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Removal of copper ions Cu (II) from industrial wastewater: A review of removal methods

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Received: 10/Jan/2016 Accepted: 15/Mar/2016

Review article

ABSTRACT

Background and aims: Nowadays heavy metals are the environmental priority pollutants and are becoming as the most serious environmental problems. In recent years removing those from diverse industrial effluents and metal cleaning have been studied. The aim of the present study was to investigate the different methods for cooper removal of cooper ions from industrial wastewater.
Methods: This study was a review research. Data were collected from different database in various articles. The various methods for cooper removal from industrial effluents were compared to each other.
Results: The present study showed the various methods for cooper removal from industrial wastewater including chemical precipitation, ion exchange, membrane filtration, flotation, electrochemical treatments, coagulation/flocculation and adsorption. High efficiency, cost-effectiveness and easy handling are important factors in the selection of the most suitable treatment systems for industrial effluents.
Conclusion: Adsorption is recommended as an effective and economical method for maintaining of cooper ions from aqueous industrial wastes because of high efficiency, cost-effectiveness and simplicity.

Keywords: Heavy metal removal, Copper, Industrial wastewater.

INTRODUCTION

With the rapid development of industries, water resource scarcity, population growth, pollution of surface and groundwater by discharging toxic wastewater and subsequent diseases may raise the necessity of reusing and treatment of wastewater.[1] The removing of toxic heavy metal ions from sewage, especially in industrial and mining waste effluents, has been widely studied in recent years.[2] Heavy metals wastewaters are directly or indirectly discharged into the environment increasingly, especially in developing countries. Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic. Toxic heavy metals of particular concern in treatment of industrial wastewaters

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include zinc, copper, mercury, lead and chromium. The presence of heavy metal ions in the aquatic system causes serious health hazards to the human beings and also other living organisms.[3-5] The wastewater from these industries frequently contain considerable amount of copper ions, which spread into the environment through soil and aquatic streams and finally gets accumulated along the food chain causing health hazards to the human beings. Copper may be found as a contaminant in food, especially shellfish, liver, mushrooms, nuts, and chocolate.[6] Copper is micronutrient element and plays an important role in the bone formation together with certain proteins and enzymes, but it produces severe toxic effects at higher concentrations.[7,8] The excessive intake of copper ions by the human beings leads to the severe mucosal irritation and corrosion, hepatic and renal damage, widespread capillary damage, Severe gastro intestinal irritation, irritation of the central nervous system, and possible necrotic changes in the liver and kidney could occur. Although a limit of 2 mg/L was proposed by the World Health Organization as the provisional guideline value for copper content of drinking water.[9-11]

The excessive amounts of Cu (II) ions in fresh water resources and aquatic ecosystem damage the osmo-regulatory mechanism of the freshwater animals. United State Environmental Protection Agency (USEPA) has set its cooper ions permissible limits as 1.3 mg/L in industrial effluents.[12] Copper were discharged from the different industries such as metal cleaning and plating baths, paints and pigments, mining, smelting, petroleum refinering, rinses as brass, fertilizer, paper board, wood pulp and printed circuit board production.[13-15] In addition, copper is phytotoxic and indeed, has been used as an algaecide to control algal blooms. A variety of treatment technologies have been applied for the removal of cooper ions including chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation-flocculation, flotation and electrochemical technologies.[5,16,17] These methods for Cu^{2+} removal from wastewater are descripting briefly as follows:

Chemical precipitation is one of the commonly employed and conventional processes for heavy metals removal from wastewater including copper. Precipitation is widely used due to its simple and inexpensive nature. The conventional chemical precipitation processes include hydroxide and sulfide precipitation, Chelation/complexation. It is difficult to comply with stringent environmental regulations using conventional chemical precipitation process. Chelating precipitants, such as dimethyl thiocarbamate, diethyl thiocarbamate have also been shown the promising results regarding Cu (II) removal from wastewater.[16] In this context, the chemicals react with copper ions to form insoluble precipitates of hydroxide, carbonates and sulfide (OH^-, CO_3^- and S^{2-} respectively) which can be separated from water by sedimentation or filtration. Sulfide precipitation is considered to be more suitable as it removes large quantities of contaminants and witness less interference with the chelating agents being utilized (Figure 1).[18] Lime precipitation can be employed to treat effectively inorganic effluent with a metal concentration of higher than 1000 mg/L.[19] Potassium ethyl xanthate has also been found to treat wastewater containing 50-1000 mg/L Cu to permissible limits and the end-products, i.e. Cu-xanthate complexes can easily be handled and treated as non-hazardous materials. Although complexation through xanthate is widely used but still the safe disposal of precipitated metal xanthate is difficult to ensure.[20]

However, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge. Other drawbacks are its excessive sludge production that requires further treatment, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal.[19]

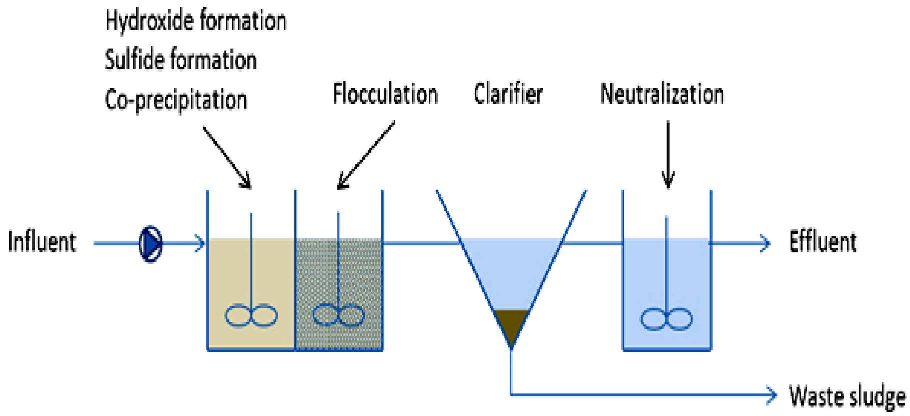

Figure 1: Co-precipitation method for copper ion removal from wastewater

Ion-exchange processes have been widely used to remove heavy metals from wastewater due to their many advantages, such as high treatment capacity, high removal efficiency and fast kinetics.[21] Ion-exchange resin, either synthetic or natural solid resin, has the specific ability to exchange its cations with the metals in the wastewater. Among the materials used in ion-exchange processes, synthetic resins are commonly preferred as they are effective to nearly remove the heavy metals from the solution.[22]

Although ion exchange is a well-established and effective technique; however, resin needs to be rejuvenated on a regular basis in order to maintain the effective removal of the targeted pollutants which can increase the cost of whole unit operation along with residual sludge production. Moreover ion exchange is highly sensitive to the pH of the solution (Figure 2).[23]

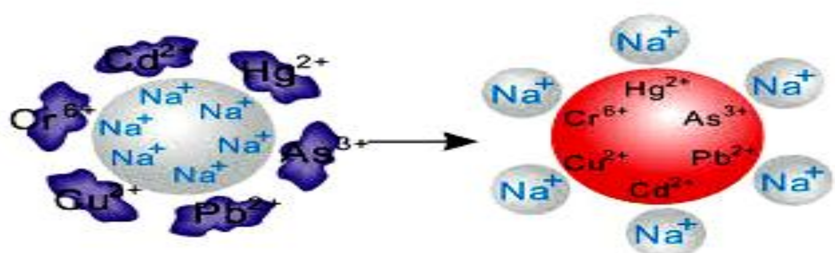

Figure 2: Diagram of ion exchange

Membrane filtration is a pressure driven separation process for Cu (II) which is based on the size exclusion and best performance (Figure 3). Nanofiltration, ultra-filtration, electrodialysis and reverse osmosis are some of the examples of the membrane filtration for the effective removal of Cu, Zn, Cd, and Cr from synthetic and real wastewater samples. The filtration process performance can be enhanced by treating the membranes with suitable chemical materials.[24,25] Ultra filtration is a trans membrane low pressure driven separation process based on particle size. It is an energy intensive process, which cannot be used alone because of the larger pore size of UF membrane than dissolved copper ion.[26] Nanofiltration (NF) is the intermediate process between UF and RO. NF is a promising technology for the rejection of heavy metalions such as cooper.[27]

Electrodialysis is a kind of membrane separation process in which the ionized species in the aqueous solution are passed following the application of an electric potential. The anions present in solution move towards anode while the cations move towards the cathode crossing the differently designed membranes. The process efficiency is romoted by increasing voltage and temperature; however, it decreases with the increasing flow rates.[28]

Reuse of wastewater, helpful in achieving stringent effluent limits, recovery of valuable material, prevention of environmental damages are some of the major advantages of this technique, but problems such as high cost, process complexity, membrane fouling and low permeate flux have limited their use in cooper ions removal.[16,23]

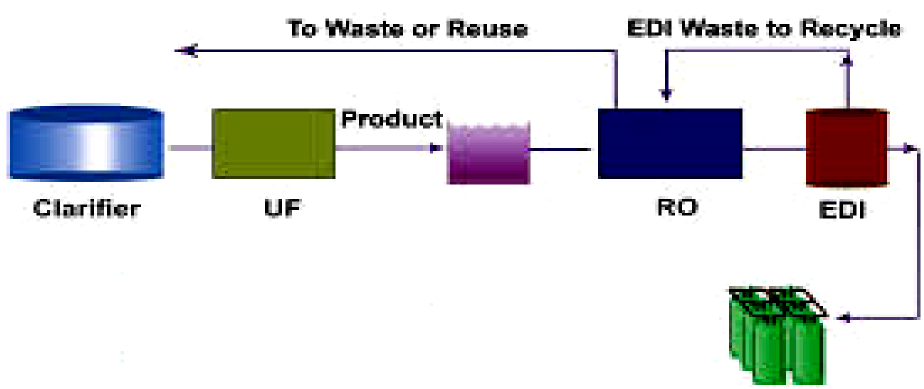

Figure 3: Usage of membrane filtration technology for copper treatment

It is a separation technique of hetero-phase system using air bubbles. Resultant flocs are collected and removed at the top.[29] Dissolved air flotation (DAF), ion flotation and precipitation flotation are the main flotation processes for the removal of metal ions from solution. Among the various types of flotation, DAF is the most commonly used for the treatment of metal-contaminated wastewater. It is to allow micro-bubbles of air to attach to the suspended particles in the water, developing agglomerates with lower density than water, causing the flocs to rise through the water and accumulating at the surface where they can be removed as sludge (Figure 4).[30] Ion flotation has been shown a promising method for the removal of heavy metal ions from wastewaters. The process of ion flotation is based on imparting the ionic metal species in wastewaters hydrophobic by use of surfactants and subsequent removal of these hydrophobic species by air bubbles.[31] Precipitate flotation process is another alternative of flotation method, based on the formation of precipitate and subsequent removal by attachment to air bubbles. Depending on the concentration of the metal in solution, the precipitation may proceed via metal hydroxide formation or as a salt with a specific anion (sulfide, carbonate, etc).[32] Flotation offers several advantages over the more conventional methods, such as high metal selectivity, high removal efficiency, high overflow rates, low detention periods, low operating cost and production of more concentrated sludge but the disadvantages involve high initial capital cost, high maintenance and operation costs.[16,33]

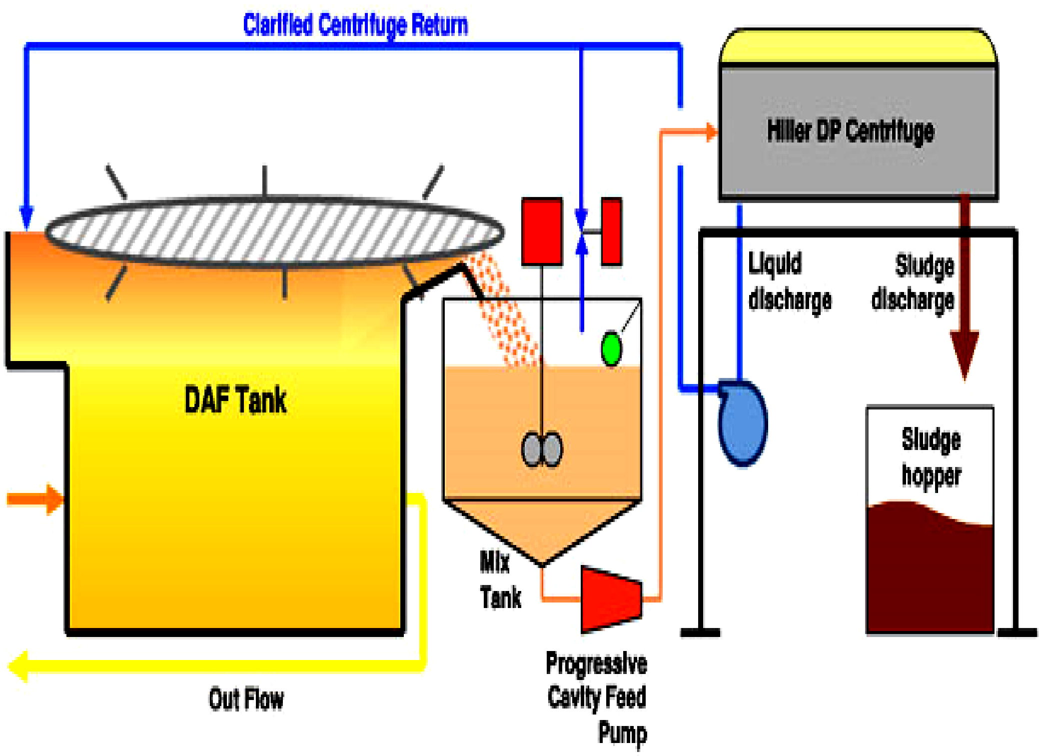

Figure 4: Cu removal using dissolved air flotation method

Electrochemical treatment is electrically supplemented with some other techniques like ultra filtration. It is being widely used to remove toxic heavy metal ions from wastewaters. However, it requires relatively large capital investment to initiate the process supplemented by long term operational and maintenance costs and the expensive electric supply delimits its applicability. The electricity can be utilized in a number of ways, such as electrocoagulation, electrofloatation and electrodeposition.[23] They are regarded as rapid and well-controlled that require fewer chemicals, provide good reduction yields and produce less sludge.[16]

Electrocoagulation involves the generation of coagulants in situ by dissolving electrically either aluminum or iron ions from aluminum or iron electrodes. The metal ion generation takes place at the anode, and hydrogen gas is released from the cathode. The hydrogen gas can help to float the flocculated particles out of the water.[34]

Electroflotation is a solid/liquid separation process that floats pollutants to the surface of a water body by tiny bubbles of hydrogen and oxygen gases generated from water electrolysis.[35] Electro deposition is technology with no presence of the permanent residues for the separation of heavy metals.[36]

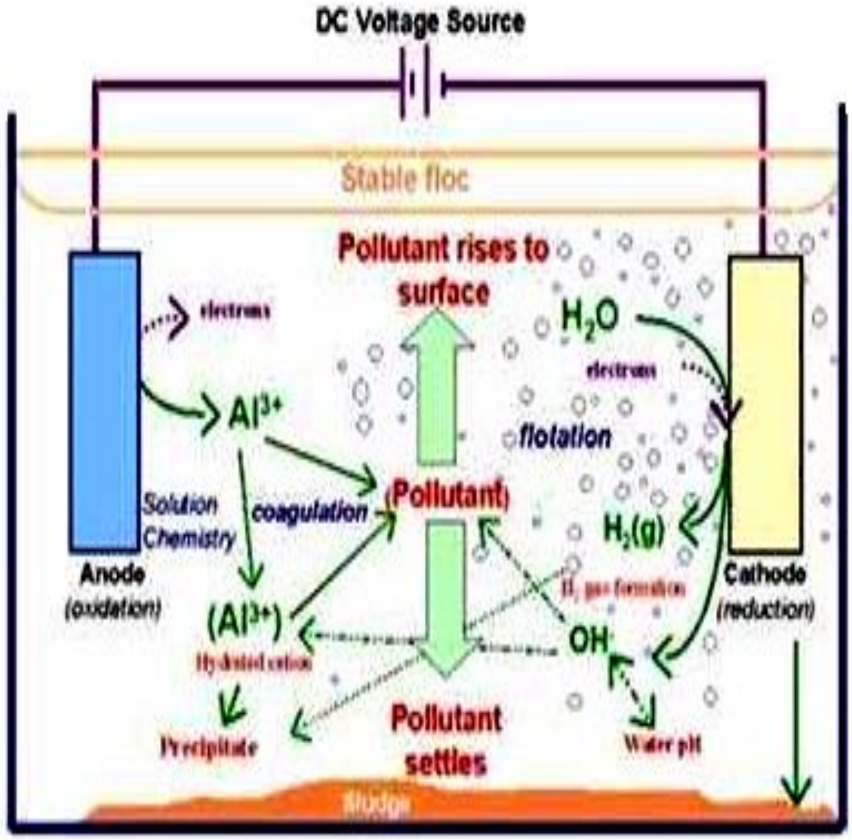

Figure 5: Electrochemical treatment for Cu removal

It is a two stepped process during which particles are destabilized at first by neutralizing the forces that keep them apart (coagulation) and subsequently the destabilized neutral particles are aggregated (flocculation) in a second step. Coagulants, such as alum, ferrous sulfate and ferric chloride is added to the wastewater to stabilize the colloids present in it and to promote the process of sedimentation which is followed by flocculation in order to develop large size flocs to make their easy removal (Figure 6). The effective pH is 11 for this removal process. The technique is not tagged to be environmentally sound and sustainable due to the operational cost and bulk of toxic sludge production.[24]

Many coagulants are widely used in the conventional wastewater treatment processes such as aluminum resulting in the effective removal of wastewater particulates and impurities by charge neutralization of particles and by enmeshment of the impurities on the formed amorphous metal hydroxide precipitates. Using coagulation-flocculation technique in removal of heavy metal from wastewater, the produced sludge has good sludge settling and dewatering characteristics. But this method involves chemical consumption and increased sludge volume generation. Therefore, coagulation-flocculation must be followed by other treatment techniques.[16]

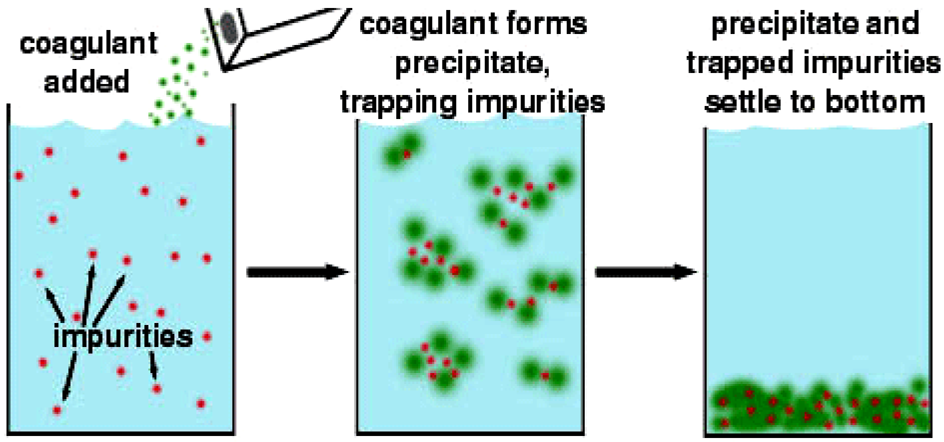

Figure 6: Cu removal using Coagulation/flocculation process

One of the most commonly used techniques involves the process of adsorption, which is the physical adhesion of chemicals onto the surface of solid. Bio adsorption is a good alternative to traditional processes. Widely available biopolymers are also being used for adsorption mainly because they are a cheap resource or a freely available resource.[37] Adsorption can be classified as physical adsorption and chemical adsorption. Physical adsorption is primarily due to Vander Waals forces and is a reversible occurrence. When the molecular forces of attraction between the substance and interface are greater than the forces of attraction between substance and the solvent, the substance will be adsorbed onto the adsorbent surface. In chemical adsorption or activated adsorption a chemical reaction occurs between the solids and the absorbed solute and the reaction is usually irreversible.[38]

Many adsorbents such as activated carbons, zeolites, clays, biomass, polymeric materials, low-cost, carbon nano-tubes and other adsorbents have been widely used for the removal of cooper ions from the wastewaters.[39-41] Presently, the application of nano-materials has emerged as a fast-developing, fascinating area of interest for removal of Cu (II) from industrial effluents because of unique characteristics of nano materials such as large surface area, a greater number of active sites, and low diffusion resistance for adsorbates. Low-cost materials, including alumina nano-powders. TiO_2 nano-rods, carbon nano-tubes, etc., have been used for the removal of Cu (II) from aqueous solutions and the experimental results suggested that the adsorption effect was quite well.[42,43] The adsorption process has been found advantageous such as: Low cost of adsorbent, easy availability, low operational cost, ease in processing as compared to other processes, reuse of adsorbent, environmentally friendly and technically feasible. But, many adsorbents have low adsorption capacities, poor regeneration abilities, and separation problems. Therefore, the research is still being available in the process for the generation of new low-cost adsorbents particularly for the removal of heavy metal ions from the water/wastewater.

METHODS

Although all the copper wastewater treatment techniques can be employed to remove heavy metals, they have their inherent advantages and limitations. Heavy metals removal from aqueous solutions has been traditionally carried out by chemical precipitation for its simplicity process and inexpensive capital cost. However, chemical precipitation is usually adapted to treat high concentration wastewater containing heavy metal ions and it is ineffective when metal ion concentration is low. Chemical precipitation is not economical and can produce large amount of sludge to be treated with great difficulties. Ion exchange has been widely applied for the removal of heavy metal from wastewater. However, ion-exchange resins must be regenerated by chemical reagents when they are exhausted and the regeneration can cause serious secondary pollution, and it is expensive, especially when treating a large amount of wastewater containing heavy metal in low concentration, so they cannot be used at large scale.

Adsorption is a recognized method for the removal of heavy metals in low concentration from wastewater containing heavy metals. The high cost of activate carbon limits its use in adsorption. Many varieties of low-cost adsorbents have been developed and tested to remove heavy metal ions. However, the adsorption efficiency depends on the type of adsorbents. Bio sorption of heavy metals from aqueous solutions is a relatively new process that has been proven very promising for the removal of heavy metal from wastewater. Membrane filtration technology can remove heavy metal ions with high efficiency, but its problems such as high cost, process complexity, membrane fouling and low permeate flux have limited their use in heavy metal removal. Using coagulation-flocculation technique in removal of heavy metal from wastewater, the produced sludge has good sludge settling and dewatering characteristics. But this method involves chemical consumption and increased sludge volume generation.

Flotation offers several advantages over the more conventional methods, such as high metal selectivity, high removal efficiency, high over flow rates, low detention periods, low operating cost and production of more concentrated sludge.[33] But the disadvantages involve high initial capital cost, high maintenance and operation costs Electrochemical process in heavy metal removal from wastewater is regarded as rapid and well-controlled that require fewer chemicals, provide good reduction yields and produce less sludge. However, electrochemical technologies involving high initial capital investment and the expensive electricity supply, this restricts its development. Although all above techniques can be employed for removing of heavy metals from wastewater, it is important to mention that the selection of the most suitable treatment techniques depends on the initial metal concentration, the component of the wastewater, capital investment and operational cost, plant flexibility and reliability and environmental impact, etc.[24]

CONCLUSION

Up to now, numerous technologies have been developed for the removal of Cu (II) from wastewater such as chemical precipitation, ion exchange, membrane filtration, biosorption, electro-coagulation etc. However, the application of these methods have been impeded by some inherent limitations, involving high capital and maintenance cost, expensive equipment, high sensitivity to operational conditions, significant energy consumption, incomplete metal removal or sludge generation. It is concluded from the above study that the adsorption is a valuable tool for controlling the level of aqueous copper pollution. The utilization of low-cost adsorbents for the treatment of wastewater containing heavy metals is helpful as a simple, effective and economic.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

ACKNOWLEDGEMENT

We gratefully thank all persons who assisted us in conducting this research.

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How to cite the article: Mohsen Arbabi, Nazila Golshani. Removal of copper ions Cu (II) from industrial wastewater: A review of removal methods. Int J Epidemiol Res. 2016; 3(3): 283-293.