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Synthesis of Green Metaloxide Nanoparticles using Aloe-Barbadensis Leaf Extract (Acid Red 28) for Dye Removal Applications

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ABSTRACT

The present study focuses on the synthesis of stable metal oxide nanoparticles (MO-NPs) using Aloe Vera Barbadensis leaf extracts via a green route approach. The MO-NPs were synthesized by the interaction of Aloe-Barbadensis leaf extract with metaloxide salt and its azodye (Congo red). These NPs were then characterized using SEM (surface morphology), XRD (Crystallography structure, peaks of MO-NPs), UV-Vis (Absorption spectrum) and FTIR (presence of functional group). The SEM images revealed the surface morphology of nano sized powder while the XRD results showed that the particle size ranged between 5-30 nm. The UV-Vis absorption spectrum revealed that the MO-NPs are iron and copper oxide respectively. FTIR data, on the other hand, indicated the hydroxyl (OH) functional group stretching due to the presence of alcohols and phenolic chemicals in the extract. Moreover, the effect of physical properties such as solution concentration, their PH and MO-NPs adsorbent dosage on percentage of dye degradation was also determined. As per results, the NPs removed about 70-80% of Congo red dye solution at optimum condition of reaction factors. The dynamics of pseudo-second order was followed in the adsorption process by MO-NPs.

*Keywords***:** *Aloe barbadensis, Metal oxide nanoparticles (MO-NPs), Cogo red.*

INTRODUCTION

The revolution in nanotechnology has been enormous from the last era to the present due to its small size and amazing properties. The NPs have shown to possess unusual properties such as magnetic, electrical, optical, physical, mechanical, and structural. In the world of nanotechnology, we deal with the manipulation of materials of very low size normally (i.e. < 100 nm) where improved properties can be easily obtained (Sathiyavimal et al. 2021). Keeping this in view, the fabrication and synthesis of NPs for desired properties imparts new developments in the field of science and technology. Different dyes and detergent industries generate and dispose untreated wastewater that is causing environmental and human health problems. Among such pollutants present in the wastewater of dyes and detergent industries is Congo red dye. Hence, the goal of the present work is to synthesize green-MO-NPs and analyze its removal efficiency for Congo red dye from solution (Pakzad et al. 2019).

Furthermore, the synthesis of NPs in a vacuum environment is not only a challenging process, but also has more cost for processing and maintenance. Hence, we used solution-based processing where no vacuum environment is required to synthesize the NPs. This leads to an expanded, environmentally friendly and less drastic reaction condition that has improved biomedical properties (Arasu et al. 2019). The most common MO-NPs methods for synthesis are physical and chemical processes, but these processes have certain drawbacks, such as being chemically more reactive, being hazardous to the environment and human, and being more toxic. Green technology is more prominent for the synthesis of NPs and has also gained benefits for the environment and society (Khalil et al. 2017).

Degradation is one of the most important properties possessed by MO-NPs sue to high surface area and ratios, hence the green synthesis route promises the stabilized NPs (Jassal et al. 2016). In this work, Cu-NPs have been fabricated using leaf extract of Aloe vera plant. The phenolic content of Aloe Vera extract is dissolved in distilled water and then used to catalyze NPs as a capping and reducing agent (Datta et al. 2017). These plant extracts contain Carboxymethyl (-O-CH2-COO-) plus Sulphonyl (-O-CH2-CHOH-CH2-O-CH2-CH2SO3). Furthermore, this plant offers deeper healing abilities and can preserve antioxidant vitamins (A, C and plus vitamin B12), choline, and folic acid with eight enzymes (Irshad et al. 2020).

MATERIALS & METHODOLOGY

PREPARATION OF ALOE VERA BARBADENSIS LEAF EXTRACT

Fresh leaves of the Aloe Vera Barbadensis plant obtained from the botanical garden of GCU Lahore, Pakistan were washed with distilled water, dissolved in 250 mL distilled water and allowed to boil for 10 minutes at 80 ^{0}C. The boiled leaves were allowed to cool down until room temperature (Jassal et al. 2016). The resulting solution (pH=4) was filtered twice using a 0.2µm filter paper to remove any impurities.

Briefly, $FeCl_3 \cdot 6H_2O$ black solution (0.01M) was added to Aloe Vera extract in a ratio of 1:1 proportion. This resulted in an immediate formation of Fe_2O_3-NPs after 10-20 minutes by reduction process. The mixture obtained was washed with ethanol for several times and then filtered and dried under a vacuum environment (at 40°C) to obtain Fe_2O_3-NPs (A et al. 2018). Aloe Vera *Barbadensis* leafs have the best reduction potential with ferric chloride salt. The nanoparticle formation was confirmed by the external color change from developed pale orange to dark red color. These Iron Oxide NPs were used in future characterization.

FABRICATION OF MO-NPS

In a 250 ml flask, 50 ml of 0.04M Cu solution (99% purity, Sigma Aldrich) was added to 25 ml of leaf extract and heated at 100 °C. After 90 minutes, the hue of the reaction mixture had changed from deep blue to dark greenish. Brown-colored copper metal precipitates suggest the production of NPs. After discarding the supernatant, the resulting solution was centrifuged at 10,000 rpm for 20 minutes at 350 °C, and solid particles were recovered. Deionized water and ethanol were used to wash the particles twice. For evaporation, the collected NPs were dried in a watch glass.

Briefly, $FeCl_3 \cdot 6H_2O$ black solution (0.01 M) was added to Aloe Vera leaf extract with ratio of 1:1 proportion. The NPs of Fe_2O_3 were immediately formed within 10-20 minutes by reduction process after heating. The mixture obtained was centrifuged and washed several times with ethanol, filtered and dried at 40 °C under vacuum to obtain Fe_2O_3-NPs (A et al. 2018). *Aloe Vera Barbadensis* leafs have been shown to possess best reduction potential with ferric chloride salt. The external colour change from the developed pale orange to the dark red colour confirmed the nanoparticle formulation.

PREPARATION OF AZO DYE STOCK SOLUTION

The preserved culture of pure *Aspergillus Niger* (NRRL 567) was extended by cultivating on the PDA media Petri plates via streaking method (Behera, 2020) and incubated at 30 ^{0}C for 96 hours. The cultures were renewed every 4 weeks.

CHARACTERIZATION/KINETIC RESULTS AND DISCUSSION

CHARACTERIZATION RESULTS

The maximum absorption peaks of the UV spectrophotometer of iron oxide and copper oxide NPs was observed between the ranges of 200-250 nm. The intense peak was due to the inter-band transition of core electrons (Morales et al. 2019). X-ray diffraction crystallographic parameter of SC: The biogenically synthesized C-1 (AV) and F-1 (AV) extract of *Aloe Vera Barbadensis* leaf extract was analyzed after adopting a wide range of experimental conditions to examine crystallographic parameters and peak indexing (Figure 1). The Fourier transform infrared spectral bands at different positions corresponded to the stretching and bending of the functional groups. The different peaks were observed between the ranges 400-4000 cm^{-1}. The broad bands were observed at 3230-3270 cm^{-1}corresponding to the hydroxyl (OH) functional group stretching due to the presence of alcohols and phenols. Peaks between a range of 2930-2925 cm^{-1} and 1605-1615 cm^{-1} indicated the C-H and amide -NH group stretching respectively. The peak at 1650.7 cm^{-1} was due to C=C aromatic bending. The topography was analyzed by the SEM model JSM (6180) at different magnifications of the instrument. According to the results shown in Figure 2. , copper oxide NPs exhibited tetragonal and iron oxide rhombohedral shape with slightly irregular shape morphology and a smooth surface. The TEM analysis revealed the size and proper crystallinity of biogenically fabricated NPs. However, copper oxides NPs were predominantly tetragonal with a diameter of approximately 10 to 40 nm .The shape of SC: F-1(AV) was rhombohedral to pyramidal with a smooth surface.

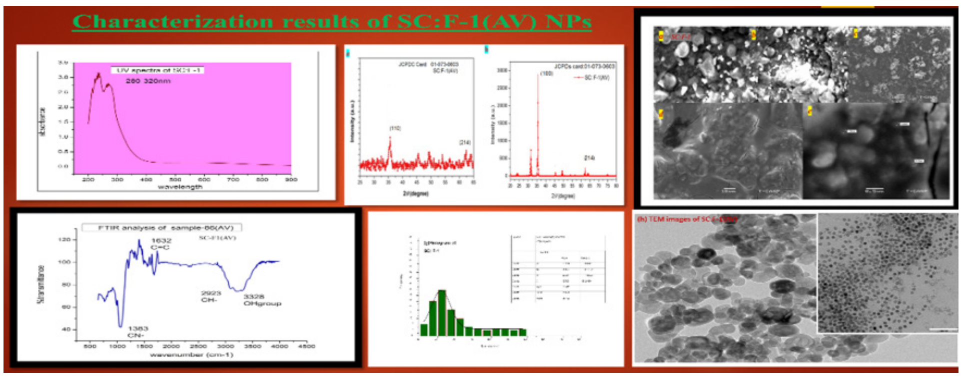

FIGURE 1. SC Characterization Results: F-1(AV)

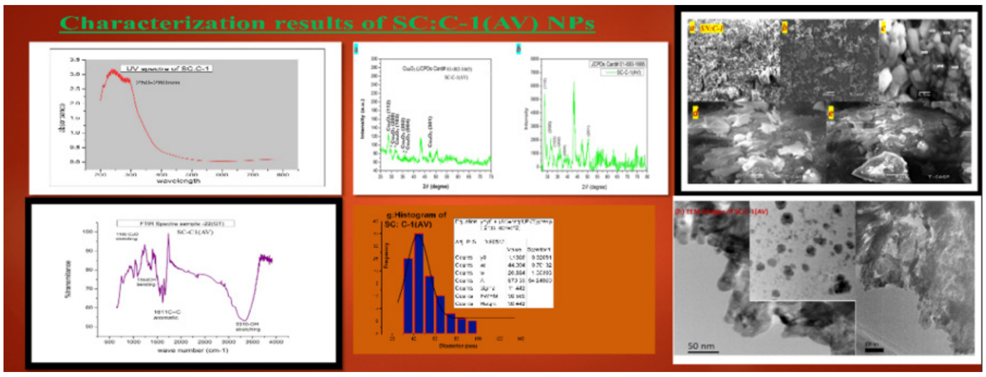

FIGURE 2. SC Characterization Results: C-1(AV)

KINETIC STUDIES OF CONGO RED DYE REMOVAL BY MO-NPS

ADSORPTION EQUILIBRIUM AND BATCH KINETIC STUDIES

The mixture of metal oxides NPs (iron oxide, and copper oxide) with 0.1 g dry powder of azodye dye and buffer solution were shacked at specific temperature 27 ^{0}C. The adsorption spectrum was analyzed by isotherm series examination of the adsorbent dose and the amount of adsorbate (Binupriya et al. 2008) also with pH and time. The dye concentrations were measured by UV-visible spectrophotometer, at least duplicated under the same condition. The batch sorption experiment was performed in 100 ml flasks (Erlenmeyer), in which 50ml of anodyne dye CR solution with 5-30 mg / l of adsorbent samples were mixed with constantly adjusted pH. The solution of dyes and nanomaterials flasks were tightly capped and agitated in an isothermal shaker at 350 rpm, to achieve equilibrium, about 30 minutes equilibrated concentrations of Congo red were analyzed by measurement of absorbance by UV-visible spectrophotometer at the wavelength range of 500-600 nm. The percentage removal of azodye dyes was calculated by the following equation:

$$\% \text{ Removal of azodye dye} = C_i - C_t / C_t \times 100$$

MEASUREMENT OF ADSORPTION PARAMETERS

For SC: F-1, and C-1, the maximum percentage of CR azodye dye removal was 88% and 87% at maximum adsorbate amounts of 95 mg/mL, 110 mg/mL and 60 mg/mL respectively. SC: C-1and F-1 showed the highest percentage removal of CR azodye dye under optimum PH of 4 and 5, respectively. Adsorbents SC: C-1 and SC: F-1 produced maximum amounts of 0.81 and 0.08 respectively. We studied the Congo red dye maximum removal time by metal oxides for samples SC: F-1 (88% in 40min) and SC: C-1 (87% in 80min). In (Figure 3), you can see the graphical representation of time's effect on adsorption.

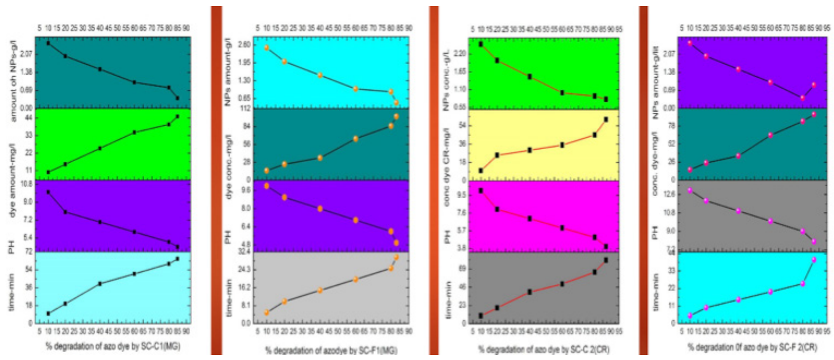

FIGURE 3. Effect of the experimental parameter on MO- NPs for % removal of Congo red dye

ANALYSIS OF EQUILIBRIUM ISOTHERMS

Isotherms of adsorption equilibrium The correlation between azodye dyes and metaloxide NPs was analyzed by Elovich, Langmuir, and Freundlich. Adsorption isotherms are the mathematical relationship between the target adsorbent (amount/gram) and the concentration of Ce in the solution (mg / L) at the equilibrium point, which is related to the removal mechanism of azodye dyes and the adsorbent's characteristics (Alamrani & Al-Aoh, 2021; Li et al. 2021; Razzaq et al. 2021). The adsorbate quantity on the reacting adsorbent was elaborated using isotherm experiments, that are typically used to explain azodye dye adsorption. The findings of several equilibrium isotherms were determined experimentally, and the favorable sorption of the azo dyes malachite green and Congo red was examined under the observed equilibrium circumstances.

ISOTHERM CURVE (LANGMUIR)

For Congo red dye for MO-NPs (SC: C-1, F-1), the separating factor KL was 0.45 and 0.43, respectively (Figure 4). The Langmuir adsorption isotherm projected the equilibrium data fitness of azodye dyes CR based on the strong monolayer maximum capacity and correlation coefficients between (0.990-0.998). The KL 1 values for samples F-1 and C-1 confirmed the favourable and practicable reaction and adsorption capacity (Qmax) of 83mg/g and 81.3mg/g, respectively.

ELOVICH ISOTHERM CURVE

Adsorption kinetics Elovich equation had been widely applied for chemical reaction mechanism and for surface coverage, which is inversely related to adsorption rate The correlation coefficient R^2 analyzed by metals oxides SC (CR): F-1(0.993) and C-1(0.996) for Congo red azodye dyes adsorption. Elovich adsorption isotherms were plotted b/w Int and qt for MO-NPs. The parameters of Elovich model α and β were calculated by the intercept of slope in linear plotted versus Int and qt. The parameters of equation β calculations from graph were 13.3 and 9.31 while α parameter 0.04 and 0.09 for copper oxide and iron oxide nano metaloxides. The data revealed that the Elovich model was better fitted than Freundlich equilibrium data.

FREUNDLICH ISOTHERM CURVE

The Freundlich equilibrium isotherm is an empirical equation, which is assessed to design heterogeneous system. The Freundlich constant adsorption capacity (Kf) and adsorption intensity (n) were analyzed by plotting graph between logCe and logqe. The Kf values were analyzed for SC: F-1 and C-1 were 12.98 and 15.98; graphically observed 0.55 and 0.75 values of 1/n respectively. The model assessment for applicability was confirmed by correlation coefficients calculations from the graph which ranges between (0.94-0.98) with greater error values confirming Freundlich adsorption isotherm fitting Langmuir model for all metaloxides samples SC: C-1 and F-1, and for CR azodye dyes (Figure 4).

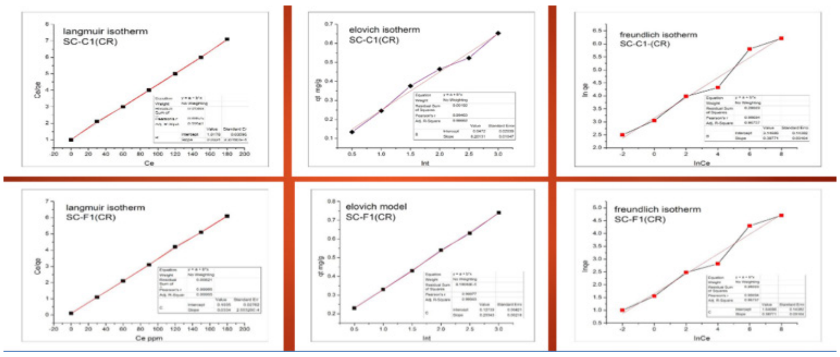

FIGURE 4. Equilibrium isotherm results of SC: C-1 and SC: F-1 for Congo red dye removal

CONCLUSION

In this study, biogenic and green fabrication with a single pot method was used to synthesize copper and iron oxide nanoparticles. No capping agents or templates were used during the process. Moreover, the predictable mechanism for biogenic synthesis required less time, low energy and easily accessible precursor, hence opening up the opportunities for various metal oxide nanoparticles. The use of plants extract (aloe barbadensis) for synthesis of metal oxide nanoparticles has fortified the manipulating of stable, ecofriendly, inexpensive, and time-effective approaches. Hence, biomaterial based synthesis methods eliminate the need to use toxic chemicals. The proteins, alcohols, polyphenols and lipids present in the plant extracts act as both chelating/reducing and capping agents. The MO-NPs, being effective adsorption of toxic azodye dyes, antibacterial and antifungal agents, are the utmost important in the outlook of industrial applications. Anti-cancer drugs loading, releasing, cytotoxicity, wound healing properties were analyzed as biomedical applications of MO-NPs. The SC: The Z-1 sample was observed to have the highest percentage of degradation of the malachite green and Congo red azodye dyes. The experimental optimization conditions of time, pH, adsorbent and adsorbate were analyzed. The Langmuir model fit better with linearity rather than Freundlich model predicted chemisorption. The elovich model also has a linear fit for all metal oxides. MO-NPs had expeditious kinetic data in good agreement (R^2 >0.99) with pseudosecond order and Langmuir adsorption isotherm. The Elovich model showed a reasonably ($R^2 \leq$0.99) value that manifested a non-fitting of the model to the calculated data in recent research for all MO-NPs. In conclusion, MO-NPs keep excellent azodye dyes degradation potential at optimum conditions. The MO-NPs have adsorption capacity for malachite green (MG) azodyes greater than Congo red (CR) azodyes.

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DECLARATION OF COMPETING INTEREST

None

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