A Review on Green Synthesized Copper Nanoparticles and Their Applications

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***Abstract*: Green synthesis of nanoparticles (NPs) is an emerging research trend in nanotechnology. Copper nanoparticles have properties like antimicrobial activity and disinfecting property. Green synthesized NPs are highly proficient for recycling and removal of heavy metal from waste waters. They could solve various water quality issues worldwide. Plant-mediated nanomaterial synthesis is economical, eco-friendly and non-pathogenic. Biomolecules required for reduction and stabilization of the metal ions are already present in the plant extract. Silver nanoparticles were synthesized within 10min and exhibited antibacterial activity against bacteria. Green-synthesized copper nanoparticles (Cu NPs) used as nano-adsorbent for the removal of Ibu, Nab, and Dic from wastewater samples. Best removal results were obtained at temperature 298 K, pH 4.5, 60 min and the adsorption process was endothermic. Paper sheets with higher copper content showed a high bacteria reduction of log 8.8 for E. coli. The CuNP paper filter has the potential to become an extremely low-cost way to purify water.**

Keywords: Wastewater Treatment; Nanoparticles; Copper; Green Synthesis; Applications; Characterization; Disinfection;

I. INTRODUCTION

Wastewater produced due to human activities in households is termed domestic wastewater i.e. wastewater from the kitchen, shower, wash basin, toilet and laundry. The strength and composition of the domestic wastewater changes on hourly, daily and seasonal basis, with the typical strength obsessed with per capita water usage, habits, diet, living standard and life style. The main reason is variation in water usage in households. Households in developed countries use more water than those in developing countries.

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A variety of green synthesized NPs are currently getting utilized in water and wastewater treatment due to their high efficiency and biocompatible nature. Green synthesis of nanoparticles (NPs) is an emerging research trend in green nanotechnology as this method is nontoxic or less toxic, eco-friendly, efficient, and cost-effective as compared to other conventional physical and chemical methods. Green synthesis of NPs employs various biological agents such as plants, bacteria, algae, and fungi, but nowadays plant-based green synthesis of NPs is gaining more attention among researchers from around the world. A variety of green synthesized NPs are currently getting utilized in water and wastewater treatment due to their high efficiency and biocompatible nature. Green synthesized NPs are highly proficient for recycling and removal of heavy metal from waste waters without loss of their stability and degradation of a spread of organic pollutants from waste waters and, thus, purify the waste waters for reuse and recycling and could solve various water quality issues worldwide[1].

Copper nanoparticles, because of their unique physical and chemical properties and low cost preparation, have been of great interest recently. Copper nanoparticles have properties like antimicrobial activity and disinfecting property. Copper nanoparticles have more surface area. The higher the area and volume, the particles become stronger, more stable and sturdy. Copper nanoparticles makes chemical and biological reactions easier. Due to their small sizes and thus large specific surface areas, nanoparticles have strong adsorption capacities and reactivity. The mobility of nanoparticles in solution is high. Heavy metals, organic pollutants, inorganic anions, and bacteria have been reported to be successfully removed by nanoparticles[2].

II. OBJECTIVES

The main objective of this project is to disinfect domestic waste water using green synthesized nanoparticles and reusing it for other purposes.

III. REVIEW WORK

GREEN SYNTHESIS OF NANOPARTICLES

Plant mediated synthesis of the nanoparticles has been in light in the recent times as it is economical, eco-friendly and non-pathogenic. The biomolecules required for reduction and stabilization of the metal ions such as proteins, amino acids, poly saccharides, terpenes, alkaloids, phenolics, saponins and vitamins are already present in the plant extract as phytochemicals, which makes it more economical and easiest way to produce NP's. The kinetics of plant-mediated nanomaterial synthesis are much higher than in other biosynthetic methods comparable to chemical nanoparticle synthesis. The aqueous extract of Alternanthera dentate was used for the rapid synthesis of silver nanoparticles 50–100nm in size. The extracellular silver nanoparticles were synthesized within 10min and exhibited antibacterial activity against Pseudomonas aeruginosa, Escherichia coli, Klebsiella pneumonia, and Enterococcus faecalis. Gold nanoparticles 20–25nm in size were synthesized showing spherical, triangular, hexagonal, and rod-shaped morphologies using Cymbopogon citratus leaf extract, and were found to boost the predation efficiency of copepod Mesocyclops aspericornis against malaria and dengue mosquitoes. Copper oxide nanoparticles were synthesized extracellularly through a colloidthermal synthesis process using a medicinal plant, Euphorbia nivulia, and the particles were proposed to be stabilized by the terpenoids and peptides present within the latex. The antibacterial activity of the particles was also assessed[3]. In a study, indium oxide (In_2O_3) nanoparticles were synthesized using indium acetylacetonate a solution

extracted from the Aloe vera plant, and the particles were characterized for their structural, morphological, and optical properties. Zinc oxide nanoparticles with hexagonal wurtzite structure were synthesized from a zinc hyperaccumulator plant, Sedum alfredii, with a mean size of 53.7nm. Furthermore, iron oxide nanoparticles were synthesized using alfalfa with four different pH values in the solution, and aggregates 1–10nm in size were obtained. It was proposed that the size of the nanoparticles could be controlled in the region of 1–4nm under optimal pH conditions[4].

Green synthesis of copper oxide nanoparticles and its effective applications in Biginelli reaction, BTB photodegradation and antibacterial activity.

Copper oxide nanoparticles (CuO NPs) were synthesized by a greener route Using Cordia sebestena (C. sebestena) flower aqueous extract, copper oxide nanoparticles (CuO NPs) were manufactured in a greener way. Particle size was found to be between 20 and 35 nm in TEM and DLS examination, and the TEM-SAED pattern ensured crystallinity and reasonable stability. These nanoparticles were tested against two gramme positive and two gramme negative harmful bacterial pathogens present in home waste water, including Bacillus subtilis (B. subtilis), Staphylococcus aureus (S. aureus), Escherichia coli (E. coli), and Klebsiella pneumoniae (K. pneumoniae). The discovery suggests that NPs could be employed in photolysis to remove contaminants from water. Furthermore, antibacterial activity against the above-mentioned pathogenic bacterial pathogens was used to determine the biological importance of green produced CuO NPs[7].

Green-synthesized copper nano-adsorbent for the removal of pharmaceutical pollutants from real wastewater samples.

Copper nanoparticles (Cu NPs) with high purity and stability were green synthesized using Tilia leaves extracts. Well-dispersed spherical and semispherical nanoparticles with particle diameters ranged from 4.7 to 17.4nm were prduced The absorption process described as spontaneous, endothermic and physical in natureThe release of Non-Steroidal Anti-Inflammatory drugs (NSAIDs) such as Ibuprofen (Ibu), Naproxen (Nab) and Diclofenac (Dic) to the aquatic system cause serious environmental problems. In this study, green-synthesized copper nanoparticles (Cu NPs) have been used as nano-adsorbent for the removal of Ibu, Nab, and Dic from wastewater samples. The best removal results were obtained at these conditions: temperature 298 K, pH ¼ 4.5, 10.0 mg Cu NPs, 60 min and the adsorption process was spontaneous, and endothermic. At these conditions, the removal percentage of Ibu, Nap, and Disc were found to be 74.4, 86.9 and 91.4% respectively. The maximum monolayer adsorption capacities were calculated as 36.0, 33.9 and 33.9 mg/g for Dic, Nap, and Ibu respectively results revealed that green-synthesized copper nanoadsorbent may be used for the removal of the anti-inflammatory drugs from real wastewater efficiently[8].

Synthesis and Impregnation of Copper Oxide Nanoparticles on Activated Carbon through Green Synthesis for Water Pollutant Removal

Explains green synthesis of CuO nanoparticles on vegetal activated carbon (VAC), using pomegranate leaf extract as reducing and stabilizing agent in the removal of multiple pollutants .Wang et al.4 adapted methodology was used for the synthesis and impregnation of the copper oxide nanoparticles. It was used coconut activated carbon as nanoparticles support. It has been found CuO nanoparticles with diameters between 104 and 165 nm and CuO measuring between 40 and 78 nm on the activated carbons surfaces. Among the samples, carbon impregnated with 1.5%Cu-24h can be highlighted, because it showed a removal similar to pure carbon for organic contaminants such as atrazine pesticide, diclofenac, caffeine and nitrate , however it increased carbon efficiency in nitrate ions removal in more than four times. So, an impregnation time of 24 h is sufficient to obtain copper oxide nanoparticles on carbon activated with a good pollutant removal potential. The impregnated carbons showed a great water pollutant removal capability, in particular nitrate, providing a non-polluting and cost-effective alternative to the conventional treatment methods[9].

Disinfection of drinking water via algae mediated green synthesized copper oxide nanoparticles and toxicity evaluation.

This paper focuses on green synthesized CuO nanoparticle which are synthesized using algal extract. The NP's have a size of 3.6nm The characteristics of the NP synthesized depend upon various factors such as stirring speed, effect of pH, concentration of algal extract, Cu+ ion concentration. The CuO NP showed antimicrobial activity against gram negative bacteria such as E-COLI. For surface water sample an optimum dosage of 50mg/L for E-COLI. Toxicity assessment was conducted on fish blood and was checked for formation of mononuclei. Cell death assessment was conducted on human gastric epithelium and Chinese hamster ovarian cell lines. Surface water is exposed to industrial and domestic waste and was more prone to disease causing bacterial growth. Activated sludge process is one of the widely use methods of disinfection, bulking is the most common drawbacks of this method. Column type Sequential Batch Reactor (SBR) haves about 87% of the COD removal efficiency. Lately, nanoparticles/powders, nano-membranes are used extensively to remove some of the heavy metals and biological substances[5]. Size of the particles are governed majorly by pH, temperature, Cu ion concentration, Incubation time. Physical and chemical synthesis of nanoparticles mostly include heavy metals and also requires lot of time for their synthesis to be carried. Green synthesis is a method which uses natural reducing agents for the synthesis. The material so synthesized are used for disinfection by immobilizing them onto surfaces such as membranes. Polyphenols or the phytochemicals in the plant extract acts as the capping agents or the catalyst during the synthesis. Microalgae contains many of these polyphenols. These green synthesized nanoparticles are non-toxic and are eco-friendly in nature. These NP's are economically feasible as they have a high growth rate, high biomass productivity[6].

Development of functionalized CuO nanoparticles for enhancing the adsorption of methylene blue dye

Water pollution by dyes is a serious environmental problem. The toxicity of dyes constitutes a great risk to the environment and human health. The nanoparticles were synthesized by the co-precipitation method using copper nitrate as the precursor. A comparison is done between the functionalised and bare nanoparticles in enhancing the adsorption activity of chitosan in adsorbing methylene blue dye. The crystallite size of CuO particles was found to be ~10 nm. The development of such functionalized nanoparticles leads to multi-functional properties such as the ability as catalysts in the presence of sunlight for degradation of dyes as well as adsorption of dyes. The BET adsorption study of the EDTA functionalized CuO nanoparticle has an enhanced surface area and also shows the presence of pores which the bare nanoparticle doesn't have. The increased surface area of the nanoparticles imparts various abilities to the nanoparticle i.e. it can enhance the adsorption activity of chitosan, and also increase photocatalytic activity. EDTA-Silane functionalized CuO nanoparticle combined chitosan was used the percentage removal of dye was 54%. Though precipitation method doesn't offer particles of uniform size, the method is cost-effective and suitable for bulk applications like waste water treatments where cost considerations are high[10].

Studies on Green Synthesis of Copper Nanoparticles Using Punica granatum

The present study aimed toward green synthesis of copper nanoparticles using various plant extracts as reducing and stabilizing agents. It might also study the antibacterial effect of the synthesized copper nanoparticles. Green synthesis of copper nanoparticles with 10mM solution of copper sulfate using 50% concentrated pomegranate fruit rind extract gave good yield of nanoparticles of medium size within 1½ to 2 hours. The aqueous solutions of varied plant extracts yielded stable copper nanoparticles as indicated by the O.D values tested using UV-Visible spectroscopy. The synthesized nanoparticles were found to be 56-59 nm, characterized by Scanning microscopy (SEM). Copper especially in its nanoscale, has significant antibacterial activity and also synthesis of copper nanoparticles is extremely cost effective. Antibacterial tests of the biosynthesized nanoparticles were administered on Gram-positive Bacteria Staphylococcus aureus by Agar well assay. The synthesized copper nanoparticles exhibited a robust antibacterial activity against Staphylococcus aureus. The copper nanoparticles are often green synthesized using fruit rind extract of pomegranate and thus these are often used as efficient antimicrobial agents against Staphylococcus aureus and therefore the study is critical currently as drug resistant infections of Staphylococcus aureus are gaining much prevalence and prominence[11].

Incorporation of copper nanoparticles into paper for point-of-use water purification

As a cost-effective alternative to silver nanoparticles, the use of copper nanoparticles in paper filters for point-of-use water purification was adopted. In this reports an environmentally benign method for the direct in situ preparation of copper nanoparticles (CuNPs) in paper by reducing sorbed copper ions with ascorbic acid. Point-of-use (POU) water purification offers an affordable and convenient way to reduce exposure to pathogenic microorganisms. Copper nanoparticles were quickly formed in less than 10 minutes and were well distributed on the paper fiber surfaces. Paper sheets were characterized by x-ray diffraction, scanning electron microscopy, energy dispersive x-ray spectroscopy, and atomic absorption spectroscopy. Antibacterial activity of the CuNP sheets was assessed for by passing Escherichia coli bacteria suspensions through the papers. The effluent was analyzed for viable bacteria and copper release. The CuNP papers with higher copper content showed a high bacteria reduction of log 8.8 for E. coli. The paper sheets containing copper nanoparticles were effective in inactivating the test bacteria as they passed through the paper. The copper levels released in the effluent water were below the recommended limit for copper in drinking water is 1ppm. This CuNP paper filter has the potential to become an extremely low-cost way to purify water[12].

Optimization and Application of Bioflocculant Passivated Copper Nanoparticles in the Wastewater Treatment

Nanotechnology offers a great opportunity for efficient removal of pollutants and pathogenic microorganisms in water. Copper nanoparticles were synthesized using a polysaccharide bioflocculant and its flocculation, removal efficiency, and antimicrobial properties were evaluated. The synthesized nanoparticles were characterized using thermosgravimetry, UV-Visible spectroscopy, Fourier-transform infrared spectroscopy (FT-IR), powder X-ray diffraction, scanning electron microscope (SEM), and transmission electron microscope (TEM). The highest flocculation activity (FA) was achieved with the lowest concentration of copper nanoparticles (0.2 mg/mL) with 96% (FA) and the least flocculation activity was 80% at 1 mg/ml[13]. The copper nanoparticles (CuNPs) work well without the addition of the cation as the flocculation activity was 96% and worked best at weak acidic, neutral, and alkaline pH with the optimal FA of 96% at pH 7. Furthermore, the nanoparticles were found to be thermostable with 91% FA at 100 ◦C. The synthesized copper nanoparticles possess great properties for disinfecting and pollutants removal in coal mine water, domestic wastewater, and river water. Over 89% of COD and BOD removal efficiency was observed for both the coal mine and river water. The remarkable properties for the removal of staining dyes and disinfecting suggest that the synthesized nanoparticles can be used in removing dye effluents, pathogens and other micro-organism from wastewater. When evaluated for antimicrobial activity against both Gram-negative and Gram-positive bacteria, they were able to inhibit and kill all the tested strains at the lowest concentration of 3.13 mg/ml[14].

Green synthesis of CuO nanoparticles via Allium sativum extract and its characterizations on antimicrobial, antioxidant, antilarvicidal activities

The green synthesis of CuO nanoparticles was synthesized by Allium Sativum extract. The powder X-ray diffraction pattern explained the high crystalline nature and the calculated crystallite size in 25−35 nm. The Fourier transform infrared spectrum described the CuO bonding nature. The particles size analyzer displayed the CuO nanoparticles in a 20−40 nm range of size. The SEM images manifested the spherical, oval-shaped morphology of CuO nanoparticles. The EDAX spectrum and mapping proved the purity of CuO with Cu and O occurrence. The phytochemical analysis listed the phytochemicals contributed for CuO nanoparticle synthesis via Allium sativum extract. The antimicrobial activity reported the efficient infection on bacteria as well as fungi. The antioxidant activity demonstrated the potential ability of free radical scavenging activity. At 21st century, CuO nanoparticles from environment friendly synthesis have special efficient application in disinfection of wastewater[15].

IV. CONCLUSION

The nano-technology in the recent years have gained importance in disinfection of water due to their characteristics such as high specific area, high surface energy, size and volume. The physiochemical properties of the nanoparticles can be easily manipulated by calculated variation in factors like pH, temperature etc. The multifunctional ability of the nanoparticles make it better compared to the conventional methods of dis-infection or filtration which used chemical reagents that impart toxicity on water and also seemed to be costly when compared to filtration using nanoparticle. Sometimes the chlorination is also in-effective due to microbial resistance.

Green synthesis among all other approaches is better as the physical approach needs more time to attain thermal stability and the chemical approach incorporates the use harmful reagents. Green synthesis under biological approach is relatively easier to carry out as it uses plant and its parts which are easier to obtain. The phytochemicals also influence the characteristics such as antimicrobial, catalytic, antibacterial properties on to the nanoparticles.

The nanoparticles synthesized by using various plant extract showed varied properties depending on the type of phytochemicals that were procured. Also the size and other distinctive properties of the synthesized nanomaterial was determined by pH, concentration of copper ions, stirring speed of the solution, concentration of the plant extract. Experimental study is necessary to decide the optimum conditions to obtain the best suitable nanoparticles for dis-infection. The characterization of the nanoparticle for various physical properties such as shape, size, surface area, surface energy was necessary to categorize the nanoparticles into various based on their usage. The instruments such as scanning electron microscope (SEM) or transmission electron microscope (TEM) shows the size and shape of the particles. UV-Visible spectroscopy was conducted to evaluate the formation of nanoparticles by analysing the graphical representation of the absorption spectrum.

A thin coating of plant extracts or the phytochemicals surrounding the nanoparticle was found which imparted their behaviour on to the NP's. The NP's showed strong anti-microbial, anti-bacterial properties against both gram negative (Escherichia coli) and gram positive (Staphylococcus aureus) bacteria by crossing the walls and compromise of the cell fluids resulting in cell death. Also the EDTA functionalized NP's showed enhanced properties such as high surface area and presence of pores which were helpful in removal of dyes up to an extent of 54%.

Immobilizing the copper nanoparticles on to membranes or fabrics made it possible to use these nanoparticles for filtration and disinfection of water and retrieval of the particles was also made easy. Such membranes were used in point-of-use filters which proved to be effective in removal of dyes and inhibit microbial growth. The copper-nanoparticles passing through the filter was well below the permissible limit for drinking water. Effect of copper nanoparticles on humans and on aquatic animals were conducted and an optimum concentration was established within which the nanoparticles proved to be safe or showed no adverse effect on the tested specimens.

Hence, use of green synthesized copper nanoparticles in disinfection of domestic waste water was found to be effective and the water treated could be used for secondary usage such as cleaning, watering plants etc. which would reduce the demand for water and provide an economical solution for costly filtration procedures such as RO and harmful and sometimes in-effective techniques such as chlorination.

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