of cadmium has been found to be higher at lower concentration of cadmium solution (25  $\text{mg L}^{-1}$ ); a maximum cadmium removal of 86.8% has been obtained for *H. valentiae* biomass. However, the effective biosorption of cadmium ( $q_e$ ) by seaweed in terms of mg of cadmium per gram of seaweed increased from 4.34 to 24.60  $\text{mg g}^{-1}$  as the initial cadmium concentration was varied from 25 to 500  $\text{mg L}^{-1}$  (Fig.3a). These authors concluded that the increase of cadmium biosorption capacity of biosorbent with an increase in cadmium concentration is probably due to higher interaction between metal ions and the biosorbent.

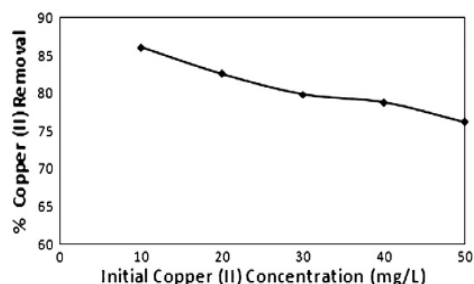
In studying the biosorption of copper onto cashew nut shell (CNS) Senthilkumar et al. [106] found that the percentage copper(II) ion adsorption decreased from 86.03% to 76.17% with the increase of the initial copper(II) ions concentration from 10 to 50  $\text{mg/L}$  (Fig. 3b). At low concentration values, a larger surface area of the CNS being available for the adsorption of copper (II) ions and the ions are adsorbed at specific sites. Whereas with increasing copper (II) ion concentrations the available sites of the adsorption became less, the specific sites are saturated with and exchange sites are filled, thus as a result adsorption percentage was less.

Chong et al. [27] observed that the adsorbed amount of Cu(II) and Pb(II) ions per unit weight of oil palm shell increased with the increase of initial concentration over the range of 5–400  $\text{mg/L}$  (Fig.3c). This is because of the reduction in the total fraction of adsorbate ions adsorbed at higher initial concentration which created a driving force to overcome mass transfer resistance that enabled the adsorbate ions to move sufficiently close to the oil palm shell to be adsorbed onto its binding sites. The authors also reported that nevertheless insufficient binding sites to accommodate excessive adsorbate ions at high initial concentration caused a reduction in fraction of adsorbate ions adsorbed [27].

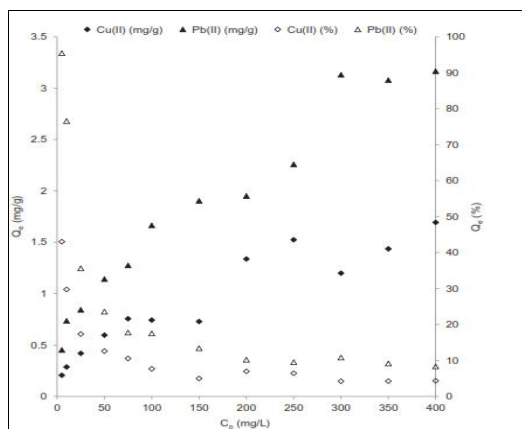




**Fig. 3a:** Effect of initial concentration of cadmium on cadmium biosorption by seaweed (adopted from reference [47])



**Fig. 3b:** Effect of initial copper (II) ions concentration for the adsorption of copper(II) ions onto CNS (the initial copper(II) ions concentration =10 to 50 mg/L, pH=5.0, CNS dose=3 g/L and time=30 min) (adopted from reference [106]).



**Fig. 3c:** Effect of initial concentration on adsorption of Cu(II) and Pb(II) ions by oil palm shell. (adopted from reference [27]).

Similarly, Chowdhury and Mulligan [107] found that the amount of As(III) adsorbed increased from 106 to 155µg/g with the increase of initial concentration from 500 to 4000µg/L but the removal efficiency decreased from 85 to 16%. Pang et al. [81] also stated that the adsorption capacity of the dead fungal biomass of *Penicillium citrinum* increased with an increase in the initial uranium (VI) concentrations from 30 to 80µg/ml. Chatterjee et al. [63] studied the effect

of different initial ions concentrations on the biosorption of Fe<sup>+3</sup>, Cr<sup>+3</sup>, Co<sup>+2</sup>, Cu<sup>+2</sup>, Zn<sup>+2</sup>, Cd<sup>+2</sup>, Ag<sup>+</sup> and Pb<sup>+2</sup> by the dead biomass of *G. thermodenitrificans* and found that the increase in initial metal concentration resulted in increase in the capacity of metal adsorption from 25 to 175mg/L with a maximum adsorption at 175mg/L for all the metals. The actual amount of copper adsorbed per unit mass of Garden Grass increased from 14.06 to 137.12 mg/g with the increase in copper concentration from 10 to 100 mg/l in the test water [21]. The increasing of initial concentration of palladium and platinum led to the maximum capacity of Indian almond leaf biomass adsorption [34]. With the increase in initial Ni(II) concentration from 10 to 750 mg L<sup>-1</sup>, the Ni(II) biosorption capacity by *Litchi chinensis* seeds rose from 5.44 to 66.34 mg g<sup>-1</sup> [18]

### 3.3. Effect of biomass dosage

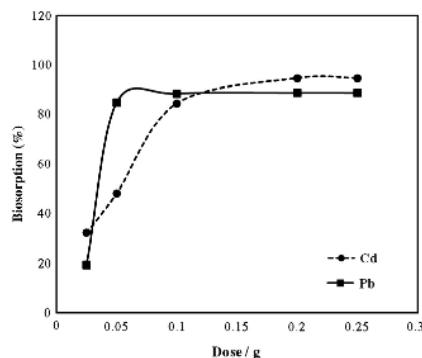
Biomass provides binding sites for the sorption of metal ions, and hence its concentration strongly affects the sorption of metal ions from the solution [108]. The amount of biosorbent used for the treatment studies is an important parameter, which determines the potential of biosorbent to remove metal ions at a given initial concentration [47].

For a fixed metal initial concentration, increasing the adsorbent dose provides greater surface area and availability of more active sites, thus leading to the enhancement of metal ion uptake [108]. At low biomass dosage, the amount of ions adsorbed per unit adsorbent weight is high. The adsorption capacity is reduced when the biomass dosage increases as a result of lower adsorbate to binding site ratio where the ions are distributed onto larger amount of biomass binding sites. However, at higher dosage, the ions adsorbed are higher due to the availability of more empty binding sites as compared to lower dosage which has less binding sites to adsorb the same amount of metal ions in the adsorbate solution [27].

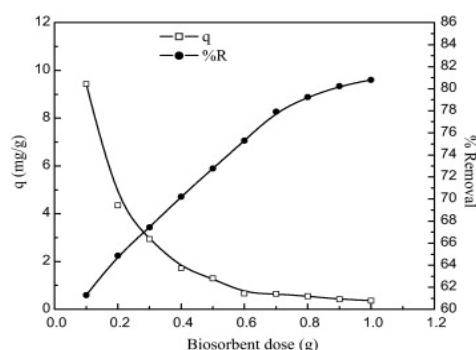
The effect of biomass dosage on metal ions biosorption was investigated by many authors. Rathinam, et al. [47] demonstrated that an increase in the amount of seaweed decreases cadmium biosorption capacity of the seaweed *H. valentiae* biomass. On increasing the quantity of seaweed from 4 to 8 g L<sup>-1</sup>, biosorption capacity decreases from 27.08 to 6.21 mg g<sup>-1</sup> for *H. valentiae* biomass. These authors indicated that the decrease in biosorption capacity may be due to splitting effect of concentration gradient between sorbate and sorbent with increasing seaweed concentration causing a decrease in amount of cadmium adsorbed onto unit weight of *H. valentiae* biomass.

In their study Abdel-Atty et al. [53] evaluated the effect of different biomass dosage of the water algae *Anabaena sphaerica* on the biosorption of Cd(II) and Pb(II) ions. The data revealed that the biosorption of Cd(II) and Pb(II) ions was increased with subsequent increasing the biosorbent dose and almost became constant at higher biomass dosage (Fig.4). This behavior could be explained by the formation of

aggregates of the biomass at higher doses, which decreases the effective surface area for biosorption.



**Fig. 4a:** Effect of the dose of *Anabaena sphaerica* biomass on the biosorption of Cd and Pb (adopted from reference [53])



**Fig.4b:** Effect of biosorbent dose on metal uptake and percentage metal removal (adopted from reference [110])

Experiments were carried out by Venugopal and Mohanty [110] to find the effect of biosorbent dose on Cr(VI) uptake and percentage adsorption by *Parthenium (P. hysterophorus L.)* weed biomass. The results revealed that percentage removal of Cr(VI) increased from 61.28 to 80.81 with increase in adsorbent dose from 0.1 to 1.0 g which is the expected trend as more active sites were available with increase in the biosorbent dose. However, at the same dose the uptake capacity of Cr(VI) decreased from 9.43 to 0.37 mg g<sup>-1</sup> due to the increased metal-to-biosorbent ratio which decreased with increasing the biosorbent dose.

Similar trend of biomass effect was reported for the biosorption of nickel by algal biomass of *Oedogonium hatei* [48], cadmium by *Streptomyces lunalinharesii* [70], copper and zinc by *Streptomyces lunalinharesii* [74], cadmium by fungus *Rhizopus cohnii* [79], copper by cashew nut shell [106], cadmium by *Lessonia kelps* [111], lead and cadmium by *Chondracanthus chamissoi* [112], etc.

According to Boschi et al. [111], the sorbent dosage influences the density of reactive groups available for metal binding and on the external surface area of the sorbent. Varying the sorbent dosage could thus influence the initial slope of the curve (resistance to film diffusion) and the equilibrium concentration. Additionally, it may affect the

concentration gradient between the surface of the sorbent and the internal groups due to the change in the concentration of the solution when the dosage of adsorbent increases.

In real applications, the most favorable biosorbent dose should be defined as the lowest quantity that gives a reasonable level of removal efficiency, and additionally, adjusts to environmental regulations to discharge metal ions in the environment [74].

### 3.4. Effect of contact time

In batch biosorption experiments, the determination of the optimum contact time required to achieve the highest removal of metal ions is one of the key factors usually assessed. Equilibrium time is one of the important parameters for selecting a wastewater treatment system [113].

In our previous studies and in agreement with many authors we have reported that basically, the removal rate of sorbate is rapid, but it gradually decreases with time until it reaches equilibrium. The rate of percent metal removal is higher in the beginning due to a larger surface area of the adsorbent being available for the adsorption of the metals. The metal uptake by the sorbent surface will be rapid initially, slowing down as the competition for decreasing availability of active sites intensifies by the metal ions remaining in solution [114].

The equilibrium time for metal ions biosorption onto various types of biomass recently reported in literature are summarized in **Table 2**.

**TABLE 2. EQUILIBRIUM TIME ACHIEVED FOR METAL IONS BIOSORPTION ONTO DIFFERENT BIOMASSES**

Biosorbent	Metal ion	Equilibrium time (min.)	Reference
Grapefruit peel	Cd (II), Ni (II)	60	[30]
Rice straw	Cd (II)	5	[16]
<i>A. leucocephala</i> bark	Cu (II), Cd (II) and Pb (II)	180	[22]
Sugarcane bagasse	Ni(II)	120	[10]
<i>Peanut shell</i>	Cu(II) and Cr(III)	20	[17]
<i>Cucumis melo</i>	Pb(II)	180	[9]
<i>Spirogyra</i> and <i>Cladophora</i> filamentous macroalgae	Pb(II), Cu(II)	30	[49]
Green algae waste biomass	Pb(II), Cd(II), and Co(II),	180	[52]
<i>Rhodococcus opacus</i>	Al(III)	5	[64]
<i>Pseudomonas aeruginosa</i> and <i>Bacillus cereus</i>	Zn(II)	30	[62]
<i>Punica granatum L.</i> peels	Pb(II)	50	[31]
Castor leaf powder	Pb(II)	30	[26]
Red macroalgae	Co(II), Cd(II), Cr(III) Pb(II)	60	[45]

Biosorbent	Metal ion	Equilibrium time (min.)	Reference
<i>Cladophora hutchinsiae</i> biomass	Se(IV)	60	[97]
Citrus paradisi L. biomass	Cd(II)	30	[32]
Bacillus strains	Pb(II)	80	[65]
<i>Chlamydomonas reinhardtii</i> algal cells	Cu(II), Pb(II)	100	[50]
Waste biomaterial of <i>Cucumis melo</i>	Pb(II)	80	[9]
Garden grass	Cu(II)	400	[21]
Brown algae	Ni(II)	120	[44]
Oil palm shell	Cu(II), Pb(II)	480	[27]
Green bean husk	Sb(III)	60	[4]
Gooseberry fruit waste	Cu(II)	60	[15]
Acacia leucocephala bark powder	Cu(II), Cd(II) and Pb(II)	180	[22]

#### 4. Biosorption Kinetics

The prediction of the biosorption rate gives important information for designing batch biosorption systems. Information on the kinetics of pollutant uptake is required for selecting optimum operating conditions for full-scale batch process [97]. The sorption kinetics is significant in the treatment of wastewater, as it provides valuable insights into the reaction pathways and mechanisms of sorption reactions [48].

Several kinetic models have been applied to fit the biosorption data of different metal ions onto various biosorbents. These models include the pseudo-first order, pseudo-second order, Elovich, intraparticle diffusion, etc.

The pseudo-first-order kinetic model (Lagergren model) assumes that metal ion binds only to one sorption site on the sorbent surface [115]. In Lagergren model, the rate of occupation of biosorption sites is proportional to the number of unoccupied sites [115]. The model is represented by:  $\ln(q_e - q_t) = \ln q_e - K_1 t$  [116].

Where  $K_1$  ( $\text{min}^{-1}$ ) is the pseudo first order adsorption rate coefficient,  $q_e$  and  $q_t$  are the values of amount adsorbed per unit mass at equilibrium and at any time  $t$ . The values of  $K_1$  and the calculated  $q_e$  can be obtained respectively from the slope and intercept of the linear plot of  $\ln(q_e - q_t)$  versus ( $t$ ).

The second order kinetic model assumes that the rate-limiting step is most likely to involve chemical interactions leading to binding of the ions to the surface by bonding as strong as covalent bonding [117]. The pseudo-second-order equation [118] based on equilibrium adsorption is expressed as:  $t/q = 1/K_2 q_e^2 + t/q_e$ ; where  $K_2$  ( $\text{g/mg min.}$ ) is the rate constant of second-order adsorption. Plots of  $(t/q_t)$  versus ( $t$ ) give the values of  $1/q_e$  as the slope and  $1/K_2 q_e^2$  as the intercept.

Elovich's equation assumes that the actual solid surfaces are energetically heterogeneous and that neither desorption nor interactions between the adsorbed species could substantially affect the kinetics of adsorption at low surface coverage [117]. Elovich's equation is given as:  $q_t = (1/b) \ln(ab) + (1/b) \ln(t)$ ; where  $a$  ( $\text{mg/g.min}$ ) is the initial sorption rate and  $b$  ( $\text{g/mg}$ ) is related to the extent of surface coverage and activation energy for chemisorption.

The criteria upon which the suitability of the model to fit the experimental data is determined include both the correlation coefficient ( $R^2$ ) and the calculated  $q_e$  value. When 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 kinetics of metal ions biosorption on various sorbents reported in many previous works mostly followed the pseudo-second order kinetics. The applicability of the pseudo-second order model to explain the kinetics of metal ions biosorption suggests that the rate limiting step in adsorption of metal ions could be chemisorption involving valence forces through the exchange of electrons between sorbent and sorbate, complexation, coordination and/or chelation [109].

Several researchers pointed out that the highest correlation coefficients for the sorption data were obtained for the pseudo-second-order model for the biosorption of metal ions onto various biomasses. Examples include: the biosorption of Cu(II) by gooseberry fruit waste [15], Ni(II) by *Moringa oleifera* bark [23], Ni(II) by brown algae [44], Cd(II) and Pb(II) by castor leaf [26], Cr(VI) by mango and neem sawdust [5], Pb(II) by *Punica granatum* peels [31], Cu(II) and Cr(III) by peanut shell biomass [17], As(III) by *Maugeotia genulflexa* algal biomass [3], Cd(II) by rice straw [16], Ni(II) by sugarcane bagasse [10], Cu(II) and Pb(II) by oil palm shell [27], Sb(III) by various plant residues [4], Cr(VI) by brown seaweed *Sargassum muticum* [54], Ni(II) by *Saccharum bengalense* biomass [119], Cd(II), Pb(II) and Zn(II) by Agave *salmiana* bagasse [120], U(VI) by rice husk [121], Cu(II), Zn(II) and Ni(II) by wheat straw [122], Ni(II) by *Litchi chinensis* seeds [18], Co(II), Cu(II), Ni(II), Pb(II) and Zn(II) by *Trichoderma reesei* [115], Zn(II) and Cd(II) by *Undaria pinnatifid* [123].

According to Ho [124] an expression of second-order rate based on solid capacity has been presented for the kinetics of adsorption of divalent metal ions onto peat biomass. The biomass contains polar functional groups such as aldehydes, ketones, acids, and phenolics which can be involved in chemical bonding and are responsible for the cation exchange capacity of peat. Thus as an example, the peat-copper biosorption reaction may be represented in two ways as:  $2P^- + Cu^{2+} \leftrightarrow CuP_2$  and  $2HP + Cu^{2+} \leftrightarrow CuP_2 + 2H^+$ , where  $P^-$  and  $HP$  are polar sites on the peat surface.

Going deeply into the biosorption mechanism, many researchers studied the application of the intraparticle diffusion model for their biosorption data. The overall rate of

adsorption can be described by the following three steps: (1) film or surface diffusion where the sorbate is transported from the bulk solution to the external surface of sorbent, (2) intraparticle or pore diffusion, where sorbate molecules move into the interior of sorbent particles, and (3) adsorption on the interior sites of the sorbent [125].

The Weber and Morris intraparticle diffusion model assumes three stages: external mass transfer and the stages of intraparticle diffusion in larger and smaller pores till the saturation of the surface [25]. The intraparticle diffusion mechanism suggests proportionality between the adsorption capacity and the square root of the time [126].

The model's equation is expressed by:  $q_t = K_i t^{0.5} + C_{b(i)}$ ; where  $q_t$  is the adsorbed quantity of phenol,  $K_i$  is the intraparticle diffusion parameter, and  $C_{b(i)}$  is the thickness of the boundary layer at stage (i) [127].

The shape of the plots of  $q_t$  against  $t^{0.5}$  gives much information about the biosorption mechanism. These plots are either presented by "one single line" or "multiple lines". If the Weber–Morris plot of  $q_t$  versus  $t^{0.5}$  gives a straight line, then the adsorption process is controlled by intraparticle diffusion only [105]. If the regression of  $q_t$  versus  $t^{0.5}$  is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step [106]. However, if the data exhibit multi-linear plots, then two or more steps influence the adsorption–sorption processes [105]. The intercept of these plots reflects also the boundary layer effect. Larger the intercept, greater is the contribution of the surface sorption in the rate controlling step [106].

When studying the mechanism of copper biosorption onto cashew nut shell Senthilkumar et al. [106] obtained linear plots at each of the tested concentrations (Fig.5a). These authors also found that the obtained plots did not pass through the origin. This deviation from the origin was attributed to the difference in the rate of mass transfer in the initial and final stages of the adsorption. This is indicative of some degree of boundary layer control and this further showed that the intraparticle diffusion was not the only rate-limiting step, but also be controlling the rate of sorption or all may be operating simultaneously.

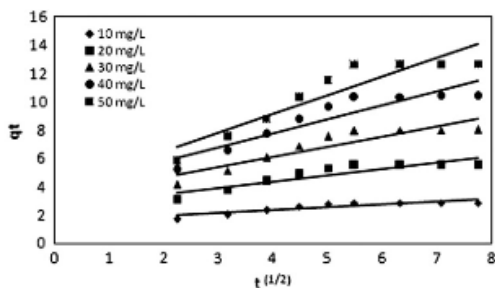


Fig. 5a: Intraparticle diffusion model for adsorption of copper(II) ions onto cashew nut shell at 30 °C (Reference [106])

On the other hand, Hossain et al. [21] in their study for the biosorption of copper onto garden grass observed two clear steps visible in the plots of  $q_t$  against  $t^{0.5}$  (Fig.5b). The first stage may be attributed to the boundary layer diffusion effect, while the second stage may be due to intra-particle diffusion effects.

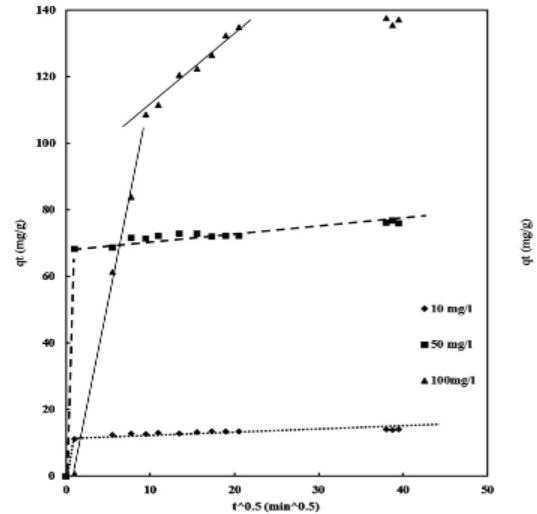
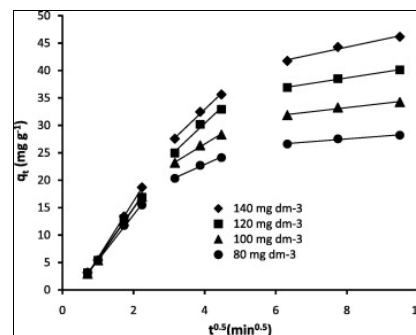


Fig. 5b: Plots of intra-particle diffusion kinetic model for the biosorption of copper by garden grass (Reference [21]).

Another  $q_t$  against  $t^{0.5}$  plot shape was reported by Ofomaja [128] for the biosorption of lead onto *mansonia* wood sawdust where the plots showed three linear parts indicating the involvement of three steps in the biosorption process (Fig.5c). The first, sharper stage can be attributed to the diffusion of biosorbate through the solution to the external surface of the biosorbent or the boundary layer diffusion of the biosorbate molecules. The second stage describes the gradual biosorption, where intraparticle diffusion is rate-limiting and the third stage is attributed to the final equilibrium for which the intraparticle diffusion starts to slow down due to extremely low biosorbate concentration left in solution. The three stages in the plot suggest that the biosorption process occurs by surface biosorption and intraparticle diffusion (meso- and micropores).



**Fig. 5c:** Intraparticle diffusion treatment of lead(II) onto *mansonia* wood sawdust at various initial lead(II) concentrations. Biosorbent dose: 2 g dm<sup>-3</sup>; solution pH: 5.0; agitation speed: 200 rpm; temperature: 299 K (Reference [128]).

This kind of multi-linearity in the shape of the intraparticle diffusion plot was also observed for the biosorption of copper ions onto sunflower hulls [25], the biosorption of Cu(II), Cd(II) and Pb(II) by *Phormidium* sp.-dominated mat [108], Cd(II) biosorption by native grapefruit biomass [32], the biosorption of Cu(II), Cd(II) and Pb(II) onto *Acacia leucocephala* bark powder [22], etc.

## 5. Biosorption equilibrium isotherms

The equilibrium relationships between adsorbent and adsorbate are best explained by sorption isotherms [129]. The biosorption isotherms describe the relationship between the mass of the adsorbed component per biosorbent mass and the concentration of this component in the solution. Determination of equilibrium parameters provides important information that allows for future design of adsorption systems [17]. Biosorption isotherms are characterized by definite parameters, which express the surface properties and affinity of the biosorbent and can also be used to compare the biosorptive capacities of the biosorbent for different pollutants [52] and [97].

Several equilibrium isotherm models were employed to fit the biosorption experimental data in order to study the nature of adsorption process. These include two parameters isotherms such as the Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and three parameters isotherms such as the Sips and Redlich–Peterson.

### 5.1. Langmuir isotherm

The Langmuir isotherm model assumes a surface with homogeneous binding sites, equivalent sorption energies, and no interaction between sorbed species [48]. In this model once a site is filled, no further sorption can take place at that site. As such, the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved [28]. The Langmuir equation developed by Irving Langmuir in 1916 [130] is represented by:  $C_{eq} / Q_{eq} = 1/b Q_{max} + C_{eq} / Q_{max}$ ; where  $Q_{max}$  (mg/g) is the maximum amount of metal ion per unit weight of biosorbent to form a complete monolayer on the surface bound at high  $C_{eq}$ , and  $b$  (l/ mg) is the Langmuir constant related to the energy of adsorption. The  $Q_{max}$  and  $b$  can be determined from the linear plot of  $C_{eq} / Q_{eq}$  versus  $C_{eq}$  [114].

The essential characteristic of the Langmuir isotherm may be expressed in terms of dimensionless separation parameter  $R_L = 1/ (1 + b C_0)$ , which is indicative of the isotherm shape that predicts whether an adsorption system is favourable or

unfavourable [114], The adsorption process as a function of  $R_L$  may be described as: Unfavorable when  $R_L > 1$ ; Linear when  $R_L = 1$ ; Favorable when  $0 < R_L < 1$ ; Irreversible when  $R_L = 0$ .

### 5.2. Freundlich isotherm

The Freundlich isotherm model applies to adsorption on heterogeneous surfaces with the interaction between adsorbed molecules, and the application of the Freundlich equation also suggests that sorption energy exponentially decreases on completion of the sorption centers of an adsorbent [28]. The empirical Freundlich equation [131] based on sorption on a heterogeneous surface is given as:  $\log Q = \log K_f + (1/n) \log C_e$ ; where ( $K_f$ ) and ( $n$ ) are the Freundlich constants characteristic of the system and are indicators of adsorption capacity and adsorption intensity, respectively [114].

The Freundlich equilibrium constants are usually determined from the plots of  $\log Q_{eq}$  versus  $\log C_{eq}$ . The  $n$  value indicates the degree of nonlinearity between solution concentration and adsorption as follows: if  $n = 1$ , then adsorption is linear; if  $n < 1$ , then adsorption is a chemical process; if  $n > 1$ , then adsorption is a physical process [28].

### 5.3. Temkin isotherm

The Temkin isotherm model [121, 132] suggests an equal distribution of binding energies over a number of exchange sites on the surface. The linear form of the Temkin isotherm can be written as [132]:  $q_e = B \ln A + B \ln C_e$ ; where  $B$  is equal to  $RT/b$  with  $R$  being the universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) and  $T$  being the absolute temperature in Kelvin.  $A$  is the equilibrium binding constant and  $B$  corresponds to the heat of sorption.

### 5.4. Dubinin-Radushkevich (D-R) isotherm

The D–R isotherm model is a semi-empirical equation where adsorption follows a pore filling mechanism. It assumes that the adsorption has a multilayer character, involves van der Waals forces and is applicable for physical adsorption processes [125, 133]. The linear form of D–R isotherm model is expressed as:  $\ln q_e = \ln q_d - \beta \epsilon^2$ , where  $q_d$  is the D–R constant (mg g<sup>-1</sup>),  $\beta$  is the constant related to free energy and  $\epsilon$  is the Polanyi potential which is defined as:  $\epsilon = RT \ln[1+1/C_e]$  noting that the universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) and  $T$  being the absolute temperature in Kelvin..

### 5.5. Sips isotherm

Sips [64,134] proposed an empirical isotherm equation, also known as Langmuir–Freundlich isotherm, which is often

expressed as:  $q_e = K_s C_e^{n_s} / (1 + a_s C_e^{n_s})$ , where  $K_s$  is the Sips constant ( $\text{Lmg}^{-1}$ ),  $a_s$  is the affinity coefficient ( $\text{Lmg}^{-1}$ ) and  $n_s$  is the heterogeneity coefficient. At low sorbate concentrations it effectively reduces to a Freundlich isotherm and thus does not obey Henry's law. At high sorbate concentrations, it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm.

### 5.6. Redlich–Peterson isotherm

The three parameters R-P isotherm incorporate three parameters and can be applied either in homogenous or heterogeneous systems [135,136]. The linear form of this isotherm is presented by:  $\ln [(AC_e/q_e) - 1] = g \ln(C_e) + \ln(B)$ , where A, B and g ( $0 < g < 1$ ) are the three isotherm constants. For a high concentration, the isotherm equation reduces to the Freundlich isotherm. In the case that  $g = 1$ , it will reduce to the Langmuir equation.

When reviewing the applicability of the different isotherms to fit the metal ions biosorption data, we have found that there is no general or even almost general trend. While some authors agreed for the better use of Langmuir model in describing metal ions biosorption [5, 49, 68, 97] other authors disagreed with this and found that the Freundlich model was the best [27, 30, 53]. Sometimes it was also noticed that some researchers suggested the applicability of more than one isotherm model [21, 119]. From the articles published between 2010 and 2013 we summarized the different trends reported by the researchers examining the isothermal modeling of their biosorption data.

Tuzen and Sari, [97] found that the coefficient of determination ( $R^2$ ) for the biosorption of selenium using green algae (*Cladophora hutchinsiae*) was 0.9956 indicating that the biosorption of the selenium ions onto *C. hutchinsiae* biomass fitted well the Langmuir model. These authors stated that in other words, the sorption of selenium using *C. hutchinsiae* was taken place at the functional groups/binding sites on the surface of the biomass which is regarded as monolayer biosorption. Biosorption isotherm data of chromium onto mango and neem sawdust at various initial metal concentrations were in good agreement with the Langmuir isotherm [5]. The Langmuir model fitted well the biosorption of lead and copper ions onto the green algae species, *Spirogyra* and *Cladophora* [49]. The biosorption of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  on *Caulerpa lentillifera* biomass correlated well with the Langmuir isotherm ( $R^2 > 0.99$ ) [137].

In the work of Bulgariu and Bulgariu, [52], the Langmuir model best-fitted the equilibrium data for the biosorption of Pb(II), Cd(II), and Co(II) on green algae waste biomass. These authors also found that the maximum biosorption capacity, which is a measure of the adsorption capacity to form a monolayer, increase in the order:  $\text{Pb(II)} > \text{Cd(II)} > \text{Co(II)}$ . Cobalt and cadmium biosorption performance by freeze-dried cells of *R. leguminosarum* bv. *viciae* STDF-Egypt19 biomass was estimated using biosorption equilibrium

measurements and the data were found to fit well with the Langmuir model [68].

The experimental data for the biosorption of Ni(II) ions onto sugarcane bagasse turned out good fits with Langmuir isotherm ( $R^2 > 0.99$ ). Therefore a chemisorption controlled mechanism can be postulated as the mechanism governing the biosorption process [10]. The Langmuir model fitted the equilibrium data for palladium(Pd(II)) and platinum (Pt(IV)) biosorption onto Indian almond leaf biomass (*Terminalia catappa* L.) better than the Freundlich isotherm [34].

The applicability of Langmuir model in the study of [20] for fitting the experimental data of the simultaneous biosorption of  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  ions onto *Trichoderma reesei* showed that the biosorption follows this model.

The experimental data obtained for the biosorption of copper(II), zinc(II), cadmium(II) and lead(II) from aqueous solutions by dead *Avena fatua* biomass were best described by the Langmuir model [29]. Langmuir model exhibited the best fit to experimental data of nickel biosorption by *Litchi chinensis* seeds [18]. The Langmuir sorption isotherm model correlated best with the U(IV) biosorption equilibrium data using rice husk for the 10–100 mg/ L concentration range [121].

The suitability of the Langmuir model for fitting the biosorption data of metal ions in the was attributed according to Meena et al. [138] attributed to three main causes: (i) the formation of monolayer coverage on the surface of biosorbent with minimal interaction among molecules of substrate, (ii) immobile and localized adsorption, and (iii) all sites having equal adsorption energies.

In contrary to those researchers that have proposed the good fit of the Langmuir model to the biosorption data of metal ions onto various biomasses, other researchers reported the Freundlich isotherm to best fit their biosorption data.

Pang et al. [81] found that the adsorption process of uranium onto non-living biomass of *Penicillium citrinum* could be well defined by both the Langmuir and Freundlich isotherms, however, Freundlich isotherm displayed a better fitting model than Langmuir isotherm. Chong et al., [27] found that the adsorption of Cu(II) and Pb(II) ions by oil palm shell showed a slightly better fit with the Freundlich compared to Langmuir. The Freundlich isotherm also had the best fit for cadmium biosorption using citrus peels [139]; cadmium and nickel biosorption onto grapefruit peel [30]; Cd(II) and Pb(II) biosorption onto the biomass of the blue green alga *Anabaena sphaerica* [53].

Other authors confirmed the more adequacy of the three parameters isotherms to explain their biosorption data. Hossain et al. [21] found that both the SIP and Redlich–Peterson isotherms better fitted with the experimental data of copper (II) removal by garden grass than the Langmuir and Freundlich models. The sorption data of lead on *Aspergillus versicolor* biomass were found to be best fitted to the Redlich–Peterson model indicating that the adsorption mechanism is a hybrid one and does not follow the ideal monolayer adsorption

behavior [80]. The equilibrium sorption data for the removal of Ni(II) ions by *Saccharum bengalense* plant biomass were better fitted to Langmuir and Sips isotherm model than any other model [119]. The Sips isotherm (Langmuir-Freundlich model) provided the closest fit to the equilibrium experimental data of cadmium biosorption using *Acidiphilium symbioticum* indicating that both physical and chemical sorption takes place simultaneously [140]. Sips isotherm was most accurately fitted to the equilibrium data of the biosorption of Cr(III) and Cu(II) by using soybean meal waste [141]. The best fit of this combined isotherm model confirms that metal biosorption continues beyond the first layer, there is a significant vertical interaction between the biosorbent and metal ions, resulting in overlapping multi-layer biosorption [142].

## 6. Application of biosorption for real wastewater treatment: case studies

Several authors attempted to apply their pilot biosorption experimental results to real wastewater samples in order to move from the experiment to the application in real world. We are summarizing the wastewater sampling protocols as well as some case studies describing the successful application of biosorption process to treat polluted water.

In order to demonstrate the practical application of the biosorption process, Vinodhini et al. [5] performed column experiment using *neem* sawdust to treat raw tannery wastewater sample collected from a common effluent treatment plant in India. The results showed that a dose of 20 g biosorbent was sufficient to achieve 99% chromium removal from wastewater volume of 1.5 L.

In order to determine the effectiveness of gooseberry fruit (*emblica officinalis*) biomass to remove copper ions from real wastewater; Rao and Ikram [15] collected electroplating wastewater from a local electroplating plant in Aligarh city. The results showed that 65% removal of Cu(II) could be achieved in batch mode and 97.6% in column process.

Ay et al. [31] evaluated the potential performance of the biomass of *Punica granatum L.* peels for the removal of lead (II) ions from real wastewater samples collected from metal processing factories in Turkey. The removal lead (II) ions at the optimum experimental conditions obtained during the batch experiment was found to be 98.07%.

Effluent samples were collected from El-Fayoum-Egypt for chemical production company to evaluate the efficiency of four algal biomasses to remove metal ions from wastewater [45]. The efficiencies of *C. mediterranea*, *G. oblongata*, *J. rubens*, and *P. capillacea* biomasses to remove metal ions ranged from 57% to 94% at a biomass dosage 10 g/L, pH 5 and contact time 60 min.

Javaid et al. [76] studied the potential use of *Pleurotus ostreatus* biomass for the removal of heavy metals from real

industrial effluents of electroplating. The results revealed that single metal removal efficiencies by the fungal biomass were 46.01, 59.22, 9.1 and 9.4% for Cu(II), Ni(II), Zn(II) and Cr(VI), respectively.

Bairagi et al. [80] determined the efficiency of *Aspergillus versicolor* biomass to remove lead from an actual system using effluent from battery industries located in Northern region of Kolkata, India. The percentage removal of lead from industrial effluent was 86% after adjusting the solution pH to 5.

The efficacy of sugarcane bagasse for the removal of chromium from tannery wastewater was evaluated by Ullah et al. [100]. In this respect, wastewater sample was obtained from a local tanning plant (Kasur, Pakistan). At the optimum conditions pre-determined during the batch biosorption studies; the maximum chromium removal from wastewater was 73%. Natural adsorbents including rice straw, rice husk, rice bran and water hyacinth roots were tested for their capability of removing copper ions from electroplating wastewater collected from Kolkata, west India. Under optimum batch conditions the results indicated that all biosorbents were effective in reducing the Cu(II) ions concentration with hyacinth roots being the most suitable [143].

## Conclusions

In the present work we aimed to highlight the “biosorption” process through the review of the recently published studies concerning the use of natural biomasses for metal ions removal from aqueous solutions:

- Waste biomasses from agricultural, fungal, bacterial and algal origins could be developed onto costly effective and environmental friendly biosorbents for metal ions removal from aqueous solutions. The biomass materials were proven to contain many “effective” functional groups that positively contribute to the metal ions biosorption process.
- Several experimental operating parameters have been found to influence the biosorption process including the solution pH, contact time, biosorbent dose and metal ion concentration.
- The pH of the solution was proven to be one of the most important factors affecting metal ions biosorption. The solution pH affects metal ion solubility as well as biosorbent total charge. The removal of metal ions is almost negligible at highly acidic pH values and increases by increasing the solution pH up to a certain limit.
- It has been generally found that the biosorption capacity increases as the initial metal ion concentration in the solution increases and on the other hand it is reduced when the biomass dosage increases.
- The kinetics of metal ions biosorption usually was found to be best described by the “pseudo-second order”

model suggesting that the rate limiting step in adsorption of metal ions could be chemisorption.

- The intraparticle diffusion mechanism was generally accepted to describe the mechanism of metal ions biosorption.
- The isothermal models including the Langmuir, Freundlich, Temkin, Sips, R-D and others have been widely employed for modeling the biosorption process.
- Several case studies have been reported for elucidating the successful application of biosorption for the treatment of real wastewater effluents.

It can be said that biosorption offers a great opportunity for a clean, cheap, and high effective process for metal ions removal from polluted water.

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