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Removal methods of copper (II) from wastewater

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Abstract
Copper in trace amount is necessary for life processes. However, with higher concentration of this element in the environment and the consequent increase in human intake, copper concentration has reached toxic levels causing various diseases and is a concern to environment. Various approaches like cementation, membrane filtration, electrochemical methods, photocatalysis and adsorption are followed to remove the copper from wastewater. This review paper gives an overview to the various methods adopted for the removal of copper from wastewater.

Keywords: Copper, wastewater, cementation, membrane filtration, electrochemical methods, photocatalysis, adsorption

1. Introduction
Population growth, deforestation, urbanization, industrialization and unsustainablity has resulted in the major three types of pollution air, soil and water. The discharge of industrial waste effluents into the environment without adequate pretreatment is the main cause of water pollution. Two types of pollutants exist: organic and inorganic. Inorganic pollutants are various heavy metal such as mercury, arsenic, chromium, cadmium, lead and copper. Pulp and paper mills, fertilizers, petroleum refineries, basic steel work foundries, nonferrous metal works, motor vehicles, aircraft plating and finishing are the major contributors of copper into the environment [1]. Higher concentration of copper causes various diseases and disorders such as liver damage, Wilson disease and insomnia [2]. Copper consumption at high dosages leads to serious toxicological concerns since it could be deposited in the brain, skin, liver and kidney [3]. Higher concentrations of copper cause vomiting, cramps, convulsions or even death [4]. 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 copper ions permissible limits as 1.3 mg/L in industrial effluents [5]. Since copper is considered one of the heavy metals, its removal before discharging becomes imperative. This paper gives an insight into the various methods that have been used to remove copper from wastewater like cementation, membrane filtration, electrochemical methods, photocatalysis and adsorption.

2. Techniques of copper removal
2.1 Cementation
Cementation is used as a general term to describe the process whereby a metal is precipitated from a solution of its salts by another electropositive metal by spontaneous electrochemical reduction to its elemental metallic state, with consequent oxidation of a sacrificial metal for the recovery of more expensive and nobler dissolved metal species present in aqueous solutions [6]. The general reaction for a cementation process is given by [7].

$$mNn^{++}nM \rightarrow nMm^{++}mN$$

Where N represents the noble metal and M the reductant metal Cementation is a general term used to describe the heterogeneous process in which the copper ions in the copper salt solution (i.e., $CuSO_4$), are reduced to zero valence at the interface of iron by spontaneous electrochemical reduction to reach the copper metallic state, with consequent oxidation of the iron and the dissolved iron species present more in the aqueous solution [8].

Cementation is one of the most effective and economic techniques for recovering toxic and/or valuable metals from industrial waste solutions [9]. Cementation method has some advantages, such as recovery of metals in relatively pure metallic form, simple control requirements, low energy consumption and is in general low cost process. The main disadvantages of the technique are excess sacrificial metal consumption [10].

Naseef *et al.* (2015) investigated the removal of copper metal ions from synthetic waste water by cementation using a rotating iron cylinder. The study covered the effect of different parameters in batch mode which are: Initial copper concentrations, pH values, rotational speed, and reaction temperature on the rate of cementation. The rate of cementation was found to increase with increasing rotational speed, temperature, and pH till a value of 2.1 and then started to decrease. As the initial copper ions concentration increased from 0.2 to 0.4 M the rate of copper ions removal increased. The rate of copper recovery ranged from 10% to 90% per hour depending on the operating conditions [11]. Shishkin *et al.* (2018), reported a new effective cementation method for recovering valuable metallic copper from industrial wastewater using Fe^0 powders. A high-speed mixer-disperser (HSMD) capable of providing a cavitation effect was used for the rapid intake, dispersion, and mixing of Fe^0 powder in an acidic wastewater solution (pH ≈ 2.9) containing copper ions mainly in the form of $CuSO_4$. Three iron powders/particles were tested as the cementation agent.Under the cavitation regime, about 90% of copper was cemented in the first five minutes and the final copper removal of 95% was achieved using all three Fe^0 powders after seven minutes of cementation [12].

2.2 Membrane filtration

Ultrafiltration (UF) is the technique under membrane separation where the transmembrane pressure required is relatively low. This method aims to eliminate dissolved as well as colloidal particles. The major limitation of this type of pressure-driven process is the larger size of the pore. The pore size for UF lies between 2 nm and 50 nm [13]. Nano filtration (NF) possesses properties between those of UF and Reverse osmosis (RO), and therefore the pore size is usually less than 2 nm [14]. The technique of reverse osmosis (RO) is the most efficient in terms of the contaminants it can separate from water. The semi-permeable membrane mostly allows water to pass and retains most of the pollutants. This technique accounts for more than 20% of the world's desalination capacity [15].

Shazlina *et al.* (2020) focussed on the fabrication of polysulfone (PSf)-clay minerals impregnated hybrid membrane for treatment of Cu (II) ions. Blending and phase inversion methods have been employed to develop clay-based membranes by the mixing of bentonite, sepiolite and zeolite in the matrix of PSf. Among all developed membranes, the membrane prepared by the mixing of zeolite demonstrated the highest adsorption (2.82 mg/g) and rejection value (97%) towards Cu (II) at low pressure (0.5 bar). Regeneration performance results confirmed the reusability of membrane up to 3–5 cycles along with 82.5-90% metal recovery [16]. Al-Rashdi *et al.* (2013) reported that the NF membrane (NF270) can recover almost 100% of copper ions in 1000 mg/L copper solution within a range of pressure between 3 and 5 bar and pH values between 1.50 and 5, which shows that the suitability of NF membranes for copper ions rejection [17].

2.3 Electrochemical methods

In electrochemical method the electricity can be utilized in a number of ways, such as electrocoagulation, electrofloatation and Electrodeposition. They are regarded as rapid and well-controlled that require fewer chemicals, provide good reduction yields and produce less sludge.

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. Electro flotation 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. Electro deposition is technology with no presence of the permanent residues for the separation of heavy metals. 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 [18].

I.A. Khattab *et al.* (2013) successfully applied packed-bed electrode cell for electrochemical removal of copper ions from dilute solutions. Removal percent of 96% approximately was attained under the following conditions: - Current density: 500 A/m^2. - Electrolysis time: 30 min. - Concentration of the supporting electrolyte, NaCl, was 0.5 M. - Initial pH of the electrolyte was 3. - Initial copper ion concentration was 100 mg/L (Using $CuSO_4$ salt) and for initial copper ion concentration >100 mg/L, longer time of electrolysis was needed to obtain high removal % [19]. Ayşe Kuleyin *et al.* (2020) investigated that copper was both removed and recovered from industrial wastewater containing copper by using the electrodeposition method. Two series of experiments were conducted by using copper and stainless steel as cathodes. In both experiments, the effects of current, pH, conductivity and initial copper concentration on the electrodeposition efficiency were investigated, and optimum values were obtained. With this method, the amount of copper removed from industrial wastewater under optimum conditions was 66% in the experiments conducted with the copper cathode and 80% in the experiments conducted with the stainless steel cathode. The copper removed from the wastewater was deposited on the cathode [20].

2.4 Photocatalysis

A treatment method which is able to remove as well as detoxify the hazardous ions is Photocatalysis reduction-oxidation. Photocatalysis reduction and Photocatalysis oxidation are reduction and oxidation induced by photon or UV light and sensitized by photo catalyst such as TiO_2. This oxide can be functioned as a photo catalyst due to its semiconductor structure, that is a structure characterized by electron filled valence band and empty conduction band, separated by a gap called as band gap energy as much as 2-3.5 eV [21]. With such structure, when a semiconductor is irradiated by UV or visible light, one electron in the valence band can be transferred into conduction band by leaving a hole symbolized as h+ which is actually a positive radical.

When the hole contacts with water and TiOH photocatalyst surface, OH radical is formed. The OH radical can act as a strong oxidizing. Meanwhile, the electron is widely used for reducing some metal ions from wastewater.
Wahyuni *et al*. (2015) studied the Photocatalysis removal of Cu (II), where the process was carried out with an initial concentration of 10 mg/L using TiO_2 with UV lamp having a wavelength within a range of 290–390 nm. The maximum Photocatalysis efficiency was reached when using 50 mg of TiO_2 at pH 5; about 45.56% of the copper ions were removed [22]. Maria C Yeber *et al.* (2009) studied the photochemical process of Cu (II) reduction by heterogeneous photocatalysis using titanium dioxide (TiO_2) Degussa P-25 and a 254 nm UV-C lamp. The aim of the work was to determine the efficiency of the Photocatalysis process to remove 100 ppm of copper (II) ion concentration from a water solution. The optimum pH (4.3) and titanium dioxide mass (0.5 g) achieved the highest efficiency, reaching 80% of copper (II) ion reduction [23].

2.5 Adsorption

"Adsorption" describes the process of mass transfer, where the material is transferred from the liquid phase directly to the surface of the solid phase, after that it is bounded with chemical and/or physical interactions. It provides many advantages compared to the other treatment techniques because of the simplicity in design and its ability to involve low investment in terms of initial cost. There are many different low-cost adsorbents that have been developed for the removal of copper ions from metal-contaminated wastewater. These adsorbents have been derived from natural material, modified biopolymers, biological wastes, industrial by-products, and nano materials [24].
Pavankumar *et al.* (2019) studied adsorption of copper using groundnut seed cake power, sesame seed cake powder and coconut cake powders as bioadsorbents. It was optimized at a pH of 5, temperature of 40 °C, initial metal concentration of 10 mg/L, contact time of 30 min and adsorbent dosage 0.75 g for groundnut seed cake powder and 1.0 g of sesame seed cake powder and coconut cake powder. Adsorption process followed pseudo-second-order kinetics. Langmuir adsorption isotherm fitted perfect for the adsorption of Cu (II) using the three adsorbents. Maximum adsorption capacity was found to be 4.24 mg/g [25]. Firas Hashim Kamar *et al.* (2015) removed copper ions from solution of the simulated wastewater using walnut shells as a natural adsorbent material in batch adsorption system. Effects of experimental parameters such as pH, contact time and adsorbent dose at different initial concentrations on the adsorption efficiency have been studied. A set of experiments were done to achieve the best conditions for the highest removal efficiency which was 79.54%. The experimental data were fitted with Langmuir and Freundlich isotherm models to determine adsorption isotherm parameters. Kinetic adsorption of experimental data was obtained as a function of time by using pseudo-first and the pseudo-second order kinetic models [26]. Suhair Saif Al Moharbi *et al.* (2020) [27] assessed the capability of *Azadirachta indica* (neem leaf) powder as a natural adsorbent in the removal of copper ions from aqueous solutions. The characterization of the adsorbent was performed using X-ray difraction, scanning electron microscopy and Fourier-transform infrared spectroscopy. Series of batch experimental studies were carried out by changing the solution pH, stirring time, adsorbent dosage and stirring speed in the removal of copper from aqueous solution using A. indica as bio sorbent. The experimental result showed that the percentage removal of copper was highest at the following optimized conditions: pH 7.0, stirring time 60 min and biosorbent dosage of 1.0 g and at 125 RPM speed [27]. Riana Ayu Kusumadewi *et al.* (2019) focussed on the effect of mixing speed, contact time, and weight of the adsorbents banana peel and water hyacinth on the efficiency of Cu removal. A maximum removal of 99.55% was observed at the adsorbent mass of 5 grams and contact time of 30 minutes using banana peel adsorbent, while using water hyacinth leaves, a maximum removal of 98.39% was observed at mass of the adsorbent of 15 grams and contact time of 60 minutes. Both the adsorbents fitted the Langmuir isotherm model of adsorption [28].

3. Conclusion

Removal of heavy metal ions and in particular copper from wastewater is of utmost importance to control water pollution. Different methods adopted to remove copper from wastewater has been analysed in this paper. The methods can be made applicable on a large scale. Removal of copper from wastewater by adsorption using agricultural wastes can be a invaluable tool in the removal of copper from wastewater.

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