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Green Synthesis of Copper Oxide Nanoparticles Using *Spinacia oleracea* Leaf for Wastewater Treatment: Effect Of pH and Concentration

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Abstract: Nanotechnology is defined as the manipulation and control of matter at the nanoscale using scientific knowledge from various industrial and biomedical applications. The nanoparticle generally refers to the individual molecules that make up the bulk of the nanomaterial. Nanoparticles are particles with a size of one to 100 nanometers (nm) and made up of three layers since they are complex molecules. This study was carried out to prepare Copper Oxide nanoparticles (CuO NPs) using the green synthesis method which is an environmentally friendly technique without using hazardous chemicals. Hazardous chemical substances lead to pollution of water which causes environmental contamination, so we used CuO NPs that were synthesized by using green method to purify the wastewater containing lead ion. Hence, the extracts of *Spinacia oleracea* were used as reducing agent. The synthesized CuO NPs nanoparticles were characterized using scanning electron microscopy (SEM), Energy Dispersive X-ray Analysis (EDX), Ultraviolet–Visible spectroscopy (UV–Vis), Fourier transform infrared spectrometry (FTIR). The two parameters of experiments, the metal ion concentration and pH were studied for the removal of Pb (II) from wastewater using the CuO NPs as nanosorbent. The synthesizing of CuO NPs was successful, the color change of the mixture of copper sulphate and spinach extract from light green to dark green indicates the succession of the synthesizing CuO NPs. The EDX and UV-Vis spectroscopy also indicated the succession of synthesizing of CuO NPs. The optimum removal efficiency of Pb (II) was found 78% and 85% for pH 7.01 and concentration of 0.002M, respectively. These factors showed that CuO NPs are good nanosorbents to purify wastewater contaminated with lead ions.

Key words: CuO nanoparticles・Green synthesis・Wastewater treatment・*Spinacia oleracea* leaf

INTRODUCTION

Nano-, is a prefix of the factor 10^{-9}, comes from the Greek word "nanos", meaning dwarf. Nanotechnology, nanomaterials, nanoscience, and nanoparticles have become popular terms not only in research, but also in everyday life. Nanotechnology is defined as the manipulation and control of matter at the nanoscale using scientific knowledge from various industrial and biomedical applications. Nanoscience is the science and study of matter at the nanoscale, which involves understanding the properties that depend on their size and structure, as well as comparing the appearance of individual atoms or molecules, or whether the difference concerns the bulk material. Nanoscale is a scale given at 1-100 nanometers (nm). This term refers to structures having a length scale relevant to nanotechnology. One billionth of a meter is a nanometer (Fig. 1). A lower limit to the mesoscopic scale is the nanoscopic scale [1-4].

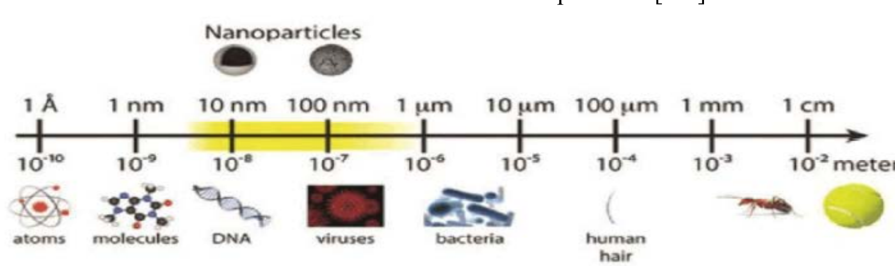

Fig. 1: Comparison of different sizes of materials with nanoscale dimensions [5].

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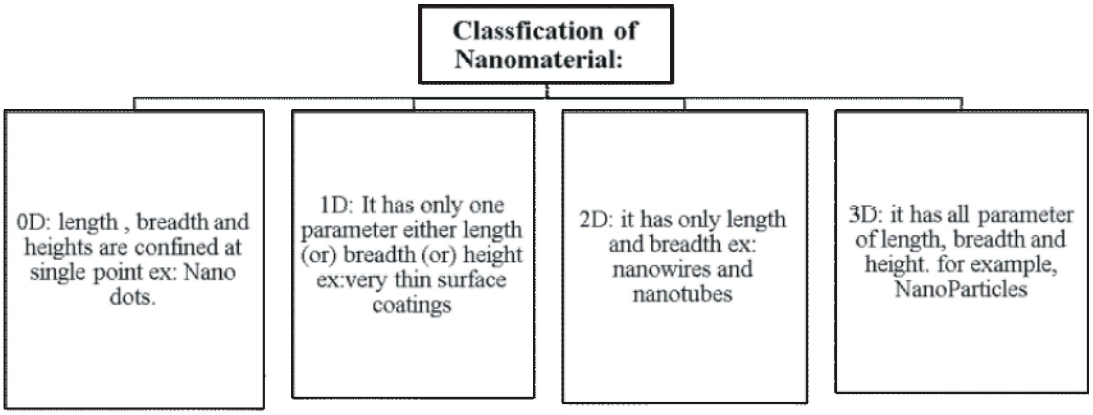

Fig. 2: Classification of nanomaterial including their definition and examples.

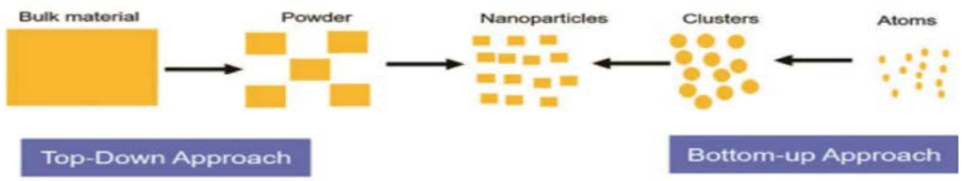

Fig. 3: Schematic illustration of the synthetic strategies of nanomaterials [10].

Nanomaterials are substances that have any external dimensions or internal or surface structure at the nanoscale. Sometimes described as possessing special characteristics resulting from the material's inherent nanoscale size. Although the terms "nanoparticle" and "nanomaterial" are frequently used interchangeably (Fig. 2), the nanoparticle generally refers to the individual molecules that make up the bulk of the nanomaterial. Nanoparticles are particles with a size of one to 100 nanometers (nm) [2, 3].

The nanoparticles are made up of three layers since they are complex molecules themselves: (a) the surface layer and can be functionalized with a wide range of small molecules, metal ions, surfactants, and polymers. (b) the shell layer, which is completely distinct chemically from the core. (c) the core, which effectively refers to the NP's core and is frequently used to describe the NP itself. Nanoparticles can be divided into many categories based on their physical properties such as size, morphology, large surface area, optical, such as the NPs' color, penetration of light and the ability of absorption and reflection. Mechanical properties are also important like elasticity, tensile strength and flexibility. Hydrophobicity, hydrophilicity, diffusion and suspension are also examples of physical properties. Sustainability of energy use newly electronics thermal conductivity, because of the magnetic and electric properties, like conductivity, semi-conductivity and resistivity. NPs also depend on the chemical properties such as chemical reactivity and stability to many factors such as heat, light, atmosphere and moisture. Redox, corrosion, anti-corrosion and flammability characteristics decide their particular uses [6, 7].

Preparation of Nanoparticles: The two primary approaches for creating nanoparticles are top down and bottom up (Fig. 3). The first technique involved "cutting" larger bits of a substance until just a nanoparticle remained to make nanoparticles. Typically, lithographic methods or etching are employed to do this; but, in special cases, ball mill grinding can also be used [6]. The main benefit of top-down techniques is that huge quantities of nanomaterials may be created quickly, whereas bottom-up procedures can create homogeneous nanomaterials with monodisperse size, shape, and atomic position. Depending on the method utilized to synthesize NMPs, the synthetic methodologies for NMPs can also be divided into physical, chemical, and biological categories. A wide range of nanoparticles, including octahedral and tetrahedral nanoparticles, are created using various synthetic techniques [8]. These nanoparticles include nanospheres, nanowires, nanocubes, nanorods, nanostars, nanoprisms, nanoplates, nano-hollow spheres, nanoflowers, nanotubes, and nanospheres. It's illustrated

Fig. 4: Schematic illustration for the synthesis of Ag NPs using different synthetic strategies as a model system [9].

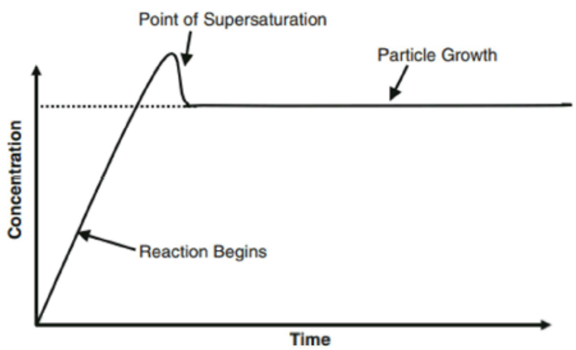

Fig. 5: A diagram showing a simplified summary of nanoparticle particle formation [6].

the various top-down and bottom-up synthetic techniques used to fabricate Ag nanoparticles as a model system in (Fig. 4) [9].

Numerous NMPs can be synthesized using these synthetic techniques. However, a bottom-up approach, in which a nanoparticle is "grown" from simple molecules, is the more practical way to produce nanoparticles on a commercial scale. Numerous techniques, including limiting the concentration, functionalizing the particle's surface, or using a micelle to template the growth, can be used to control the size of the nanoparticle. The bottom-up strategy uses the supersaturation principle to regulate particle size (Fig. 5) [6].

The concentration of the final material increases quickly in the early stages of the reaction, but precipitation doesn't start until the saturation limit gets reached (explained by the dotted line). If the process proceeds quickly enough, the saturation limit may be reached before material precipitates from solution. These initial particles will then serve as the starting point for the final particles, and in an ideal system, any additional creation of the final substance will take place at the particle surface, resulting in particle growth. The reality might be far more complex than this explanation suggests [11]. Yet this idea is a key component of all bottom-up strategies. The reaction medium, which can have a significant impact on the particle's final characteristics and surface chemistry, accounts for most of the changes in the reaction [6].

Now, after getting a brief idea about the basic methods for synthesis nanoparticles, it will be explained in detail.

1- Top-Down Synthetic Method: The fundamental idea of top-down synthetic techniques is to reduce massive materials to the appropriate nanometer scale dimensions. These synthetic methods use traditional workshop or microfabrication techniques to mill, cut, mold, and carve large-scale materials into precise sizes and shapes [12].

2- Bottom-Up Synthetic Method: This method involves slowly assembling nanoparticles from atoms and molecules according to their chemical characteristics while exposing them to capping ligands or surfactants. The idea behind this technique is based on molecular self-assembly and/or molecular recognition. When synthesizing nanoparticles, a variety of capping ligands are available to control the development of the particles [13].

This methodology allows for the creation of homogeneous nanoparticles as opposed to the top-down method used to create them. When NMPs are manufactured utilizing a bottom-up technique, their size, shape, and composition can all be easily customized attributable to their perfect crystalline structures [10]. The technique used in our research is called green synthesis which belongs to the category of bottom-up and we will talk about it in detail.

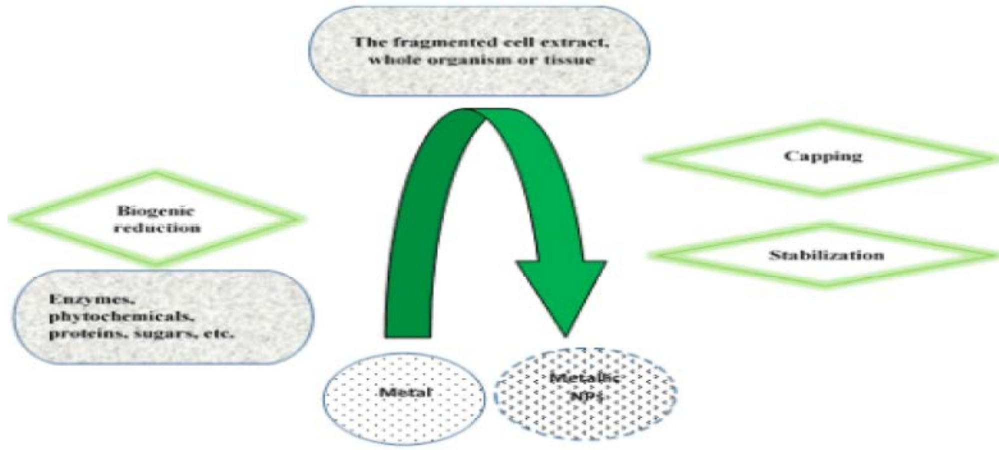

Fig. 6: Biological synthesis of nanoparticles [21].

Green Synthesis Methods: An environmentally friendly technique to create nanoparticles is by using the biological method, which is provided as an alternative to chemical and physical methods. Additionally, this procedure does not require expensive, toxic or dangerous substances. The biological technique, which has been utilized frequently in recent years, allows for the synthesis of metallic nanoparticles with a wide range of sizes, shapes, compositions, and physicochemical characteristics [14].

Utilizing biological agents like bacteria, actino-bacteria, yeasts, molds, algae, and plants, as well as their by-products, synthesis can be completed in a single step. Proteins, enzymes, phenolic compounds, amines, alkaloids, pigments, and other molecules found in plants and microorganisms undergo reduction-based nanoparticle production [15-20].

Traditional chemical and physical techniques show a risk of toxicity to the environment and the cell when using reducing agents for the reduction of metal ions and stabilizing agents to prevent unwanted agglomeration of the created nanoparticles. Additionally, the shape, size, and surface chemistry of the generated nanoparticles are thought to be toxic. These substances are already present in the biological organisms used in the green synthesis process, which produces biocompatible nanoparticles. The creation of nanoparticles by biological processes is depicted in (Fig. 6) [21].

Plants, which have a high capacity for metal detoxification, reduction, and accumulation, are promising, rapid, and cost-effective in the removal of metal-borne contaminants. Metallic nanoparticles with varied morphological characteristics can be created both inside and outside of cells. Extracts from plant parts including leaves, roots, and fruits are added to a solution of metal ions to start the synthetic process. The bioinduction of metal ions into nanoparticles is carried out by the materials included in the plant extract, such as sugar, flavonoid, protein, enzyme, polymer, and organic acid, which function as a reducing agent [17, 22-26].

The physical and chemical properties that we discussed earlier make the NP's special and convenient applicants for many applications and be classified into many types [27].

Applications: Nanoparticles have many applications in different fields based on their properties, these applications include: Medicines and Therapeutics, Manufacturing and Materials, Mechanical Industries, Electronics, Cosmetics and Sunscreen, Power Generation, Food, Catalysts and Environment The environment is our field of research.

Environment: The manufactured material uses can make the concentration of the NPs higher in groundwater and soil, which can show the most important exposure avenues for estimating the environmental risks. Because of ratio of high surface area to mass, natural NPs can contribute in the solid/water splitting of pollutants that can be absorbed to the NPs surface area, co-precipitated during the natural NPs formation or enclosed by aggregation of NPs that have the pollutants adsorbed to their surface. Most environmental applications can be categorized into: (i) Environmentally safe renewable products, like green chemistry or pollution prevention. (ii) Material treating that are polluted with hazardous compounds. (iii) Sensors for environmental stages [28].

Environmental improvements use NPs, because of their success in treating the air, water and soil and decontaminate them [7].

Cleaning polluted soil and treating it is done by injecting NPs into particular target areas for heavy metal pollution, toxic industries waste, etc. [7]. These NPs can be harmful to environment, so it's important to understand their speed, reactivity, eco toxicity and persistence [28]. Treating wastewater and water by using nano-filters is an important application of NPs [7]. The membrane in the nano-filter stops large molecules, and it can, with less energy, purify surface water and well water. Bacteria, viruses, pesticides, pollutants of organic origin and Ca & Mg salts can be removed from water. It's a safe process to the environment, because there are no chemicals used. Filters are categorized by their pores size, and they're categorized into nano-filters, micro-filters and ultra-filters. Nano-filter doesn't cost a lot like the other filters, plus they have the ability to eliminate viruses and bacteria [29].

MATERIALS AND METHODS

Materials: Spinach leaves, Distilled water, Hydrated Copper sulphate solution 0.1 M and Lead nitrate solution (0.01, 0.008, 0.005, 0.002 M).

Equipments: Beaker 500 ml, Hot plate, Glass rod, Filter paper whatman no.42, Erlenmeyer flask 250 ml, Stirrer, Glass watch, Mortar and pestle, Funnel and Volumetric flask 100 ml.

Method:

Preparation of Plant Extracts: Spinach leaves were collected from a local vegetable market. Then, we prepared the spinach extract by washing the spinach leaves with distilled water and drying them at room temperature for 48 h. Then it was grinded, and we added 25 g in a standard beaker filled with 500 mL of distilled water, the solution is heated for 5 min at 60°C. After heating and leaving the solution to cool down, we filtered it twice and stored the extract at the refrigerator and used it within a week as a reducing agent for preparing CuO Nps.

Preparation of CuO NPs: In the green synthesis method, 80 mL of copper sulphate ($CuSO_4$) at a concentration of 0.1 M in a 250 mL Erlenmeyer flask placed on a magnetic stirrer (Fig. 7) added to it 20 mL of spinach extract, every 1 ml of extract is slowly added to the solution and stirred for 3 min till all the extract is used (Fig. 8). Finally, the mixture was stirred for half an hour where the solution changes when adding the spinach extract to the green colour (Fig. 9), the obtained nanoparticles are denoted as CuO NPs. The mixtures were left for 7 days at room temperature then was separated using a centrifuge (6000×g cycles) for 15 min and the nanoparticles were obtained after leaving the mixture to dry at room temperature shown in (Fig. 10).

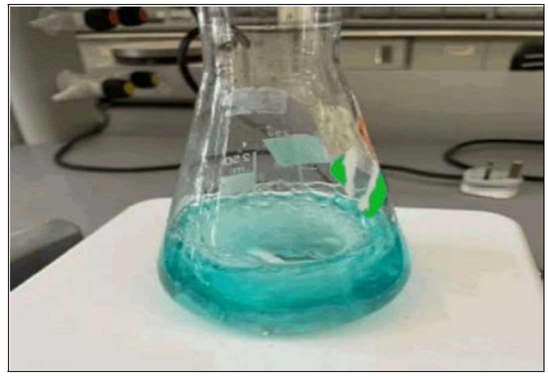

Fig. 7: Solution of copper sulphate.

Fig. 8: Addition of Spinach extract to copper sulphate solution.

Fig. 9: Change the color of $CuSO_4$ after adding Spinach extract.

Fig. 10: CuO NPs after dry.

Detection and Characterization of CuO NPs: The main detections of CuO NPs were accomplished by visual observation of the change in the color of the mixture. The synthesized nanoparticles have been characterized by UV–Vis spectroscopy. Scanning Electron Microscopy (SEM) coupled with Energy dispersive X-ray (EDX) was used to explore the surface morphology and size of the synthesized CuO NPs as well as its elemental composition. Fourier transform infrared spectrometry (FTIR) is used for nanoparticle samples to confirm the synthesis by analyzing the chemical bonds present.

Preparation of Wastewater and Metal Ion Treatment Experiment: We have prepared synthetic wastewater containing lead. Two factors were studied. The first factor was studying the effect of the different metal concentrations (0.01, 0.008, 0.005, 0.002 M), and the concentration was fixed at 0.01 M at the pH experiments. The second factor was the pH of the solutions. We prepared three solutions of different range of pH (5-9), acidic, basic and neutral by neutralization process with NaOH (0.01M), the pH was fixed at 5.19 when studying the other factor. The experimental experiments were done by stirring 0.2 g of CuO NPs in 30 mL solution of lead metal ion, with concentration range from 0.002-0.01 M for 120 minutes. The removal percentage of the nanosorbents can be estimated with the following equation [30].

$$\%R = \frac{C_0 - C_f}{C_0} \times 100$$

C_o is the metal ion initial concentration (M), C_f is the metal ion concentration (M) at equilibrium, R is the removal percentage of the studied metal ions.

RESULTS AND DISCUSSION

Characterization of Nanoparticles The SEM micrographs of the CuO NPs presented in (Fig. 11) show that the prepared CuO NPs were mostly spherical in shape. The SEM micrographs revealed that the synthesized CuO NPs were in the nanometer range of 1 micro. The elemental components of the prepared CuO NPs were assured using Energy-dispersive X-ray (EDX) and the peaks obtained are shown in (Fig. 12). It is shown that the prepared CuO NPs are mainly composed of Cu, O and C with small traces of other materials. In EDX patterns show a strong signal peak at 0.5 keV representing Cu atoms. The detected carbon and high oxide peaks are due to the phytochemicals already present in plant extract which is added in large volume. The phytochemicals in the extracts are the main cause for the formation of complexes with the copper salt that reduces the ions to form nanoparticles. Hence, we observed the color transformation in the prepared Solutions (Fig. 13). UV–Vis spectroscopy is used in the range of 200-400nm. (Fig. 14) indicates a

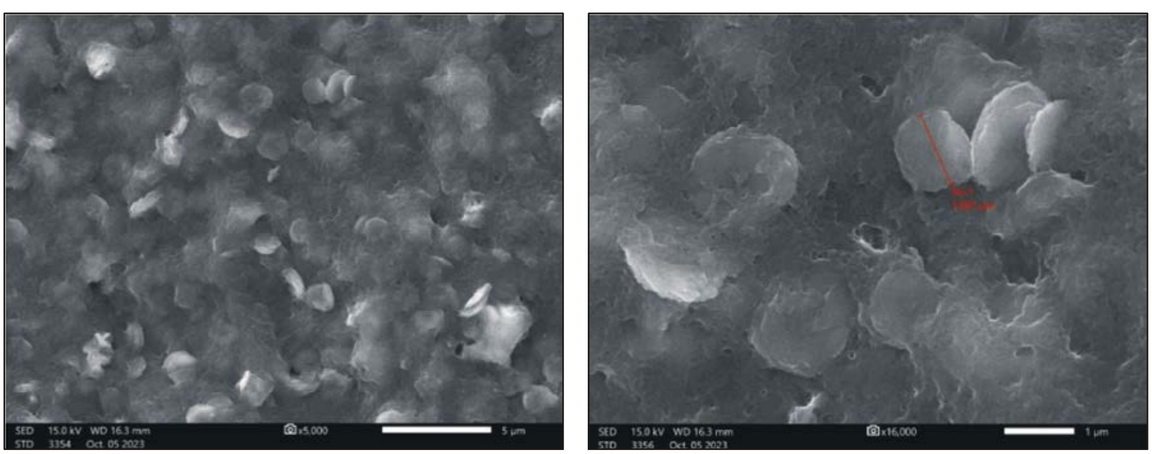

Fig. 11: The SEM micrographs of the CuO Nps.

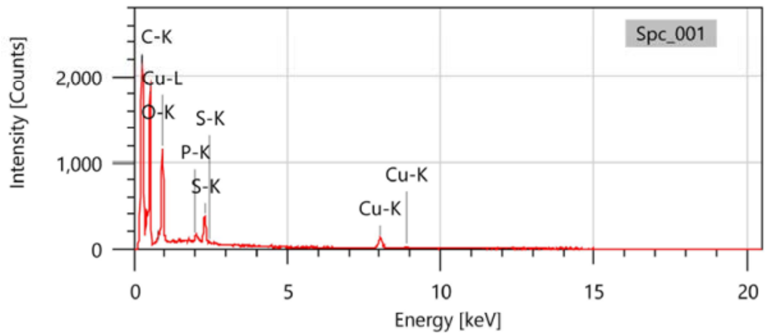

Fig. 12: EDX spectra of CuO Nps.

Fig. 13: Color transformation in the Solution of CuO.

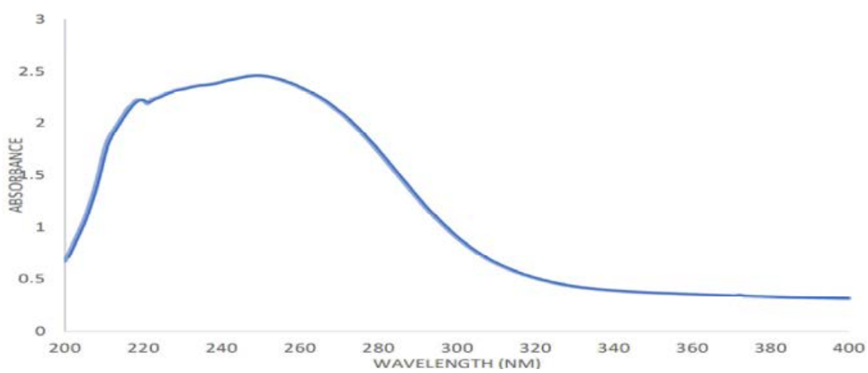

Fig. 14: Uv-Vis spectra of CuO Nps.

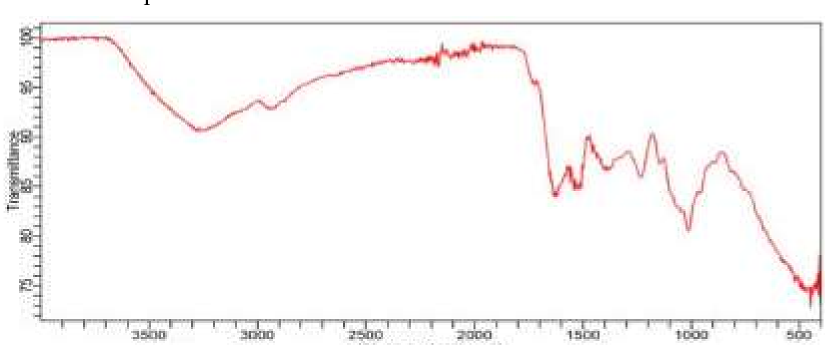

Fig. 15: FTIR spectra of CuO Nps**.**

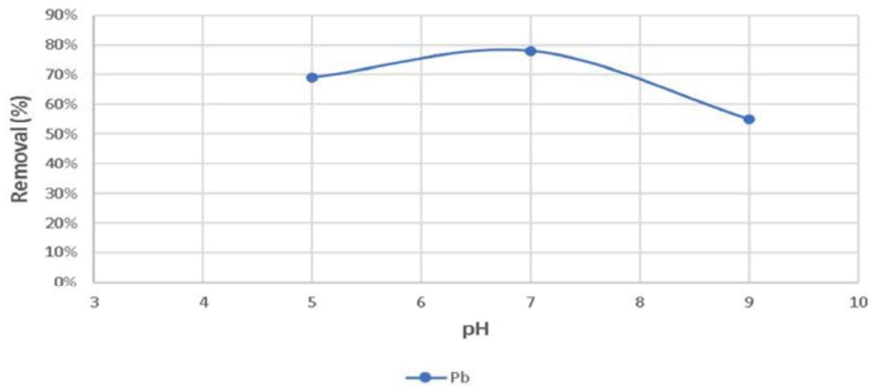

Fig. 16: The effect of pH of CuO NPs on heavy metal adsorption.

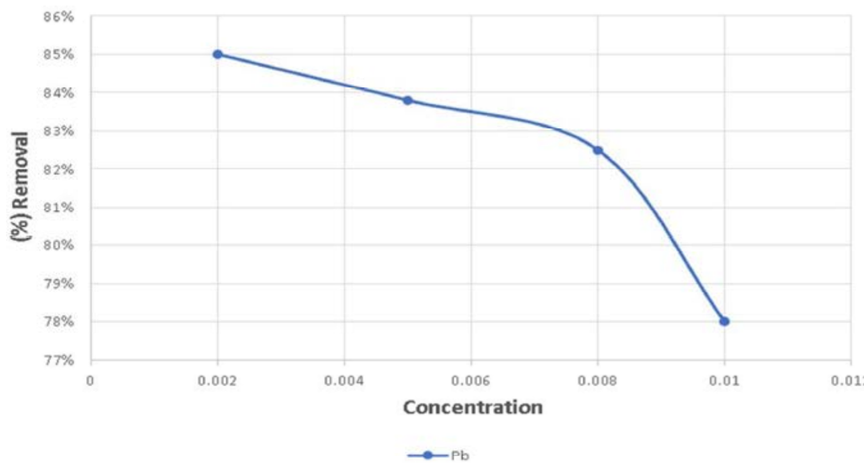

Fig. 17: The effect of concentration on heavy metal absorption.

noticeable peak at 248.91 nm due to the inter band transition of the core electrons of the CuO NPs. The FTIR spectrum of CuO NPs is presented in (Fig. 15). The sharp peak around 500-600 cm^{-1}, this is a characteristic peak for CuO stretching vibrations, which directly indicates the presence of copper oxide (CuO). This peak appears between 500-600 cm^{-1} and is a strong indicator of the metal-oxygen bond in CuO nanoparticles. The absorption peaks around 3400-3600 cm^{-1}corresponds to the OH stretching vibration indicating the presence of hydroxyl groups. The absorption peaks around 1600-1650 cm^{-1} correspond to the H-O-H bending vibration, which further confirms the presence of water molecules either from moisture or from the synthesis method. The C-O functional group shows peaks in the range of 1000-1300 cm^{-1} in an FTIR spectrum [31].

Metal Ions Treatment Experiments:

Effect of pH: The pH of the solution has a major role in the removal of heavy metals from wastewater. In order to determine the impact of pH on Pb (II) adsorption on CuO NPs, pH values ranging from 5 to 9 at equilibrium time were used. Because of the decreased positive charge of the nanosorbent, which results in less electrostatic repulsion between the nanosorbent's surface and metal cations as well as less competition between the metal cations and hydrogen atoms or the functional groups of the nanosorbents, the removal percentage of the metal ions reached its maximum value which is 78% when the pH value increased to the neutral level 7. Furthermore, the metal ions precipitated at pH levels higher than 7shown in (Fig. 16) [32].

Effect of Initial Concentration of the Selected Metal Ions: The removal percentage is inversely proportional with the concentration as shown in (Fig. 17), where the removal percentage decreases when the concentration of the metal ions increases, and this relationship was indicated from the adsorption of the metal ions at different concentrations. This relationship shows a significant connection between adsorption efficiency and the metal concentration. The increase of initial concentration will lead to decreasing the removal percentage from 85% to 78%, this is because the nanosorbents have a certain number of active sites, and increasing the concentration will make these sites saturated and not be able to adsorb more Pb (II) ions [33].

CONCLUSION

The synthesizing of CuO NPs was successful using spinach leaves extracts as reducing agent, the colour change of the mixture of copper sulphate and spinach extract from light green to dark green indicates the succession of the synthesizing CuO NPs. The EDX, UV-Vis spectroscopy and FTIR also indicated the succession of synthesizing of CuO NPs. Also, it was found that the adsorption application of CuO NPs on the removal percentage of Pb (II) depends on several factors, such as pH and metal ion concentration. The optimum removal efficiency of Pb (II) was found 78% and 85% for pH 7.01 and concentration of 0.002M, respectively. These factors showed that CuO NPs are good nanosorbents to purify wastewater contaminated with lead ions.

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