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Removal of Copper from Aqueous Solution using Various Activated Carbons: A Short Review

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Abstract: *Copper has fundamental importance for human life and health but it is potentially toxic as well like all other heavy metals. United State Environmental Protection Agency has set its* Cu^{2+} *permissible limits as 1.3 mg/L in industrial effluents. These limits suggest more stringent requirement for the removal of copper from aqueous environment, which necessitated the development of innovative and cost-effective technique. The research carried out for copper removal has been summarized in the current review paper.*

Keywords: *Heavy metal; Copper; Adsorption; Isotherm*

1. INTRODUCTION

The term “heavy metal” is collectively applied to a group of metals (and metal-like elements) with density greater than 5 g/cm^3 and atomic number above 20[1] . Environmental contamination due to copper is caused by mining, printed circuits, metallurgical, fiber production, pipe corrosion and metal plating industries [2]. The other major industries discharging copper in their effluents are paper and pulp, petroleum refining and wood preserving.

Copper may be found as a contaminant in food, especially shell fish, liver, mushrooms, nuts and chocolates. Any packaging container using copper material may contaminate the product such as food, water and drink [3]. In some instances, exposure to copper has resulted in jaundice and enlarged liver. It is suspected to be responsible for one form of metal fume fever [4]. Copper containing sprays are linked to an increase in lung cancer among exposed workers [5] .The world Health Organization recommended a maximum acceptable concentration of Cu (II) in drinking water to be less than 1.5mg /L [6].

In the present review we have summarized the recent development in preparation of activated carbon and analyzed the copper removal with respect to effect of various parameters, removal efficiencies, kinetics of the solute uptake, modeling approach and isothermal studies.

2. Various Adsorbents used for Copper Removal

Yargıç et al, (2014) investigated the biosorption of copper (II) ion from aqueous solutions by hydrochloric acid treated tomato factory waste to identify metal ion removal efficiency of biosorbent. According to the pH effect experiments the maximum % metal removal was achieved at pH 8 as 92.08%. Optimum biosorbent dosage and initial copper (II) concentration were found as 0.2 g/50 mL solution and 50 ppm, respectively [7].

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J.C Moreno and L. Giraldo prepared Activated carbons (ACs) by pyrolysis of cassava peel in presence of zinc chloride (chemical activities). Different concentrations were used to produce impregnation ratios of 40, 70, 110 and 160 wt.%. Activation was carried out under argon flow by heating to 823 K with 1 h soaking time. The porous texture of the obtained ACs was characterized by physical adsorptions of N_2 at 77 K and CO_2 at 273 K. The impregnation ratio had a strong influence on the pore structure of these ACs, which could be easily controlled by simply varying the proportion of $ZnCl_2$ used in the activation. Thus, low impregnation ratio led to essentially microporous ACs. At intermediate impregnation ratios, ACs with wider pore size distribution (from micropores to mesopores) were obtained. Finally, high impregnation ratios yielded essentially mesoporous carbons with high surface area and pore volume. The four best-fit three-parameter isotherms Sips, Toth, Radke–Prausnitz and Vieth–Sladek suggests that the sorption capacity of activated carbon of cassava peel to uptake copper ions to be 55 mg / g.[8].

Ferooze et al, (2015) compared the removal efficieny of Cu (II) from aqueous solution using polyaniline and polyaniline/ potassium ferricyanide composite and investigated the results by UV–visible spectroscopy. The adsorption of Cu(II) by polyaniline and polyaniline/ferricyanide composite was found to be dose dependent. The adsorption kinetic results of Cu(II) showed that adsorption reached equilibrium within 180 min in case of polyaniline and 60 min for polyaniline/ferricyanide composite and their measured adsorption capacities are 38.265 and 41.625 mg g^{-1} respectively[9].

M. Yilmaz1 et al (2010) evaluated the ability of Enterococcus faecium, a lactic acid bacterium (LAB), to remove copper(II) ions from water. The effects of the pH, contact time, initial concentration of copper(II) ions, and temperature on the biosorption rate and capacity were studied. The initial concentrations of copper(II) ions used to determine the maximum amount of biosorbed copper(II) ions onto lyophilised lactic acid bacterium varied from 25 mg L^{-1} to 500 mg L-1. Maximum biosorption capacities were attained at pH 5.0 and 6.0. Temperature variation between 20°C and 40°C did not affect the biosorption capacity of the bacterial biomass. The highest copper(II) ion removal capacity was 106.4 mg per g dry biomass. The correlation regression coefficients show that the biosorption process can be well defined by the Freundlich equation. The change in biosorption capacity with time was found to fit a pseudo-second-order equation [10].

Badriya Al-Rashdi et al, (2012) synthesized Diboron trioxide/titanium dioxide (B_2O_3/TiO_2) nano-size adsorbent and used it to remove Cu (II) from water by adsorption. The BET surface area was 222.4 ± 6.8 m^2/g. B_2O_3/TiO_2 was effective in removing copper and the maximum adsorption capacity was 82.0 mg /g [11].

Hasfalina et al, (2012) investigated the adsorption of Copper (II) from aqueous solution by kenaf (Hibiscus cannabinus, L) fibres using fixed bed column .The highest bed capacity was obtained at 47.27 mg /g using 100 mg/L of initial Copper (II) and 6 mL /min flow rate. The results showed that kenaf fibres can be an effective adsorbent for Copper (II) removal [12].

Xiu-Hui Zhao et al, (2015) prepared Tartaric acid (TA) modified multi-walled carbon nanotube (MWCNT-TA) and studied the adsorption properties for bivalent copper ion [Cu(II)].The adsorption kinetics could be better described by the pseudo second-order model, and the adsorption matches with the Langmuir isotherm. The results indicated that MWCNT-TA possessed higher adsorption capability for Cu(II) than pristine MWCNTs or TA[13].

Ying-bo et al, (2014) investigated Cu^{2+} adsorption from simulated aqueous solution using a modified spent shiitake substrate (MSSS). The results showed that the MSSS has a high adsorption efficiency and removal performance. The Cu^{2+} removal rate of the MSSS reached above 95% [14].

Nasehir Khan et al, investigated the adsorption of Cu (II) onto rice husk based activated carbon (RHAC) in batch mode with variation in operational parameters such as initial Cu (II) concentration, contact time and adsorbent dosage. Langmuir and Freundlich isotherm models were used to test the adsorption data. Maximum monolayer adsorption capacity of Cu (II) onto RHAC was 112.43mg/g at 298 K. It was observed that the adsorption of Cu (II) onto RHAC could best be described by the Langmuir and pseudo-second-order respectively for adsorption equilibrium and kinetic studies [15].

Senthil Kumar et al, (2011) investigated cashew nut shell (CNS) as a biosorbent for the removal of copper ions from aqueous solutions. Batch experiments were carried out to investigate the effect of solution pH, CNS concentration, contact time, initial copper (II) ion concentration and temperature on sorption efficiency. The copper adsorption was favored with maximum adsorption at pH 5.0. The percentage of copper ion removal onto the CNS decreased with increasing temperature. The equilibrium adsorption data were fitted to Langmuir and Freundlich adsorption isotherm models and the model parameters were evaluated. The adsorption of copper ions could be described by the pseudo-second order kinetic model. Thermodynamic quantities such as Gibbs free energy (ΔG^o), the enthalpy (ΔH^o) and the entropy change of sorption (ΔS^o) have also been evaluated and it has been found that the sorption process was feasible, spontaneous and exothermic in nature [16].

Hongmei Jin et al, (2016) conducted experimental and modeling investigations to examine the effect of biochars pyrolyzed from anaerobically digested algae-dairy-manure slurry (DAS) on removing aqueous Cu (II) before and after activated by 2 M KOH solution. Results showed that the highest adsorption capacity of pristine biochars was 21.12 mg /g. The Elovich model and Freundlich

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adsorption isotherm model can preferably describe the adsorption process, which indicated that Cu(II) was chemisorbed on heterogeneous surface of DAS-derived biochars. The activated biochar showed enhanced Cu(II) adsorption ability with an adsorption capacity of 50.71 mg/g, which was more than 3.36 times of pristine biochars. Increase of surface area and changes of porous texture, especially the functional groups on the surface of activated biochars are the major contributors to its more efficient adsorption of Cu(II) [17].

U. Gayathri, et al, (2011) exploited low cost and efficient sorbents for the removal of copper from aqueous solution using Cynodon dactylon carbon. It was observed from the experimental results that almost 90-100% copper can be removed from the aqueous solution. Adsorption kinetics and equilibrium have been investigated as a function of initial copper ion concentration. pH, contact time and adsorbent dosage. Kinetics studies suggested that the adsorption allowed first order reaction. Equilibrium data were analyzed using Langmuir and Freundlich isotherm models. On the basis of experimental results and the model parameters, it can be concluded that the carbonaceous Cynodon dactylon is effective for the removal of copper ion from aqueous solution [18].

Vanessa C. G. et al (2011) evaluated the copper ion adsorption capacity of sugarcane bagasse in natural and chemically modified with citric acid and sodium hydroxide. Adsorption analyses in batch system were carried out in function of contact time with theadsorbent and adsorbate concentration. Flame atomic absorption spectrometry was used to determine the copper concentrations. Adsorption experimental data were fitted to Langmuir and Freundlich linear models, and the maximum adsorption capacity was estimated for copper ions in function of modifications. The required time for the adsorption to reach equilibrium was 24 h and the kinetics follows the behavior described by the pseudo-second order equation. Besides, a significant improvement of the copper adsorption has been observed after the bagasse treatment, where the maximum adsorption capacity was31.53 mg g^{-1} for copper using modified bagasse with nitric acid according to Langmuir isotherm linear model [19].

Ahsan Habib et al (2007used orange peel, sawdust and bagasse used as adsorbents for the removal of Cu (II) from aqueous solution. The effects of contact time, pH, concentration, dose and ionic strength on the removal of Cu (II) have been studied. Moreover, treated sawdust has been used as an adsorbent for the same. The equilibrium adsorption capacity of the adsorbents for Cu (II) was obtained by Langmuir isotherm. The ionic strength effect on the removal of Cu (II) from its aqueous solution indicated that the removal followed ion-exchange mechanism.

Conclusion

It is concluded from the above literature survey that the adsorption using activated carbons is a valuable tool for analyzing aqueous copper solution. It is simple, effective and economical means of water treatment.

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