Removal of Cr and Cu using Nanomaterials - A Review

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Abstract - The different techniques have been utilized for water and wastewater treatment expulsion of overwhelming metals so far some of which are exceptionally effective. The advancement nanofiber, nanotube and nanoparticles their application in expulsion of substantial metals is turning into a noteworthy region of research. The study revaluated that maximum removal of chromium (Cr) was observed by using Iron Nanoparticles absorbent with removal efficacy of 100%. The study revaluated that maximum removal of copper (Cu) was observed by using **electrospun chitosan blend nanofibers** absorbent with removal efficacy of **99.5%.**

Keywords — *Nanofiber, Nanotube, Nanoparticle, Removal of chromium, Removal of copper, Heavy metals.*

I. INTRODUCTION

The various methods of removing the heavy metal ions from water and wastewater have been proposed. The various conventional methods are developed such as chemical treatment, filtration, distillation, precipitation, UV radiation, ion exchange, adsorption, electrochemical technologies etc. The various filtration methods use ceramic filters, biosand filters, charcoal bed and activated carbon bed. The filters are effective in removing organic contaminants, unable to handle high turbidity and bacteria growth on filter media. In concoction precipitation, evacuation of metals is accomplished by the expansion of coagulants, for example, lime, press salts alum, and other natural polymers. The main drawback of this method is the production of large amount of sludge containing toxic compounds. Nanomaterials are characterized as materials under 100 nm in no less than one measurement. At nano scale, materials have some new size-subordinate properties, for example, substantial surface to volume proportion, reactivity, fast disintegration and adsorption which are not the same as the mass material, Sushma and Richa (2015). Nanotechnology based multifunctional and profoundly productive procedures are giving reasonable answers for wastewater medications that don't require incorporated frameworks or vast foundations, Sulekha (2016). In this paper literature review has seen made on use of nonmaterial for removal of copper and chromium.

II. REMOVAL OF CHROMIUM (Cr)

A. Use of Nanoparticle removal of Chromium (Cr)

Hu et al. (2005) used maghemite nanoparticles for removal of chromium. The study was conducted by varying the adsorption capacity, pH, temperature, initial concentration. The maximum adsorption is 90% at pH 2.5 and adsorption within 15 min. The characterization of nanoparticles is

X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS). The study revealed that maghemite nanoparticles can be produced in large quantity using the sol–gel method, the adsorption capacity of magnetic nanoparticles is higher by considering the larger surface area and highly active surface sites. **Hu et al. (2007)** used magnetic nanoparticles for removal of chromium. The study was conducted by varying adsorption capacity, pH, shaking rate. The adsorption efficiency is 99.5% at pH 2.with shaking rates from 100 to 400 rpm. The characterization of nanoparticles is transmission electron microscopy (TEM), X-ray diffraction (XRD). The study revealed that six kinds of ferrites, $MeFe_2O_4$ (Me = Mn, Co, Cu, Mg, Zn, Ni) were synthesized in nanoscale using a simple method and tested for the adsorption/desorption of Cr (VI) from synthetic wastewater. **Liu et al. (2010)** used Nanoscale zero-valent iron (NZVI) for removal of chromium. The study was conducted by varying pH, initial concentration, adsorption capacity, temperature. The removal rates of Cr (VI) using bare NZVI and CS-NZVI beads were 83% and 82%, at pH 6.4 The characterization of nanoparticles is scanning electron microscope (SEM), Fourier transform infrared (FTIR). The study revealed that the role of chitosan in Cr (VI) reduction by CS-NZVI beads, as well as elemental composition of final products, and evaluate the influence of different factors on the Cr (VI) removal by CS-NZVI beads. **Sharma et al (2009)** used Iron Nanoparticles for removal of chromium. The study was conducted by varying pH, contact time, initial concentration, adsorbent dose, and temperature. The maximum removal is 100% at pH 2. The characterization of the nanoparticles is X-ray diffraction (XRD) and transmission electron microscopy (TEM).

B. Use of Nanofiber of removal Chromium (Cr)

Bhaumik et al (2011) used polypyrrole-polyaniline (PPy-PANI) nanofibers for removal of Chromium. The study was conducted by varying pH, dose of adsorbent, contact time, concentration and temperature. The removal efficiency increases from 57.3% to 99.8% with an increase in adsorbent dose from 10 mg to 50 mg. maximum adsorption capacity of the PPy-PANI nanofibers for Cr (VI) was 227 mg/g. The characterization of nanofiber is Fourier transforms infrared spectroscopy (ATR-FTIR), field-emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HR-TEM). The study revealed that synthesizing the nanofibers lies in the fact that incorporation of PANI into the growing polymer chain of PPy provides an increase in surface area that may enhance the Cr (VI) adsorption compared to its polypyrrole homopolymer counterpart and as well overcomes the limitations of the rareness of new conjugated Π bond-containing monomers. **Chen et al (2014)** used Polypyrrole-sepiolite nanofibers for removal of chromium. The study was conducted by varying pH, contact time, adsorption capacity and temperature. The maximum adsorption capacity is 95 % at pH 2 and temperature 25^0c. The nanofiber characterized by scanning electron microscopy (SEM), X-ray spectrometer (EDX).The fibers are $1-2$ μm in length and $20-30$ nm in diameter. The study revealed that the growth orientation of PPy nanofibers and the resulting PPy-sepiolite nanofibers exhibit high efficiency for Cr (VI) removal. **El-Sherif et al. (2013)** used cysteine-modified polymer nanofibers for removal of chromium. The study was conducted by varying pH, contact time and adsorption capacity. The maximum adsorption capacity is 99 % at pH of 5.5 and an exposure time of 45 min. **Lin et al (2010)** used polyacrylonitrile (PAN)/ferrous chloride ($FeCl_2$) composite porous nanofibers for removal of chromium. The study was conducted by varying pH, initial concentration and adsorption. The Cr-removal capability is more than 110 mg/g. The characterized by field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). The study revealed that the PAN/ $FeCl_2$ composite porous nanofibers could be good candidates for efficient Cr-removal from wastewater and for the deep-purification of pollutant water.

C. Use of Nanotube removal of Chromium (Cr)

Moosa et al. (2015) used Carbon Nanotubes for removal of chromium. The study was conducted by varying pH, initial concentration, and adsorption capacity. The maximum adsorption efficiency is to be 99.83% for CNTs at 25 mg; and pH 6. The characterization of nanotube is Fourier Transform Infrared Spectrophotometer (FTIR), specific area measured by the BET 63.17 m^2/g. **Huang et al (2015)** used magnetic multi-wall carbon nanotubes for removal of chromium. The study was conducted by varying adsorbent dosage, initial concentration, temperature and pH. The

characterization of nanotube is transmission electron microscope (TEM) and X-ray diffraction (XRD).The diameters of the MWCNTs were 20nm to 40 nm, the length 2 μm, and the specific surface area is $200 m^2$/g.

III. REMOVAL OF COPPER (Cu)

A. Use of Nanoparticle removal of Copper (Cu)

Yuwei and Jianlong (2011) used magnetic chitosan nanoparticles for removal of Cu (II). The study was conducted by varying the initial concentration and adsorption. The maximum sorption capacity is to be 35.5 mg/g. The magnetic chitosan nanoparticles is characterized by means of X-ray diffraction (XRD), transmission electron microscope (TEM), Fourier Transform infrared spectroscopy (FTIR), vibrating sample magnetometer (VSM) and energy dispersive X-ray spectrometer (EDS). The nanoparticle size in the range of 8–40 nm and FTIR analysis is $-NH_2$ and $-OH$ were involved in the removal mechanism of Cu (II). The study revealed that prepared magnetic chitosan nanoparticles through a simple one-step in situ co-precipitation method. Their performance characterized, and the sorption property for removing Cu (II) from aqueous solution. **Adeli et al. (2012)** used sodium dodecyl sulphate-coated Fe_3O_4 nanoparticles (SDS–Fe_3O_4 NPs) for removal of Cu (II), Ni (II) and Zn (II). The study was conducted by varying pH, contact time and adsorption. The maximum adsorption of metal ions between pH values 5 and 6 and adsorption capacity 24.3, 41.2 and 59.2 mg/g for Cu (II), Ni (II) and Zn (II) with 1 min of contact time. The study revealed that to assess the performances of MNPs for the removal of the heavy-metal ions, to achieve the possible regeneration of MNPs for reuse, and to explore the mechanisms of metal adsorption onto MNPs. **Bai et al. (2011)** used elemental selenium nanoparticles for removal of copper. The study was conducted by varying contact time, pH, initial concentration, and temperature. The maximum adsorption capacity is 0.89 g /g at pH 3and temperature 298.15K. The elemental selenium nanoparticles is characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and energy dispersive X-ray (EDX). The study revealed the function of ascorbic acid and investigates the effects of factors on the removal of copper, to determine the adsorption parameters from the adsorption isotherms and the kinetic equations. **Feitoza et al. (2013)** used Maghemite nanoparticles (MNPs) for removal of copper. The study was conducted by varying pH, adsorbate/adsorbent concentration and temperature. The adsorption capacity is $Cu^{2+}$of 625 mg/g at pH 6.5 and 25^0c. The nanoparticles is characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), magnetization measurements, dynamic light scattering (DLS), Fourier transform infrared (FTIR), and thermo-gravimetric analysis (TGA).

B. Use of Nanofiber removal of Copper (Cu)

Haider and Park (2008) used chitosan electrospun nanofiber for removal of copper and lead. The study was conducted by varying the pH, adsorption time and temperature. The equilibrium adsorption capacities for Cu (II) and Pb (II) were 485.44mg/g and 263.15mg/g The study revealed that remarkable characteristics of the chitosan electrospun material are the high surface area per unit mass, spongeous nature with small pores and wet absorption, which may cause fast and increase adsorption due to more exposure of the chitosan nanofiber's functional groups to the metal ions. **Jiang et al. (2012)** used Polyaniline (PANI) nanofibers for removal of copper and lead. The study was conducted by varying the pH, adsorption time and agitation speed. The removal of Cu^{2+} and Pb^{2+} in this PANI/CA composite with milli/nano hierarchical structure surpassed 90% at pH 3-7 and The adsorption kinetic results of Cu^{2+} and Pb^{2+} showed that the adsorption reached equilibrium within 120 min and 40 min. The study revealed that prepared PANI nanofibers on the surface of CA beads via competitive adsorption-restricted polymerization. The Cu (II) and Pb (II) ions removal properties of the PANI/CA hierarchical adsorbent were evaluated in terms of the sorption kinetics and sorption isotherm, the effects of solution pH and the CA particle size. Desorption studies of pre-adsorbed samples in Cu $(NO_3)_2$ or Pb $(NO_3)_2$ bulk solutions (10 mg/L). **Kampalanonwat and Supaphol (2011)** used ultrafine polyacrylonitrile (PAN) fiber for removal of Copper (II). The study was conducted by varying the initial pH, initial concentration and adsorption time. The initial concentrations (40-800 ppm) and the maximal adsorption capacity of the H-ePAN fiber mats for the Cu (II) ions was determined to be 31.3 mg /g at pH 5. The study revealed that prepared nonwoven matrices of ultrafine fibers from commercial PAN microfibers, of increasing the surface area. The surface of the electrospun PAN fibers reacted with a sodium hydroxide (NaOH) ethanolic/aqueous solution to introduce chemical functionality that is capable of chelating metal ions. **Nthumbi et al. (2011)** used electrospun chitosan blend nanofibers for removal of Pb and Cu. The study was conducted by varying the initial concentration, pH, adsorption capacity. Adsorption capacity for Pb and Cu of 56.54 mg/g and 5.75 mg/g. Adsorption for Pb (II) at pH 4.25 and for Cu(II) at pH 5.5 and for removal of Pb and Cu, with removal efficiencies of 100% (Pb) and 98.6% (Cu) in pond water; and 97.2% (Pb) and 99.5% (Cu) in wastewater. The characterization of chitosan and its polyacrylamide blend, using C^{13}-NMR, FTIR, SEM, and BET. The surface area of the chitosan and Chi-PAA blend showed the surface area to double from 1.44m^2/g to 2.84m^2/g. The study revealed that to develop a flow sorbent, based on chitosan polyacrylamide biopolymer blend cross-linked with glutaraldehyde as a rigid and stable nanomaterial, with high dynamic adsorption capacity for the removal of heavy metals in contaminated water.

C. Use of Nanotube removal of Copper (Cu)

Ge et al. (2013) used Sulfonated multi-walled carbon nanotubes for removal of copper. The study was conducted by varying pH, initial concentration and adsorption. The adsorption capacity for Cu (II) was enhanced 58.9% at pH 2-6. The Sulfonated multi-walled carbon nanotubes characterized by SEM, FTIR, Raman, XPS, and BET. The study revealed that the functionalization of MWCNTs by concentrated H_2SO_4 at elevated temperatures which introduced the hydrophilic functional groups $-HSO_3$ onto MWCNTs. **Chao-Yin Kuo (2009)** used as-grown and modified multi-walled carbon nanotubes for removal of Copper. The study was conducted by varying pH, initial concentration, adsorption capacity and temperature. Initial concentration of Cu is 43mg/L at pH 6 with temperature 320 K. The study revealed that the equilibrium and thermodynamics of the adsorption of Cu^{2+} onto CNTs. The copper adsorption capacity is increased herein by modifying the surface of as-grown CNTs by H_2SO_4 and $H_2SO_4/KMnO_4$. **Li et al (2010)** used carbon nanotubes (CNTs) for removal of copper. The study was conducted by varying pH, initial concentration, and adsorption capacity. Adsorption capacity of CNTs/CA is 67.9 mg/g at concentration of 5 mg/L and removal efficiency of CNTs/CA is 69.9% at pH of 2.1. The study revealed that to utilize the excellent formability of alginate to support and fix CNTs. The composites not only make full use of the good heavy metal adsorption properties of CNTs and alginate, but also prevent micro-sized CNTs from breaking off the composites to cause second micro-pollution to water. **Salam et al. (2012)** used Multi-walled carbon nanotubes (MWCNTs) for removal of copper (II), lead (II), zinc (II) and cadmium (II). The study was conducted by varying contact time, metal ions concentration, pH, and adsorption capacity. Removal of Cu (II) increased gradually from 12.41 to 90.63%, at pH 2.0 to 6.0 with temperature298 K. Multi-walled carbon nanotubes characterized by FTIR, XRD, and BET.

IV. CONCLUSION

Adsorption study on the removal of heavy metals such as chromium (Cr) and copper (Cu) has been carried using nanofiber, nanotube, nanoparticles. The study revaluated that maximum removal of chromium (Cr) was observed by using Iron Nanoparticles absorbent with removal efficacy of 100%. The study revaluated that maximum removal of copper (Cu) was observed by using electrospun chitosan blend nanofibers absorbent with removal efficacy of 99.5%.

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