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Cu(II) removal from aqueous solutions: A Review

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ABSTRACT: Copper is a widely known toxic as well as poisonous metal to the living organism with a permissible concentration of 50 µg/litre in aqueous solutions. It is necessary to provide a suitable, environment friendly and cost effective copper removal process to save the world. The biosorption technique was found to be an effective method for the treatment and removal of copper from aqueous solution. The use of eco-friendly and low-cost biosorbent as well as biosorbent regeneration are the effective means of using biosorption techniques for the removal of copper from aqueous solutions. However, this review present the various techniques used in the treatment and removal of copper from aqueous solution with emphasis on biosorption technique.

Keywords: Biosorption, Copper (II) ions, ion exchange, adsorption, aqueous solutions.

INTRODUCTION

Copper is a metallic element that occurs naturally as a free metal, or associated with other elements in compounds that comprise of various minerals. Most copper compounds occur in +1 Cu(I) and +2 Cu(II) valence states. Copper (Cu) and its alloys are used extensively in domestic and industrial applications, (Stern *et al.*, 2007) and it is an essential trace element for human health that plays an important role in carbohydrate and lipid metabolism as well as in the maintenance of heart and blood vessel activity, but it is potentially toxic as well like all other heavy metals when in excess. The excessive amount of Cu(II) in the environment can cause serious health issues such as nausea, headache, dizziness, respiratory difficulty, hemolytic anemia, massive gastrointestinal bleeding, liver & kidney failure and even death. The US EPA (1991) has established 50 µg/litre as the practical quantification limit for copper in drinking water. Copper may be found as a contaminant in food, especially shellfish, liver, mushrooms, nuts, and chocolate. Elevated environmental levels of Cu(II) come from variety of sources, such as mining, metal cleaning, plating baths, pulp, paper and paper board mills, refineries, fertilizer industries etc. (Zahra, 2014). Unfortunately, Cu(II) is a persistent, bioaccumulative and toxic chemical that does not readily break down in the environment and is not easily metabolized (Khraisheh, *et al.*, 2004). Due to the toxic nature of copper to the environment, various techniques have been employed in order to remove the metal from the pollutants especially the aqueous solutions. Some of the methods include precipitation, ion exchange, adsorption/biosorption processes among others. However, this paper reviews the various methods of Cu(II) ions removal from aqueous solution with emphasis on biosorption technique.

DIFFERENT TECHNIQUES FOR COPPER REMOVAL

1. Precipitation-Coagulation and Flocculation: The easiest physical and chemical method of treatment that removes metal ions from wastewater by gravity is precipitation. Hydroxide or sulphides are the most common chemicals used as a result of their ability of forming precipitates that are insoluble and can be easily adsorbed on the particulate surfaces. This speeds up the rate of agglomeration there by forming sludge which can then be removed through physical process such as flotation, filtration or sedimentation (Metcalf and Eddy, 1979).

Normally, two steps are followed in the agglomeration of particles. In the first step, the forces that are in charge for the particles to be stable are lowered as a result of the addition of chemicals and in the second step, as a result of mixing due to mechanical action the particles collide there by resulting in agglomeration. Coagulants are the general name giving to the chemicals used and equipment's specifically design for their application need to be in place so as to allow easy mixing of the coagulant chemicals with the water. Also destabilisation of the particles known as flocculation is carried out so as to increase the rate formation of the agglomerate (Montgomery, 1985).

The hydroxide precipitation and coagulation-flocculation methods were used by Fongmoi *et al*., (2009) to treat wastewater containing lead, zinc, copper, and iron. The concentrations of heavy metals in the synthetic wastewater range from 1 to 14 mg/L for lead, 5-90 mg/L for zinc, 3 to 90 mg/L for copper and 5 to 45 mg/L for iron. Individual Zn(II) and Cu(II) with concentrations below 90 mg/L and Fe(III) with concentrations below 45 mg/L were removed up to 99% by the precipitation method in the pH range of 8.7 to 9.6, 8.1 to 11.1, and 6.2 to 7.1, respectively.

2. Chemical Precipitation: Chemical precipitation is another method used for the treatment wastewater. In this method chemicals are added to the waste water which then forms particles that settle and the contaminants can be removed by decantation (Edward, 1995). pH is one factor that chemical precipitation depends on the process of heavy metals removal from waste water. pH adjustment is not just for neutralisation purpose only but also a process that aid the removal of unwanted substances from the waste effluent. If the pH of waste water containing toxic metals is adjusted properly, the ability of the toxic metals to be soluble in the waste water is reduced, thereby making the possibility of the precipitate to settle and then filtered. Normally, lime, $Ca(OH)_2$ and caustic soda, (NaOH) are used for the chemical precipitation to from hydroxides of metal.

The removal of Cu(II) ions from waste waters by the use of 20% (sodium carbonate) Na_2CO_3 and 15% caustic soda (NaOH) solutions as agents of precipitation was studied by Negrea *et al.*,(2008). Numerous process of precipitation were studied: the reliance of pH on reaction mass and also volume of precipitating chemical used, the increase of the volume with time and the dependency of the pH on the concentration of copper.

The hydroxides of metals are basically insoluble in solutions and their solubility has a minimum level of pH. Different metals have different hydroxide precipitation values as shown in Table 1.

Table 1: Hydroxide precipitation values for different metals

Metals	**Tin**	**Iron**	**Aluminium**	**Lead**	**Copper**	**Chromium**	**Zinc**	**Nickel**	**Cadmium**
pH Concentration	1.0-4.5	4.3	5.2	6.3	7.1-7.3	6.5-7.3	8.3-8.5	9.2-9.4	9.7

Source: (Montgomery, 1985).

If different metal ions are present in a wastewater, it is often very difficult for the precipitation to be controlled; this makes it necessary to carry out more than one precipitation process at different pH values for an effective removal of the various metals. The process of metal removal by using hydroxide lime is the most common method use, but likewise precipitation using sulphides can also be used to remove metals from the effluent even at a lower concentration (Montgomery, 1985).

3. Chemical Oxidation/Reduction: Another chemical treatment that is very important substitute for heavy metals removal is redox reaction (oxidation and reduction reaction). Oxidation is the process of removing electrons from ion, molecules or atom while oxidation is their addition. These two reactions happen to take place in one single reaction there by formulating the name redox reaction. The process of hexavalant chromium reduction to trivalent chromium in large scale electroplating system is the most common and important reduction process been used and normally, sulphur dioxide is used as a reducing agent. Cyanide waste which is also found in metal finishing industries is also treated using oxidation in which alkaline chlorination is used to convert it into less toxic cyanite and then another chlorination to oxidise it to nitrogen and carbon dioxide gas. The chlorination normally takes place at a pH greater than 10 (Dojlido, 1993).

4. Ion Exchange: Ion exchange is a treatment method in which ions can be transferred from a solid phase to liquid phase or liquid phase to solid phase and it is a physical-chemical process mainly used in the treatment of hardness. The ions are normally held by an electrostatic force on the solids surface which is then exchange for ions that are in a solution and in contact with the solid surface. The exchange of ions takes occurs on the solid surface there by classifying the process as sorption process which uses chemical and electrical mechanism of ions exchange between the solids and the liquid solution. Both natural and synthetic ion exchange mechanism uses group of ions that are maintained by electro neutrality of the opposite charge ions (Montgomery, 1985).

Ion exchange treatment method is widely applied in treatment of permanent hardness of Ca^{2+} or Mg^{2+} for both industrial and domestic water as well as complete demineralisation of industrial water. The hardness removal known as softening normally replace magnesium or calcium ions with sodium ions. But for demineralisation, two steps are involved. In the first step H^+ ions are been replaced with all cations in a cation exchanger, and secondly $OH^-$are replaced with anions in an anion exchanger. The treatments of metals like lead, uranium, gold, copper and silver and for pharmaceutical industries, hospitals and laboratories and also in nuclear power reactors are other areas where ion exchange is applicable (Metcalf and Eddy, 1979).

Ion Exchange technique is preferred because of low sludge generation in comparism to other treatment methods and has better removal efficiency. Gaikwad *et al.*, (2010) carry out a factorial design of experiments to study the effect of pH, flow rate, height of bed and concentration of initial copper metal. The metal removal efficiency was determined after 100 minutes of the treatment.

5. Adsorption: “Adsorption is the ability of the adsorbate to adhere or attach to the adsorbent. It is a well established technology to remove dilute pollutants as well as to recover valuable products from aqueous streams” (Igwe and Abia, 2006).

It has also been applied in the recovery of some biological materials, organic compounds and metals and has the tendency for the solid surface to be covered with one or more layers of molecules attracted to the surface from its gaseous or liquid surrounding (Alan *et al.*, 2007). On an industrial scale, adsorption has played a vital role in the process of purification and separation over the last decades. Purification, such as removal of hydrogen sulphide (H_2S) and obnoxious fumes as well as removal of organic compounds from wastewater is one of the earliest applications of adsorption. Other applications are odour and colours removal from edible oils, decolourisation in the sugar industry, solute removal in tobacco manufacturing and removal of non-useful hydrocarbons in oil refining (Mckay, 1996).

Recently adsorption is been applied in the immobilisation of microbial cells and enzymes for conducting biochemical reaction as conversion of edible oils and wastewater treatment by biosorption (Ruthven, 1984). Adsorption has proven by many researches in the field of wastewater treatment as an effective and economically viable process (Ozturk and Kavak, 2005). In the application of adsorption, there are four major adsorbents that are widely applicable; these include activated silica gel, carbon, zeolites and activated alumina (Yang, 2003). The adsorbent which has been widely accepted is granular activated carbon. Among metal that have been removed by the granular activated carbon are copper, chromium and lead (Wase and Foster, 1997).

6. Biosorption: Biosorption is a physiochemical procedure that takes place in a certain biomass which allows it to accumulate and attach contaminants onto its cellular structure (Volesky, 1990).

Though the use of biomass for environmental purposes has been in practice for long, researchers are hopeful that the method will lead to an alternative economical method for the removal of heavy toxic substances from wastewater.

Even though biosorption and bioaccumulation are used synonymously, they are very different in how they do away with contaminants. Biosorption is a metabolically passive process, it does not need the use of energy, and the quantity of contaminants an adsorbent can take away, depends on the adsorbents composition and the kinetic equilibrium. Adsorption of the contaminants takes place on the structure of the cells, while bioaccumulation is energy dependent from living organisms and requires respiration. The contaminants are adsorbed and transferred within the cell surfaces (Velasquez and Jenny, 2009).

Biosorption have been seen as a new technology, and has been put to use in various applications for a very long time. The most commonly used of biosorption is activated carbon filters. They have the ability to filter water and air by the process of binding the contaminants to their porous and surface area structure. Activated carbon structure is generated as the result of charcoal treatment with oxygen. Biosorption technique is an alternative to other conventional methods of toxic heavy metals removal due to its low cost biosorbent and the ability to regenerate the biosorbent.

Biosorption have several applications in different industries especially the heavy metals processing ones, which include metal plating, metal processing, mining, battery manufacturing and metal finishing operations. Biosorption is a new alternative to other methods of heavy metal ions removal from wastewater especially industrial wastewater, due to their numerous disadvantages like high cost, partial metal removal and generation of sludge. Low cost, minimisation of sludge production, metal recovery, ability to regenerate the biosorbent and non-requirement of additional chemicals is what makes biosorption to have more advantages over other conventional methods (Kratochvil and Volesky, 1998).

Biosorbents for metal removal comes under different types of categories such as fungi, bacteria, industrial wastes, algae and agricultural waste (Vijayaraghavan and Yun, 2008). Hence, biosorption is a good applicant for the removal of toxic metals from large volume and lower concentration of aqueous solutions.

Copper metal removal by biosorption has so far been investigated throughout the last decades using different biosorbents (Veglio and Beolchini, 1997). The Table 2 shows the comparison of different technologies for the removal of heavy metals.

Table 2: Comparison of Technologies to Heavy Metals Removal

Method	***Advantage***	***Disadvantage***
Precipitation-coagulation	• Sludge Settling • Dewatering	• High cost • Large consumptions of chemicals
Chemical precipitation	• Simple • Inexpensive • Most metals can be removed	• Large Amount of Sludge produce • Disposal Problems.
Ion exchange	• High regeneration of materials • Metal selective	• High Cost • Less Number of Metals removed
Chemical Oxidation	• Increase possibility of contacts with contaminants	• Chemical handling and storage required
Adsorption	• large specific surface area	• Expensive • Large Amount of Sludge produce
Biosorption	• Low cost • possibility of metal recovery • regeneration and recycle of biosorbent	

6.1 Micro-organism based biosorbents: There are various microorganisms reported by different researcher that are effective in copper removal from aqueous solution, this include fungi, bacteria, algae and others (Vijayaraghavan and Yun, 2008).

Equilibrium and modelling study on copper biosorption by live cells of *Penicillium cyclopium* using fuzzy knowledge-based system was performed by Ianis *et al.,* (2006). The Cu(II) ion uptake was found to be highly rapid and strongly dependent on the biomass and Cu(II) ions concentration.

Jha *et al*, (2011) evaluated the efficiency of fungus and bacteria for the Cu(II) removal capacity. The result indicated that fungal strain *A. lentulus* absorb maximum amount of copper and have a high absorbing capacity.

Biosorption of Cu(II) ions using *Thiobacillus ferrooxidans* was found to be an effective bacterial bioaccumulation process. The result shows that bacteria has the ability to grow on Cu(II) ions concentration as high as 800 ppm (Hossain and Anantharaman, 2005).

Isotherm and thermodynamic studies of the biosorption of Cu(II) ions by *Erythrodontium barteri* were carried out by Babarinde *et al*, (2007) as a function of different parameters. The results of various studies show that *E. barteri*biomass has some capacity to absorb Cu(II) ions from solution. The study on contact time shows that the biosorption is time dependent and maximum biosorption was obtained after 150 min.

The biosorption behaviors and mechanisms of a novel exopolysaccharide (EPS), which is secreted by a mesophilic bacterium (named *Wangia profunda* (SM-A87)) isolated from deep-sea sediment, for heavy metals Cu(II) and Cd(II) have been studied by Zhou *et al.,* 2009 The optimum biosorption capacities were observed at pH 5.0 for Cu(II) with 48.0 mg/g and pH 6.0 for Cd(II) with 39.75 mg/g.

Continuous biosorption studies are of very important in evaluating the technological practicability of a process for real applications. The packed bed column has been a convenient, effective and most economical process of biosorption. Several research of batch biosorption of copper has been carried out by various researchers. However, very few researches exist on column studies for Cu(II) biosorption (Vijayaraghavan and Yun, 2008).

In a study carried out by Mukhopadhyay *et al*., (2008), Cu(II) biosorption was investigated in a column using pre-treated *Aspergillus niger as* biomass. The influence of flow rate, bed height and metal ion concentration of 10mg/l were measured. The column equilibrium capacity and the amount of metal loading on the biomass surface were evaluated. Based on the observation, pre-treatment of *Aspergillus niger* increases based on the enhanced activity of the surface reactive groups.

The ability of free and polysulphone immobilized biomass of *Arthrobacter sp*. to remove Cu(II) ions from aqueous solution were studied in batch and continuous systems by Hasan, and Srivastava (2009). The Langmuir and Freundlich isotherm models were applied to the data and was found to fit the sorption data indicating that sorption was monolayer and uptake capacity (Q) was 175.87 and 158.7 mg/g for free and immobilized biomass respectively at pH 5.0 and 30^0C temperature, which was also confirmed by a high correlation coefficient, a low RMSE and a low Chi-square value.

Among various biosorbents, algae have a high capacity of metal-bonding, most likely as a result of the abundant existence of various groups as hydroxyl, carboxyl, amino and sulphonic, groups. Batch studies were conducted by Gupta *et al*, (2006) to study the kinetics and isotherms of Cu(II) ions biosorption using green alga *spirogyra* species biomass. The studies show that *Spirogyra* species is an efficient adsorption material for Cu(II) removal.

The maximum capacity of Cu(II) biosorption have been found to be 133.3 mg Cu(II)/g of dry weight of biomass at an algal dose of 20 g/L in 120 min of contact time, with initial Cu(II) concentration of 150 mg/L and optimum pH of 5.

Vijayaraghavan *et al*., (2005) carried out the biosorption of copper, cobalt and nickel by marine green alga *Ulva reticulate* in a packed bed up-flow column. The experiment studied the effect of bed height and flow rate. It was found that at a bed height of 25 cm, the metal uptake capacity of *Ulva reticulata* for copper was 56.3 mg g^{-1}. Also the sorption capacity per unit bed volume of copper was found to be 2580 mg l^{-1}.

Also biomass of brown marine algae of *Sargassum fluitans* was used for the biosorption of Cu(II) by Kratochvil *et al.* (1997). Biomass pretreatment with 1% (w) solution of $CaCl_2$ and with 0.1 M HCl resulted in 75mg/g of Cu uptake

In another different study, using red alga (*Palmaria palmate) and* beer draff *(Brewery waste)* have been used for the removal of Cu(II). The highest maximum adsorption capacity derived from Langmuir isotherm was found as 12.7 mg/g and 9.01 mg/g for, red alga (*Palmaria palmate) and* beer draff *(Brewery waste)* at a pH of 5–6 (Yang *et al.*, 2011).

Sorption studies using the dead biomass of spirogyra spacie for copper removal were carried out by Bishnoi and Garima (2004) to study the influence and optimization of the biosorption of Cu(II). It was observed that spirogyra species possessed better specific uptake capacities for Cu(II).

Another study by Sivaprakash, *et al*. 2010 carry out Batch and continuous sorption studies to remove copper (II) from aqueous solution using marine alga, *Sargassum tenerrimum*. Maximum copper uptake of 174.23 mg/g was observed according to the Langmuir model at an initial pH of 6. The copper loaded biomass was eluted using 0.1 M HCl and no damage to the biosorbent was caused. Effects of operating parameters such as bed height and flow rate were studied in a packed column and the metal uptake decreased with increase in flow rate.

A basic investigation into the removal of copper ions from aqueous solutions by *Sargassum* sp. was conducted in batch conditions by Antunes *et al*., (2003). Results indicated that for shaking rates higher than 100 rpm no significant changes in copper accumulation were observed, as well as for pH values between 3.0 and 5.0. No marked effect on the biosorption of copper was detected for temperatures between 298 and 328K. The Langmuir model better represented the sorption process, in comparison to the model of Freundlich. The process followed a second order kinetics and its calculated activation energy was 5.2 kcal/mol. Due to its outstanding copper uptake capacity (1.48 mmol/g biomass) *Sargassum* sp. proved to be an excellent biomaterial for accumulating and recovering copper from industrial solutions.

6.2 Agricultural based biosorbents: Most agricultural based biosorbent are cheap and readily available and are composed of lignin and cellulose as the main constituents. A variety of functional groups are present in the binding process. The functional groups present in biomass molecules are: acetamido groups, carbonyl, phenolic, structural polysaccharides, amido, amino, sulphydryl carboxyl groups, alcohols and esters (Rao *et al*., 2010)

Sawdust, an inexpensive material has been utilized as an adsorbent for the removal of Cu(II) from waste water for their safe disposal by Ajmal *et al.*, (1998). The effects of contact time, pH, concentration, temperature, dose, particle size of the adsorbent and salinity on the removal of Cu(II) have been studied. The equilibrium nature of Cu(II) adsorption at different temperature (30±508C) has been described by the Freundlich and Langmuir isotherm and a tentative mechanism has been proposed. Also the results reported by Larous *et al*, (2005) explain the retention mechanism as an ion exchange process for binding the divalent metal ions to the sawdust.

Teak leaves (*TectonagrandisL.f)* are found to be good potential biosorbents for the removal of Cu(II) ions from aqueous solutions. Rathnakumar *et al*., (2009) studied the biosorption of Cu(II) ions using teak leaves. The experiments were carried out at different initial concentrations of Cu(II), biosorbent dosages, pH and temperature. It was noticed that the percentage bisorption of Cu (II) ions increases at lower concentrations of Cu (II) (0.2 g l^{-1}). This is due to the available sites for sorption at lower concentrations compared to the moles of metal ions present.

The capacity of wheat shell adsorption for Cu(II) was studied at different agitation speeds, pH and initial metal concentrations by Basci *et al*, (2004). The maximum efficiency at a pH of 5 and a 12.0 g/l of wheat shell concentration was found to be 99%.

The use of spent tea leaves as a cost effective and non-conventional adsorbent for the removal of Cu(II) ions was carried out by Bajpai and Jain, (2010). The biosorption capacity was found as 90.9 and 68.4 mg/g^{-1} at 27^0C and 37^0C as evaluated using the Langmuir isotherm.

The adsorption of copper in a batch and continuous mode using neem leaves has been carried out by (Febriana *et al.*, 2010). The maximum adsorption capacity of neem leaf powder was found to be 18.29 mg/g. Langmuir equation represents the adsorption equilibria better than Freundlich. Also thermodynamics data indicated that the adsorption process is spontaneous, irreversible and endothermic.

Another study conducted by Sulaiman *et al.* (2010), for biosorption of copper using oil palm leaves shows the adsorption capacity of copper to be 11.22mg/g at a temperature of 30^0C. The adsorption was found to be exothermic with the heat of adsorption as (ΔH) -39.84 KJ/mol.

The litter of natural trembling poplar (*Populus tremula*) forest (LNTPF) was used for the biosorption of Cu(II) ions in a batch adsorption experiments The efficiency of copper uptake by the used LNTPF increases with a rise of solution pH, adsorbent concentration, agitating speed, temperature, and with a decline of particle size and initial Cu(II) concentration. The biosorption process was very fast; 94% of Cu(II) removal occurred within 5 min and equilibrium was reached at around 30 minutes (Dundar *et al*, 2008).

Another study by (Huang, 2007), fish scales of Tilapia *Niloticalinnaeus* were used as adsorbent in the investigation of copper biosorption capabilities. This was carried out under different biosorbent to copper mass ratios and contact times. The results show that larger amounts of biosorbent added and longer contact times yielded higher biosorption percentage.

The effect of pH, biosolid dosage, initial copper concentration, and contact time on copper removal from aqueous solutions using biosolids (waste sludge cake) was investigated through batch experiments. The copper removal increased by time and initial metal concentrations, based on the observations, the main mechanism of copper removal should be the formation of insoluble complexes between Cu^{+2} and anionic species such as CO_3^{2-}, SO_4^{2-} and OH taking place in the structure of biosolids The biosolid was found as an efficient and economic material for the removal of copper from aqueous solutions. (Sarioglu *et al* 2007)

In order to get information about the sorption sites and mechanism responsible for the capture of metallic ions by the biomass of Maitenus truncate, Carvalho *et al.*, (2003) investigate the sorption of copper by dried leaves of Maitenus truncate, using Fourier transform infrared spectroscopy (FTIR) and electron paramagnetic resonance (EPR). From FTIR measurements, it was conclude that the presence of copper ions in the biomass affects the bands corresponding to CMC vibrations of carbon rings of the biomass

Pre-treatment of biosorbents by the use of different types of modifying agent such as base solutions (sodium carbonate, calcium and sodium hydroxide), organic and mineral acid solutions (Citric acid, tartaric acid, hydrochloric acid, nitric acid), organic compounds (formaldehyde, ethylenediamine, methanol), oxidizing agent (Hydrogen peroxide), dye (reactive orange) can extract soluble organic compounds and enhance chelating efficiency (Ngah and Hanafiah, 2008).

Studies on copper removal using rubber leaves that are chemically modified were carried out by Ngah and Hanafiah, (2008). The rubber leaves were modified using formaldehyde solution and the results shows efficient removal of the Cu(II) ions. Soluble organic compounds release was overcome since COD (chemical oxygen demand) values were very low after adsorption. Desorption experiments are important as they clarify the performance of adsorption, desorption experiment using 0.02 mol L^{-1} HCl, EDTA and HNO_3solutions shows that 80% of Cu(II) ions on the adsorbent were desorbed.

Acid-modified sawdust using hydrochloric acid (HCl) was found to be suitable for the removal of copper from artificial wastewater. The high adsorption capacity per unit cost makes this material a promising and economical alternative for biosorption (Argun *et al.*, 2007).

Biomodified Palm Shell biosorbent was evaluated in terms of adsorption capacity to remove copper and zinc metal ions from aqueous solutions. Comparison of the adsorption data of the biomodified and original palm shell activated carbon showed higher uptake of metal ions by the hybrid biosorbent. The highest capacity of the hybrid biosorbent was observed at pH 5 and comprised 22 mg/g and 19 mg/g for copper and zinc, respectively (Issabayeva and Aroua, 2011).

Cinnamomum camphora leaves powder (CLP) was investigated as a biosorbent for the removal of copper ions from aqueous solutions. The biosorbents before and after adsorption were measured by EDS and FT-

IR. Kinetic data and sorption equilibrium isotherms were carried out in batch process. The adsorption kinetic experiments revealed that there are three stages in the whole adsorption process.

It was found that Cu(II) adsorption onto CLP for different initial Cu(II) concentrations all followed pseudo-second order kinetics and were mainly controlled by the film diffusion mechanism. Batch equilibrium results at different temperatures suggest that Cu(II) adsorption onto CLP can be described perfectly with Langmuir isotherm model compared to Freundlich and D–R isotherm models, and the characteristic parameters for each adsorption isotherm were also determined. Thermodynamic parameters calculated show that the adsorption process has been found to be endothermic in nature. The analysis for the values of the mean free energies of adsorption (Ea), the Gibbs free energy and the effect of ionic strength all demonstrate that the whole adsorption process is mainly dominated by ion-exchange mechanism, accompanied by a certain amount of surface complexation. (Chen, *et al*., 2010).

The biosorption of Cu(II) from aqueous solutions by Pleurotus cornucopiae was investigated as a function of initial pH, contact time, initial metal ion concentration and biosorbent concentration Danıs (2010) The aim of the study was to understand the mechanism that govern Cu(II) removal and find a suitable equilibrium isotherm and kinetic model for Cu(II) removal in a batch reactor. The removal percentage of Cu(II) was increased with an increase in pH, biomass concentration and a decrease in Cu(II). Pleurotus cornucopiae exhibited the highest Cu(II) uptake of 25 mgg^{-1} of biomass at pH 5 in the presence of 100 mgL^{-1} Cu(II) at 298 ^{o}K.

The effect of chemical pretreatment on Cu(II) biosorption by *Marrubium globosum* subsp. *Globosum* leaves was carried out by Yazıcı, *et al.*, (2008). The results showed that pre-treating the biomass with alkali solutions (laundry detergent, sodium hydroxide and sodium bicarbonate, 0.5 M) improved the biosorption capacity of biomass (45.90, 45.78 and 43.91%, respectively) compared with raw biomass. Pre-treatment with sulfuric and nitric acid solutions, 0.5 M, increased the biosorption capacity of biomass by 11.82 and 10.18%, respectively, while there was no considerable change in the biosorption capacity of biomass (0.35%) after pretreatment with formic acid solution, 0.5 M.

Furthermore, sodium chloride and calcium chloride, 0.5 M, pretreatments resulted in the improvement in biosorption capacity of biomass (31.38 and 26.69%, respectively). FT-IR analysis revealed that hydroxyl and carboxyl functional groups were mainly responsible for Cu(II) biosorption.

Copper uptake by sour orange residue (SOR) was reported by Khormaei *et al*., (2007). Equilibrium isotherms and kinetics were obtained and the effects of solution pH, temperature, and particle size were studied in batch experiments. Maximum uptake was observed at pH 5. With an increase in temperature from 20 to 50^{o}C, copper removal decreased by about 20%. Additional chemical treatment of the biosorbent by NaOH, increased the biosorption capacity.

In another study by Lu *et al.*, (2008), a series of orange peel cellulose biosorbents has been specifically prepared by different chemical modifications to understand the mechanism of copper adsorption from chloride solutions. The different biosorbents and raw orange peels were characterized using elemental analysis and Fourier transform infrared spectroscopy (FTIR). The acidic and basic sites and pH of zero charge were also determined. The influences of pH, contact time, initial copper concentration and solid/liquid ratio on copper removal were examined. The maximum adsorption capacity of copper was 1.22 mol/kg, using orange peel esterified by 0.6 mol/L citric acid at 80 °C after 0.1 mol/L NaOH saponification.

The ability of chaff to adsorb heavy metal ions from aqueous solution was investigated in a fixed-bed column by Han *et al.*, (2005) the adsorption/desorption recycles of chaff were shown, and the results indicated that chaff could be recycled to remove heavy metal ions.

The Thomas model was applied to adsorption of copper and lead at different flow rate and different influent concentration to predict the breakthrough curves and to determine the characteristic parameters of the column useful for process design. The model was found suitable for describing the biosorption process of the dynamic behavior of the chaff column.

Table 3(a): Capacity of Cu(II) adsorption by Micro-organism based biosorbents

Adsorbent	Q mg/g	*Reference*
A. lentulus	500	Jha *et al*, (2011)
exopolysaccharide	48.0	Zhou *et al*., 2009
Aspergillus niger	13.4	Mukhopadhyay *et al*.,
Arthrobacter *sp*.	175.87	Hasan, and Srivastava (2009).
spirogyra species	133.30	Gupta *et al*, (2006)
Palmaria palmate	12.7/9.01	(Li *et al*., 2011).
Dead spirogyra species	34.94	Bishnoi and Garima (2004)
Ulva reticulate	74.63	Vijayaraghavan *et al*., (2005)
Sargassum fluitans	214	Kratochvil, *et al.* (1997)
Sargassum tenerrimum	174.23	Sivaprakash, *et al*., 2010
spirogyra species	133.30	Gupta *et al*, (2006)
Palmaria palmate	12.7/9.01	(Li *et al*., 2011).

Table 3(b): Capacity of Cu(II) adsorption by agricultural based biosorbents

Adsorbent	Q mg/g	*Reference*
Sawdust	15.50	Ajmal *et al*., (1998)
TectonagrandisL.f	166.78	Rathnakumar *et al*., (2009)
wheat shell	10.84	Basci *et al*., (2004)
Saltbush leaves	68.00	Sawalha *et al*., (2007
spent tea leaves	90.00	Bajpai and Jain, (2010)
Neem leaves	18.29	Febriana *et al*., (2010).
Oil palm leaves	11.2	Sulaiman *et al*., (2010)
Populus tremula	18.92	Dundar *et al*., (2008)
Tilapia *Niloticalinnaeus*	82	Huang, 2007
Maitenus truncate	25	Carvalho *et al*., (2003)
rubber leaves	8.71	Ngah and Hanafiah, (2008).
Acid-modified sawdust	3.62	(Argun *et al*., 2007).
Biomodified Palm Shell	22	(Issabayeva and Aroua, 2011)
Marrubium globosum	12.46	Yazıcı, *et al*., (2008).
sour orange residue	52.08	Khormaei *et al*., (2007).
Thuja orientalis	19.23	(Nuholgu and Oguz, 2003)
Cinnamomum camphora	16.76-17.87	(Chen *et al*., 2010)
Pleurotus Cornucopiae	25	Danis 2010
Chaff	1.98	Han *et al*., (2005)
Sawdust	3.742	Larous *et al*,

CONCLUSION

This review shows the various techniques used in the treatments and removal of copper from aqueous solution with preference to biosorption technique. There are various biosorption parameters studied to evaluate their effects on Cu(II) removal efficiency, some of which includes: contact time, pH, temperature and biosorbent concentrations. Evaluation of isothermic and thermodynamic parameters has also been outlined as important factors which can be use for scale up and process development from small scale batch process to a large continuous process. The major advantages of biosorption over other techniques include: eco-friendly, low-cost, regeneration/recycling and safe disposal of loaded biosorbent.

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