

**Adsorption of Cu (II) ions from aqueous solution using pyridine-2, 6- Dicarboxylic acid cross-linked chitosan as a green biopolymer adsorbent.****Ibraheem Olayiwola Bisiriyu**

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**Abstract:**

In this study, Cross linked Chitosan (CCS) has been synthesized by anchoring a bi-functional Ligand, namely Pyridine-2, 6-Dicarboxylic acid (PDC) with chitosan through ion exchange. The functionalized biopolymer was characterized by elemental analysis (CHN), spectral (UV visible, FTIR and solid state  $^{13}\text{C}$  NMR), thermal (TGA and DSC), structural (powder XRD), surface and morphological (BET and SEM) analyses. The PDC-CCS was employed to adsorb Cu (II) ion from aqueous solutions. The influences of various operating parameters such as PH, temperature, initial concentration of Cu (II) ion and contact time on the adsorption capacity of PDC-CCS have been investigated. The results showed that the maximum adsorption capacity of PDC-CCS for Cu (II) ion was 2185.64 mmol $\cdot$ g $^{-1}$  and that the adsorption capacity rapidly reached equilibrium within 60 min and strongly depends on PH and temperature. Langmuir and Freundlich adsorption models have been applied to describe the equilibrium data. It was shown that the PDC-CCS had given good correlation with both isotherm models and the adsorption kinetics of Cu (II) ion could be best described by the pseudo-second-order kinetic model. The use of bottom ash of expired drugs incineration for removal of Cu (II) ions from aqueous solution has been investigated. Analytical techniques have been employed to find characteristics of adsorbent materials. The removal of Cu (II) was conducted in batch system, and the effects of pH, adsorbent dosage, initial concentrations of copper ions, and contact time on adsorption efficiency were studied. Optimum adsorption was achieved at a pH 5 and equilibrium was established within 15 min of the process. The equilibrium adsorption data were analyzed using eight adsorption isotherm models: Langmuir, Freundlich, Temkin, Redlich–Peterson, Dubinin–Radushkevich, Toth, Harkin–Jura and Halsey isotherms. The energy value obtained by application of Dubinin–Radushkevich model was 2.593 kJ/mol indicating that physisorption was the

dominant mechanism of sorption. The values of the correlation coefficient ( $R^2$ ) of the isotherms gave the best fit ( $>0.99$ ) with the Langmuir, Toth, and Redlich–Peterson isotherms. The adsorption capacity (QM) from the Langmuir isotherm for Cu (II) was found as 13.335 mg/g. The equation constant  $n$  of Toth isotherm model is found to be close to 1 (0.945), confirming that the adsorbent studied presents homogeneous surface under conditions used. It is concluded that bottom ash of expired drugs incineration can be used as an effective adsorbent for removing Cu (II) from aqueous solution. Herein we report the green recovery of toxic metals [namely: Cd  $^{2+}$ , Cr  $^{3+}$ , Mn  $^{2+}$ , Pb  $^{2+}$ , and Ni  $^{2+}$ ] from water utilizing a biopolymer: 2, 6-pyridine dicarboxylic acid cross-linked chitosan (PDC-CCS) as the adsorbent. Adsorption studies were performed at a previously determined optimum adsorption conditions for Cu (II) [i.e. temperature = 30 °C, pH of about 7.5, contact time = 60 mins and initial metal ion concentration of 2.5 mM]. At the RI-PB/def2-SVP level of theory, the Density Functional Theory (DFT) approach has been used to evaluate adsorption energy for metal ions. Selectivity studies were performed at pH 4.20, 5.56, 6.65 and 7.61. While Mn (II), Cd (II) and Ni (II) were strongly adsorbed at higher pH (7.5), Cr (III) and Pb (II) were seen to be strongly adsorbed at lower pH (around 4.0). Selectivity studies revealed that PDC-CCS can be utilized for simultaneous removal of the metals at pH 4.2; selective adsorption of Mn (II) at pH 5.56 as well as simultaneous-selective removal of Ni (II) and Mn (II) near neutral pH. The maximum adsorption limit of PDC-CCS for Mn (II), Cd (II) and Ni (II), were found to be 1258.79, 1118.70 and 829.62 mmol/g respectively. When compared with some relevant previously used adsorbent, PDC-CCS shows an exceptional adsorption capacity. Consequently, a successful biopolymer adsorbent for the treatment of water contaminated by hazardous metal.