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EFFICACY OF NANOPARTICLE SYNTHESIZED SPINACH VARIETY IN BIOREMEDIATION OF COPPER FROM CONTAMINATED WATERS

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ABSTRACT

The green synthesis of iron oxide nanoparticles was studied, using *Amarnthusblitum* variety of spinach as a reducing agent. UV-visible spectroscopy, X-ray diffractometer (XRD), Fourier transform infrared spectroscopy, and scanning electron microscopy (SEM) were used to examine the structural and morphological properties of the produced Fe_3O_4 nanoparticles. SEM investigation revealed that the synthesized nanoparticles are spherical, highly crystalline, and agglomerated, with sizes ranging from 30 to 65 nm. Nanoparticles were used as an adsorbent to remove copper from wastewater. The adsorption of copper onto iron oxide nanoparticles from aqueous solution was investigated by varying contact time, adsorbent dosage, and agitation speed. Copper removal was 98% with 350 rpm agitation, 60-minute contact period, 0.05g adsorbent dosage, pH of 6±0.2at room temperature. The equilibrium adsorption data were evaluated using Freundlich and Langmuir isotherms, and the Freundlich model best describes copper adsorption. The kinetic analysis revealed that the adsorption of copper follows pseudo-second-order models with rate constants of 0.9838. The current study demonstrates that Fe_3O_4 nanoparticles can be used as effective green adsorbents for the removal of copper from wastewater.

Key words: Adsorption, *Amaranthusblitum*, Copper, Fe_3O_4 nanoparticles, Green synthesis, Spinach

INTRODUCTION

The relatively young area of nanotechnology focuses on inventions that function at the nanoscale and have wide-ranging real-world applications (Nakum and Bhattacharya, 2022). The advantages of nanoparticles over conventional wastewater treatment methods are being studied by a large number of researchers. In large-scale wastewater treatment applications, several conventional approaches are limited because they are energy-intensive and impractical (Gautamet al, 2016; Abdelbasir et al, 2020 and Benassai et al, 2021).The removal of heavy metals from wastewater has become a major international concern. Diverse technologies have been developed to tackle this problem. Many nanomaterial have been developed to remove heavy metals from contaminated water due to the manometer effect, which provides nanotechnology its unique features. Although nanotechnology is still in its early stages, interest in it is (Hamidreza et al, 2017; Almomani et al, 2020 and Khoso et al, 2021).

Researchers have recently focused a lot of attention on iron oxide-based nanomaterial because of their remarkable properties and straightforward adsorption approach separation procedures. Using iron-based nanomaterial increased the adsorption capacity, which enhanced overall performance and simplified the magnetic field-assisted separation procedure (Dave et al, 2014; Aragawet al, 2021; Zhang et al, 2013 and Sameenaet al, 2020). In recent years, zerovalent metal nanoparticles have proven to be effective in treating and remediating contaminated water. Nanoscalezerovalent iron (nZVI) has garnered significant attention as a potentially novel adsorbent for the remediation of many heavy metals, including mercury (II), chromium (VI), copper (II), nickel (II), and cadmium (II) (Parvin et al, 2019 and Baruah et al, 2019).

Agro-based nanoparticles have proven to be an excellent heavy metal remediation method due to their capacity to absorb heavy metals (Aswathi et al, 2023; Darshan et al, 2023 and Modi et al, 2022). Agricultural waste has gained a lot of attention for its high removal effectiveness and financial advantages when used to remove heavy metals from wastewater (Shaukat et al, 2022). The sorption mechanism of biomass can involve a variety of processes, such as chemisorption, complexation, surface adsorption, diffusion through pores, and ion exchange (Tade et al, 2020).

Green approaches have been touted as environmentally beneficial since they produce environmentally friendly products and by products (Miessyaet al, 2020 and Lakshmanan et al, 2021). Green solutions are also highlighted as cost-effective because they consume less energy, eliminate the need for expensive chemicals, and create dangerous end products (Parveenet al, 2016 and Rashidet al, 2022). Through a reduction mechanism, the phytochemicals function as reducing agents in the production of nanoparticles, transforming metal ions into nano forms (Bawazeer et al, 2021, Shafey, 2020 and Lingraju et al, 2020). The green manufacture of iron oxide nanoparticles consists mostly of three steps: selecting the solvent medium (precursor), the biological source-related reduction agent, and non-toxic stabilizing agents (Ezhilarasiet al, 2016 andEzhilarasi et al, 2018).

Adsorption has been demonstrated to be an efficient method of treating industrial waste effluents, offering numerous advantages such as affordability, accessibility, financial gain, user-friendliness, and effectiveness (Sukmana et al, 2021 and Rathi and Kumar, 2021). Heavy metal biosorption is a relatively new technology that has showed considerable promise for eliminating pollutants from aqueous effluents. Biosorption is gaining popularity as an alternative to current technologies for removing and/or recovering toxic metals from wastewater (Beni and Esmaeili, 2020; Barquilha et al, 2017; Barros et al, 2022 and Bulgariu and Bulgariu,2018) . The two primary benefits of biosorption technology are its capacity to efficiently reduce the concentration of heavy metal ions to incredibly low levels and the use of reasonably priced biosorbent materials (Brazesh et al, 2021). The process of metal adsorption and biosorption on agricultural wastes is complex and impacted by a variety of factors. Some of the mechanisms involved in the biosorption process include chemisorption, complexation, adsorption - complexation on the surface and pores, ion exchange, micro precipitation, heavy metal hydroxide condensation on the bio surface, and surface adsorption (Demirbas, 2008 and Torres, 2020).

Copper (Cu) is one of the most widely utilized metals in a number of industrial and agricultural applications (Masindi and Muedi, 2018 and Saydeh et al, 2017). Copper (Cu) is a heavy metal used in a wide range of applications, including water pipes, metal processing, batteries, the pulp and paper industries, and electronic circuits (Afzalet al, 2022; Wanget al, 2023 and Hamid et al, 2022). Copper is an essential trace metal for microorganisms and humans, but too much can be harmful. Many enzymes require copper to function properly, making it a necessary metal. It stimulates plant growth by providing structural strength to the plants, and it also contributes to photosynthesis via the electron transport chain. It also serves as a catalyst for cell wall metabolism and hormone signalling (Kumar et al, 2021 and Shabbir et al, 2020).

Copper is frequently found in high concentrations in wastewater. Furthermore, even in little concentrations, copper is an extremely poisonous metal. Copper-contaminated wastewater must be treated before being released into the environment (Husak, 2015 andChowdhury et al,2018). Cu is non-biodegradable, poisonous, and easily accumulated in living creatures, particularly in the human body, even at low quantities. They can cause serious illnesses such as cancer, nervous system damage, and kidney failure, and they can be deadly in large doses (Alicia et al, 2020). Cuproenzymes, which are involved in redox reactions, can convert copper from Cu2+ to Cu+. This change of state can potentially be dangerous since it produces superoxide and hydroxyl radicals. Copper has been proven in tests to break DNA strands and cause bases to oxidize using oxygen free radicals and hydroxyl radicals. Cupric and cuprous forms of copper cause DNA breakage through the genotoxic benzene metabolite (1, 2, 4-benzenetriol), more than iron (Moreno and McCord, 2017; Desaulniers et al, 2023 and Ge et al, 2022).

Handling heavy metals is particularly important because of their recalcitrance and persistence in the environment. Several remediation approaches have been developed for treating heavy metal-contaminated water (Qasem et al, 2021; Vidu et al, 2020; Hussain et al, 2021 and Deniz et al, 2022). These methods include adsorption, reverse osmosis, solvent extraction, membrane filtering, and chemical precipitation, biosorption, advanced oxidation processes, ion exchange, and chemical coagulation-flocculation (Omar et al, 2023; Vareda et al, 2019; Carolin et al, 2017; Pohl, 2020; Khulbe and Matsuura, 2018 and Qiu et al, 2021).The nature of heavy metals, the permitted limit and the influent and effluent concentrations all influence the treatment chosen for heavy metal management in a given context (Vareda et al, 2019; Alalwan et al, 2020; Renu and Singh, 2017; Saleh et al, 2020).The current study aims to develop iron oxide nanoparticles for the efficient removal of copper from waste water.

MATERIAL S AND METHODS

Collection of agricultural waste and green synthesis of nanoparticles

Spinach variant Amaranthusblitum was collected from various areas in Kerala (Palakkad) and Coimbatore (Thirumalayampalayam), India. Samples were prepared in accordance with established methods (Buarki et al, 2022). Spinach aerials were crushed after air drying. Using a water bath, the samples were homogeneously mixed in water at 80°C. After filtering the crude extract solution, the filtrate was oven dried for 48 hours at 45°C. The powdered dry extract was mixed with an appropriate amount of distilled water. In each solution, $FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ were added at a 2:1 molar ratio. NaOH was used to bring down the pH to around 11±0.2. Following centrifugation, the precipitates were dried in an oven at 70°C. Without extract, the same procedure was repeated for the blank.

Characterization of Green synthesized nanoparticles

The synthesized Fe_3O_4 nanoparticle samples were analysed using a UV spectrophotometer to determine their absorption spectra from 200 to 400 nm. The nanoparticle sample was examined under a scanning electron microscope (SEM) to assess its form. The functional groups on the surface of Fe_3O_4 nanoparticles were identified using Fourier transform infrared (FTIR) analysis. At a 4 cm^{-1} resolution, the scanned spectra ranged from 200 to 4000 cm^{-1}. XRD analysis can reveal a material's chemical composition by identifying its crystalline phases (Nkele and Ezema, 2021 and Jayawardena et al, 2021).

Batch mode studies of copper adsorption by nanoparticles

The adsorption efficiency of the prepared Fe3O4 nanoparticles was examined using $CuSO_4$ solution as an adsorbate and nanoparticles as adsorbent using batch experiments. Here, a specific amount of Fe_3O_4 nanoparticles was added to synthetic solution of $CuSO_4$ prepared. The initial concentration of $CuSO_4$ was kept at 100 ppm. The mixture was shaken using a mechanical shaker at a speed of 300 rpm. The parameters studied during the batch experiment include contact time (10 – 90 mints), adsorbent dosage (0.01 – 0.07 g/35 mL) and agitation speed (50 – 350 rpm) at pH 6±0.2 and temperature at 30±0.5℃. Sample of $CuSO_4$ is withdrawn from each flask and filtered in order to separate adsorbent from the aqueous solution and the content of each flask was analysed for the presence of copper after the adsorption process (Shirsath and Shirivastava, 2015).

The adsorption capacity (q_e) was determined using the mass balance expression Equation (1)

$$qe = \frac{V(Co - Ce)}{M}$$

The adsorption capacity (q_t) at time t was determined using Equation (2)

$$Qt = \frac{V(Co - Ct)}{M}$$

In the Equations (1) and (2), Co is the initial metal ions concentration, Ce is the concentration of metal ions in solution (mol/L) at equilibrium, *Ct* is the concentration of metal ions in solution (mol/L) at time t in solution, V is the volume of initial metal ions solution used (L) and M is mass of adsorbent used (g).

Adsorption isotherms

The adsorption isotherm depicts the relationship between the adsorbate in the surrounding phase and the adsorbate adsorbed on the surface of the adsorbent at equilibrium and constant temperature. Understanding the adsorption isotherm is essential to maximizing adsorbent use and explaining how solutes interact with adsorbents (Saleh, 2020).

The linearized forms of Langmuir and Freundlich isotherms used to describe the adsorption process respectively are:

$$\frac{1}{qe} = \frac{1}{qm} + \frac{1}{qmKL}\frac{1}{Ce}$$

$$lnqe = lnKf + \frac{1}{N}lnCe$$

Where,

K_f is Freundlich constant or maximum absorption capacity (4.614), C_e (mg/L) is the equilibrium concentration of adsorbate in solution, Q_e is the quantity of metal adsorbed on the surface of the biosorbent (mg/g), $1/n$ is the Freundlich constants characteristics of the system, indicating the adsorption capacity and the adsorption intensity where n = 1.2, Q_m is the maximum adsorption capacity and K_L is Langmuir constant and its value is 0.003.

RESULTS

Characterisation of green synthesised nanoparticles

UV Visible Spectroscopy

UV Visible spectroscopy was utilized to ensure the formation of iron oxide nanoparticles. Figure 1 shows the ultraviolet-visible spectrum of Fe_3O_4 nanoparticles. The adsorption band formed between 250-270 nm. The absorption peaks are also attributed to the presence of alkaloids, phenolic acids, flavonoids, tannins, terpenoids and carbohydrates (Balu et al, 2020). There is a distinctive absorption peak in the 300–400 nm wavelength regions, indicating the formation of iron oxide nanoparticles. Additionally, polyphenol is linked to the peak that was found between 300 and 400 nm. Iron oxide nanoparticles were found to have an intense absorbance at about 250 nm from the UV-visible spectrometer examination, indicating that the produced particles were photosensitive in the UV region (SRajendran and Sengodan2017).

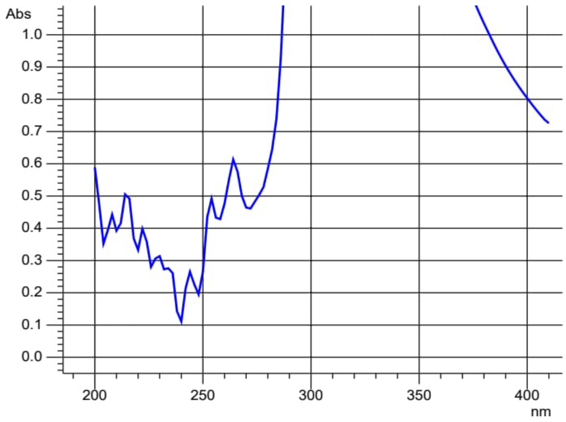

Figure 1:UV Visible spectra ofFe_3O_4 nanoparticles

Scanning Electron Microscopy

The structural and morphological properties of green synthesised iron oxide nanoparticles were studied using SEM analysis. Figure 2 shows the synthesised Fe_3O_4 nanoparticles with 10 kV electron high tension using scanning electron microscopy. The morphological form indicates that the nanoparticles are spherical nature. They generate a cluster of nanoparticles with an average crystalline size of about 50 nm and are a highly crystalline aggregate. Morphological traits are beneficial for metal adsorption. The increased surface tension of ultrafine nanoparticles may be responsible for nanoparticle aggregation. Consequently, pressure that cause particles to stick to one another result in sub-micron-sized entities. With the exception of a few cubic ones, the SEM image of the encapsulated nanoparticles clearly demonstrates that they are spherical in shape. The SEM demonstrated that the aggregation of nanoparticles was caused by the sample's solution form. Encapsulated iron oxide nanoparticles have a desirable structure that promotes metal adsorption (Poguberović et al, 2016; Gaharwar et al, 2019; Fenekansi et al, 2022 and Aqib et al, 2023).

nanoparticles have a desirable structure that promotes metal adsorption[70-73].

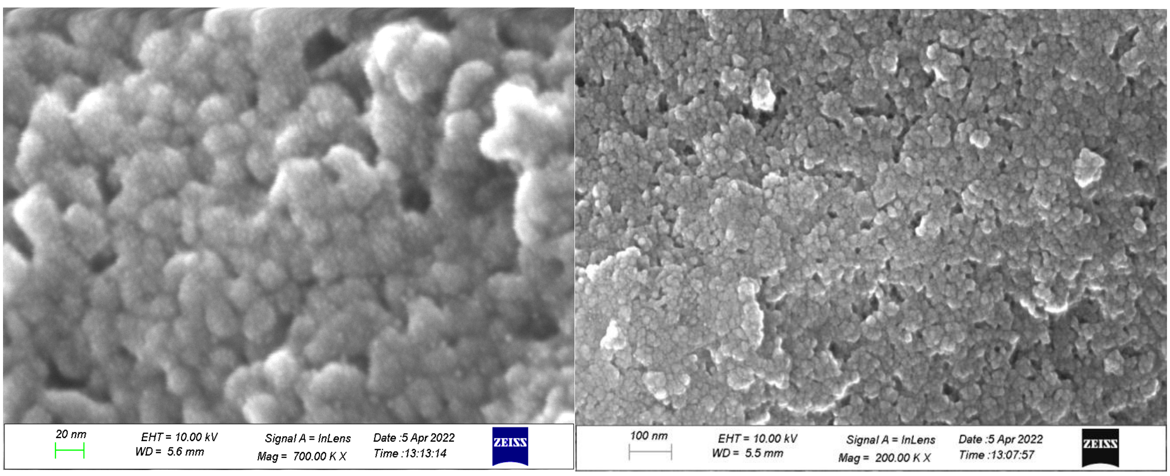

Figure 2:SEM images of Fe_3O_4 nanoparticles

Fourier Transform Infrared Spectroscopy

The FTIR spectrum of Fe_3O_4 nanoparticles synthesised from *Amaranthusblitum*is shown in figure 3. This result indicates the presences of various functional groups in spinach extract. The peak at 3137.015 cm^{-1} is due to asymmetric stretching of alkanes (-CH_2-). A peak at 2132.741 cm^{-1} refers to the C≡C stretching. The peak at 1637.588 cm^{-1} attributes to stretching vibration in amide (-C=O-). The peak at 1382 cm^{-1} indicates N-O stretching vibration due to the presence of nitro compounds. A peak at 1036.843 cm^{-1} corresponds to C-N stretching vibration or the presence of nitro compounds. The peak at 601.301 cm^{-1} is the characteristics of C-Br stretching vibration which indicates the presence of alkyl halides (Kanwal et al, 2021; Hwang et al, 2014 and Saranya et al, 2017).

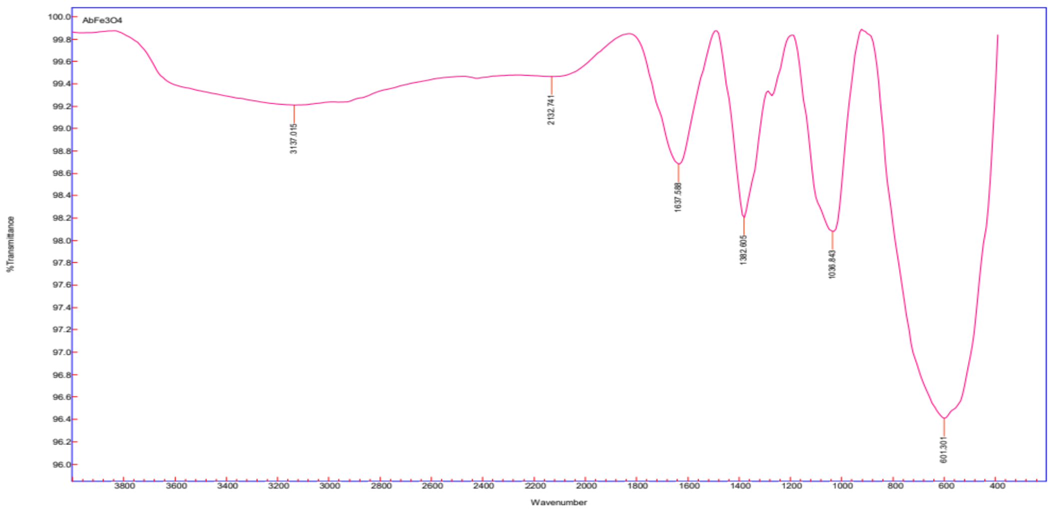

Figure 3: FTIR spectrum of Fe_3O_4 nanoparticles

X-ray diffraction analysis

Figure 4 shows the XRD spectrum of iron oxide nanoparticles synthesised from *Amaranthusblitum*. There are nine strong intense peaks at 2θ of 24, 28, 32, 41, 45, 50, 59, 67 73° and the diffracting planes are 200, 311, 222,400, 422,511, 440 and 622. The sharp peak indicates that the nanoparticles synthesised have crystalline structure of face centred cubic. The existence of several diffraction peaks shows the development of iron nanoparticles. The adsorption of organic compounds from the spinach extract, which acts as a capping and stabilizing agent, was found to be responsible for the wider shoulder peak (Liu et al, 2018). The small peak can be regarded as the presence of α-Fe (Hjiri et al, 2020 and Shukla et al, 2015). The decrease in the peak intensity of "Fe" could potentially be attributed to variations in the electron densities of the host materials, contingent upon multiple factors including structure and scattering factor (Revathy et al, 2021 and Katta et al, 2024).

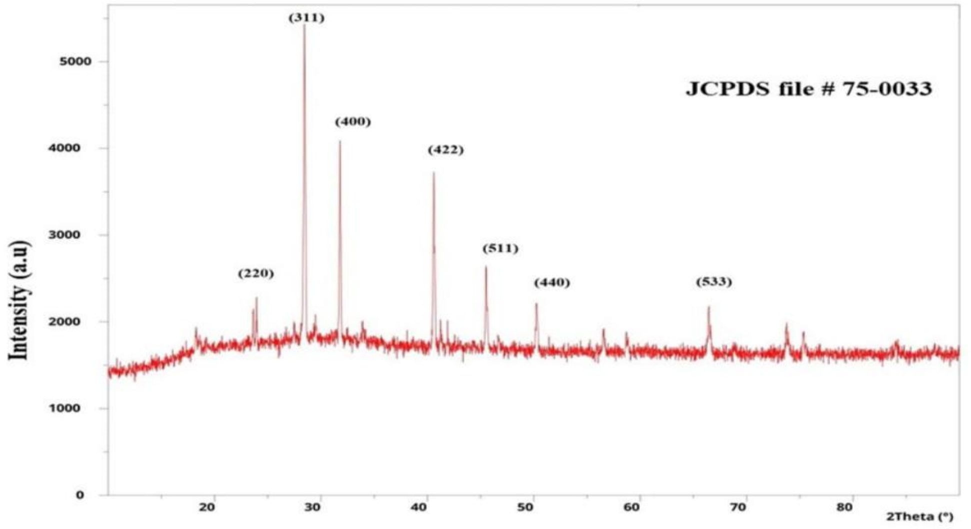

Figure 4: XRD spectrum of Fe_3O_4 nanoparticles

Batch mode studies of copper adsorption by nanoparticles

Effect of adsorbent dosage

Figure 5 shows the effect of adsorbent dosage on copper adsorption. Using Fe_3O_4 nanoparticles in the range of 0.01-0.07 g/35 mL, the effect of adsorbent dosage on copper adsorption from waste water was studied. The other parameters including temperature = 30°C, beginning concentration = 100 ppm, pH = 6, contact time = 60 minutes, and agitation speed = 300 rpm are kept at optimal levels. The rate at which copper is eliminated is directly proportional to the absorbent dosage. A maximum removal of 99% is achieved at an adsorbent dosage of 0.06 g/35 mL and 0.07 g/35mL. By increasing the adsorbent dosage, the availability of sorption sites rises, and hence the rate of copper adsorption increases. After a particular adsorbent dosage, all of the copper is adsorbed to the adsorbent, and no more adsorption occurs as the adsorbent dose increases (Attarad et al, 2023 and Phuengprasop, et al, 2011).

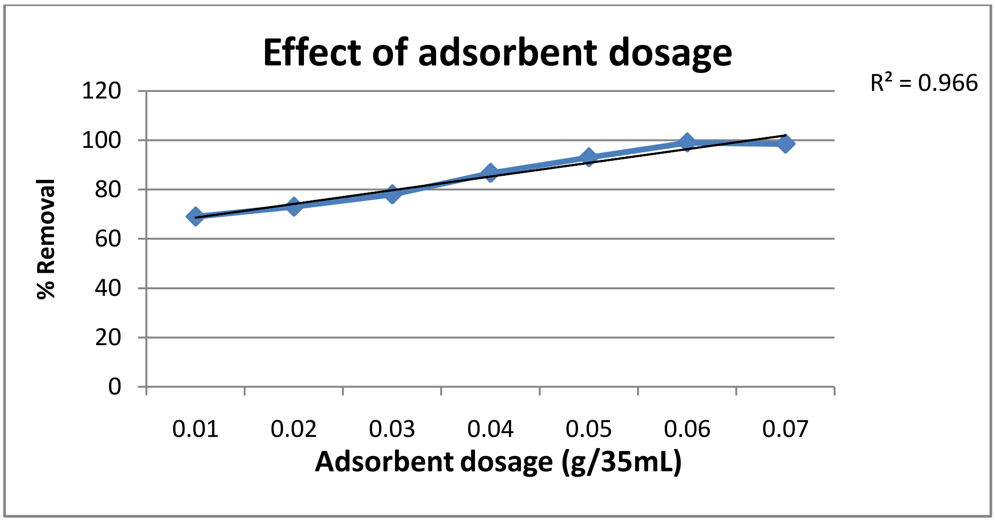

Figure 5: Effect of adsorbent dosage

Effect of agitation speed

Different agitation rates ranging from 50 to 350 rpm were used to investigate the effect of speed on copper adsorption by nanoparticles. Other parameters, including temperature (30±0.5°C), starting concentration (100 ppm), pH (6±0.2), contact time (60 minutes), and adsorbent dosage (0.06 g/35 mL), remained unchanged. Figure 6 shows that when agitation speed increases, the proportion of elimination rises and then stabilizes. The greatest removal achieved at 300 rpm, after which it becomes constant. Because of the existence of active sites on the adsorbent's surfaces, adsorption started quickly. However, as the active sites get saturated, the rate of adsorption decreases. The shift in metal ion adsorption from ion exchange to chemisorption could possibly account for the decrease in metal ion removal percentage (Redwan et al, 2023).

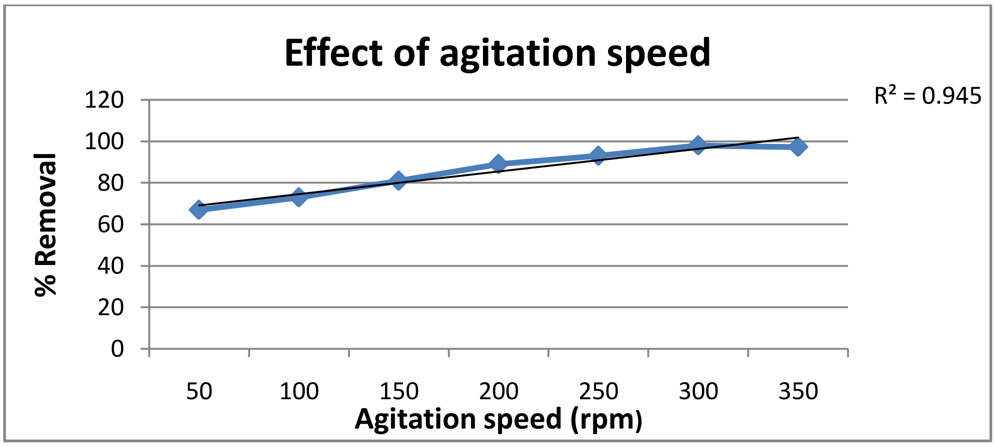

Figure 6: Effect of agitation speed

Effect of contact time

To determine the influence of contact time on copper adsorption by nanoparticles, contact times ranging from 10 to 90 minutes were tested. All other parameters remained unchanged (temperature = 30℃, starting concentration = 100 ppm, pH = 6, agitation speed = 300 rpm, and adsorbent dosage = 0.06 g/35 mL). Maximum copper adsorption occurs at 60 minutes, after which the rate of adsorption becomes constant. The sorption rate was high in the early stages due to the higher number of active sites available on the surface of Fe_3O_4 nanoparticles. As time passes, the number of active sites decreases, thereby stabilizing the adsorption process (Kahrizi et al, 2018 and Hosseini et al, 2019).

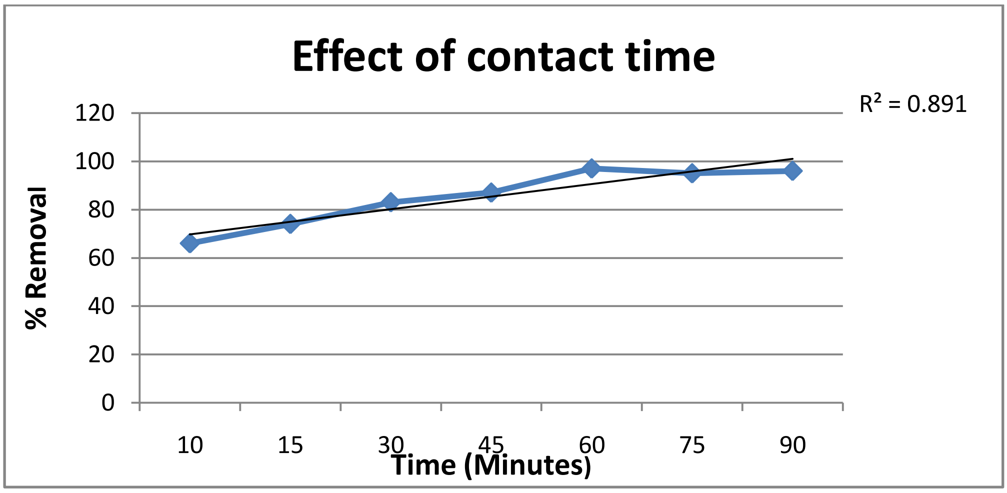

Figure 7: Effect of contact time

Adsorption isotherm and kinetics

Adsorption isotherm is a graph that shows the relationship between the amount adsorbed by a unit gram of sorbent and the amount of metal ions left in an experimental medium after equilibrium, as well as the distribution of metal ions between the solid and liquid phases. To study the relationship between amount of copper adsorbed by nanoparticles, Langmuir and Freundelich isotherm models were used. Figure 8 and 9 show the fitting of the adsorption data with linearized form of the two isotherms. Value of correlation coefficient R^2 was used for the assessment of models. The R^2 value of Langmuir isotherm was 0.8264 and Freundelich isotherm was 0.9838. The R^2 value of Freundelich isotherm was greater than Langmuir isotherm. From this it is clear that adsorption is better described by Freundelich model (Ahmadi and Izanloo, 2023).

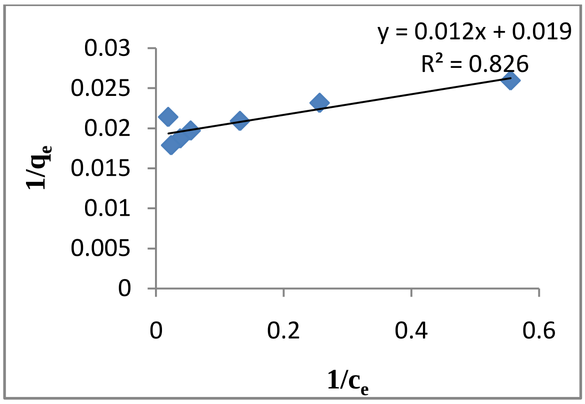

Figure 8: Langmuir isotherm model of Amaranthusblitum

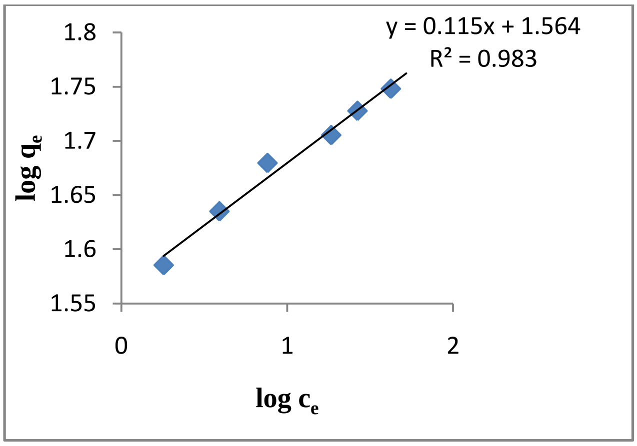

Figure 9: Freundelich isotherm model of Amaranthusblitum

DISCUSSION

The present study deals with the effective removal of copper from waste water using nanoparticles from spinach. Batch mode studies of different parameters prove that these nanoparticles are efficient for copper removal. The elimination of pollutants from wastewater, including heavy metals, has grown to be a major global issue. Various technologies have been created to address this issue (Renu and singh, 2017 and Odumbe et al, 2023).Because of the outstanding qualities that come from the nanoscale effect, numerous nanomaterial have been designed to remove heavy metals from polluted water. Nanotechnology is still in its infancy, but interest in it is growing (Yaqoob et al, 2020 and Hamidreza et al, 2017). One well-known adsorbent for water remediation is the use of nanomaterial based on iron oxide nanoparticles to remove heavy metals. Their significant physiochemical properties, low cost of operation and simple regeneration in the presence of an external magnetic field make them more appealing for the purification of water (Gutierrez et al, 2017). The utilisation of surface modification strategies for iron oxide nanoparticles in water remediation enhances the effectiveness of iron oxide in eliminating heavy metal ions from aqueous solutions (Huang and Keller, 2015). Adsorption is an efficient and inexpensive procedure where the appropriate adsorbents in an atmosphere favouring adsorption are used in methods for extracting metals or dyes from a water source (Kumar, 2019). Nano-bioremediation is one of the new rising techniques for remediation of contaminations utilizing green synthesized nanoparticles. Nano-bioremediation is yet another territory, however, quickly pulling in much intrigue among researchers. Such a significant number of biogenic nanoparticles have been tried and yielded excellent outcomes. The biosynthetic green incorporated nanoparticles could develop as a superior and more secure option in contrast to traditional strategies(Sekar et al, 2023).

CONCLUSION

Nanoparticles made from various agricultural waste products are currently frequently used in the adsorption of heavy metals from industrial wastewater. In this study, iron oxide (Fe_3O_4) nanoparticles were produced using a simple co-precipitation approach, with spinach aerial parts extract serving as a unique stabilizing and capping agent. UV-Visible spectroscopy, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscope (SEM) analysis were used to assess the structural, optical, and morphological properties of the produced Fe_3O_4 nanoparticles. The SEM investigation reveals that the nanoparticles are spherical in shape, extremely crystalline, and highly agglomerated, appearing as a cluster of nanoparticles with a size range of 50 nm. The Debye-Scherrer relation was used to determine the crystalline size of nanoparticles, which was found to be approximately 42 nm. The Fe_3O_4 nanoparticles were then utilized as an adsorbent for removing copper from waste water. The adsorption data was fitted to Freundlich isotherm with correlation coefficient R^2 value 0.9838. The kinetics investigation shows that both spinach kinds adsorb in second order. These findings demonstrate that Fe_3O_4 nanoparticles synthesized by spinach as a capping agent can be used to effectively remove copper from waste water using adsorption processes.

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