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Biosynthesis of metal oxide nanoparticles by using *Aloe barbadensis* leaves extract and study of application in Congo red (Acid red 28) dye removal

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Abstract
In this study, stable metal oxide nanoparticles were synthesized by using *Aloe barbadensis* leaf extracts. The present study tracing of an object is a green synthesis of nanoparticles by the interaction of leaf extract and metal oxide salt and its azo dye (Congo red) degradation efficiency. The characterization was performed by XRD, SEM, FTIR, UV spectroscopy. The XRD analysis showed that average particle size was between 5-30nm by Scherrer equation. The effect of variables like concentration, time, PH, adsorbent dosage also examined in this present study on % degradation of dye. The nanoparticles removed about 70-8% of Congo red dye from solution at optimum condition of reaction parameters. The kinetics of pseudo second order was followed by adsorption process by MO-NPs.

Keywords: *Aloe barbadensis*, SEM, Metal oxide nanoparticles, Congo red, XRD, adsorption

Introduction
Nanotechnology deals with the manipulation of matter at low size normally less than 100nm [1]. Recent development in the field of science and nanotechnology has lead to a new concept of synthesizing nano-sized particles of desired size and shape wastewater characteristics, such as dyes, detergents used in the process are the parameters that have caused a serious effect on health. In this study, we intended to remove Congo red dye from its aqueous solution by metal oxide nanoparticles [2].
Hence, there is a scope to develop new methods for the synthesis of nanoparticles which should be required in-expensive, less drastic reaction condition and eco-friendly. Degradation and biomedical properties [3]. Metallic nanoparticles can be prepared by the chemical and physical method. These methods have certain flaws like toxic chemicals and also dangerous to the environment. Developing research in green chemistry employed prominent part in nanotechnology to gain benefit to the society [4]. Nanoparticles have dye degradation property due to increase surface area and mass ratios. Therefore, the need for the development of a reliable, biocompatible, benign and eco-friendly process to synthesize nanoparticles. Green synthesis has been engaged in synthesis of highly stabilized nanoparticles. Copper nanoparticles were synthesized by leaf extract of Aloe vera plant. Phenolic content in plant extracts dissolved in water, degradable and used to catalyzed synthesis of the nanoparticle as capping and reducing agent [5].
Nanoparticles show unusual structural, electrical, optical and magnetic properties. Several clinical trials are being conducted to further evaluate the use of aloe vera gel for a variety of disorders. Aloe vera juice is commonly used as an ointment and skin abrasions Functional groups in aloe vera contain, Carboxymethyl -O-CH2-COO- and Sulphonyl -O-CH2-CHOH-CH2-O-CH2-CH2SO3-. This ancient plant may offer deeper healing abilities. Aloe vera keep antioxidant vitamins A, C, and plus vitamin B12**,** folic acid, and choline. It contains eight enzymes [6, 7]. These chemicals salicylic acid and anthraquinones (Aloin, Emodin, aloetic acid, anthranol, cinnamic acid, and anthracene) are responsible for the reduction of copper Polyphenols in aloe vera plants leaves extract like aloin can act as chelating, capping and also reducing agents for nanopartical formulation. This was one-step processes in which no surfactants and other capping agents used [8].

Experimental
All the chemicals in this present study were analytical grade and pure and purchased from

Sigma Aldrich company. Aloe vera leaves were taken from the nearby botanical garden of the institute GCU Lahore.

Fabrication of MO-NPs by *Aloe barbadensis* leaves extract

Preparation of *Aloe barbadensis* leaves extract

Fresh leaves of *Aloe barbadensis* plant were purchased from the botanical garden of the institute GCU Lahore. The leaves extract were prepared by washing leaves with distilled water. The obtained leaves material were dissolved in 100 mL of water in a 250mL flask and allowed to boil for 10 min at 80 ^{0}C and then allowed to cool down at room temperature (35^{0}C) [9]. The resulting solution was filtered twice using a 0.2-micrometre filter paper to remove any impure particles. The calculated PH of that solution was PH 4 at room temperature.

Briefly, 0.01 M $FeCl_3 \cdot 6H_2O$ black solution was added to Aloe broadness leaves extract in a 1:1 proportion. The nanoparticles Fe_2O_3-NPs were immediately obtained after 10-20 minutes by reduction process after heating 60-80 ^{0}C. The obtained mixture was centrifuged and washed several times with ethanol and then filtered, dried at 40°C under vacuum to obtain the Fe_2O_3-NPs [10]. *Aloe barbadensis* leaves have the best reduction potential with ferric chloride salt. The nanoparticle formulation was confirmed by the external colour change from developed pale orange to dark red colour. These iron oxide nanoparticles were used in future characterization shown in (Figure 3.5)

Fabrication of Metal Oxide Nano Particles

50 milliliters solution of. 04M solution of copper sulfate (99% purity Aldrich Company) was added into 25mL Aloe Vera leaves extract in a 250 mL Erlenmeyer flask with constant shaking with a stirrer under heating at temperature100–120 °C range. The Color of the reaction mixture was turned from deep blue to dark greenish after 90 mint. After some time, brown colour precipitates of copper metal indicate the formation of nanoparticles. Then the resultant solution underwent centrifugation by using (Beckman JA-17 rotor model), at 10,000 rpm for 10-15min, at room temperature 35 ^{0}C and solid particles were collected after discarding the supernatant. The particles were washed twice with deionized water and ethanol. The collected NPs were dried in a watch glass for evaporation of extra liquid.

Briefly, 0.01 M $FeCl_3 \cdot 6H_2O$ black solution was added to Aloe broadness leaves extract in a 1:1 proportion. The nanoparticles Fe_2O_3-NPs were immediately obtained after 10-20 minutes by reduction process after heating 60-80 ^{0}C. The obtained mixture was centrifuged and washed several times with ethanol and then filtered, dried at 40°C under vacuum to obtain the Fe_2O_3-NPs [10]. *Aloe barbadensis* leaves have the best reduction potential with ferric chloride salt. The nanoparticle formulation was confirmed by the external colour change from developed pale orange to dark red color. These iron oxide nanoparticles were used in future characterization shown in (Figure 1).

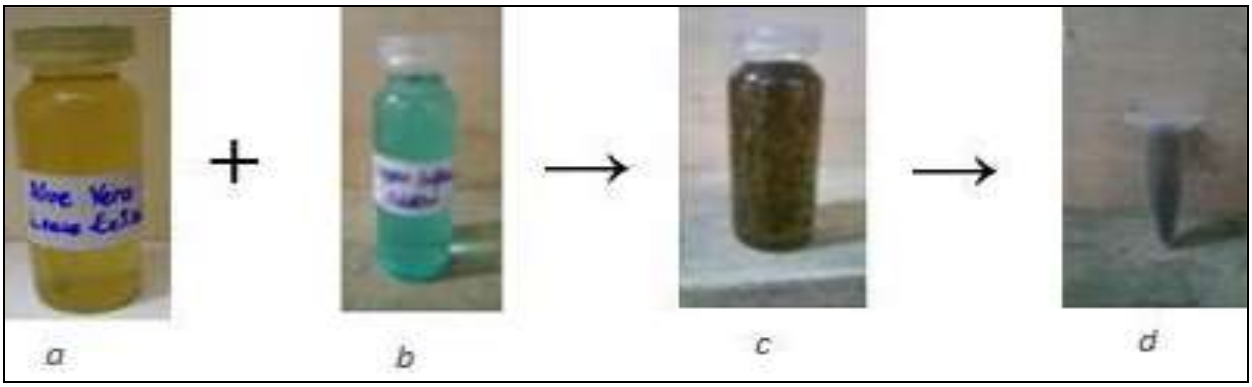

Fig 1: Process of synthesis of metaloxide nanoparticles

Characterization Results of Metal Oxide Nanoparticle

The maximum absorption peak of UV spectrophotometer of iron oxide and copper oxide NPs was noted between the ranges of 200-250 nm. The intense peak was due to the inter band transition of the core electrons of the sample, while that of a peak around [11-13]. X-ray diffraction crystallographic parameter of SC: C-1(AV) and F-1(AV) biogenically synthesized by *Aloe barbadensis* leaves extract was analyzed after adopting a wide range of experimental conditions to examine crystallographic parameter and peak indexing (Figure 2) The Fourier transform infrared spectral bands at different positions corresponded to stretching and bending of the functional group present. The different peaks observed between the ranges 400-4000cm$^-$ The broad bands observed at 3230-3270cm^{-1}corresponded to the hydroxyl (OH) functional group stretching due to the presence of alcohols and phenolic compounds of extract. The peaks between a range of 2930-2925cm^{-1} and 1605-1615cm^{-1} indicated the C-H and amide -NH group stretching respectively. The peak at1650.7cm^{-1} was due to C=C aromatic bending. The topography was analyzed by SEM model JSM (6180) at a different magnification of instrument. According to the results shown in the (Figure 3) the analysis of mostly copper oxide nanoparticles exhibited mostly tetragonal and iron oxide rhombohedral shape with little bit irregular shape morphology with a smooth surface. The TEM analysis revealed the size and proper crystallinity of biogenically fabricated nanoparticles. The size of biogenic fabricated nanoparticles were influenced by the synthesis method. However, copper oxides nanoparticles 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.

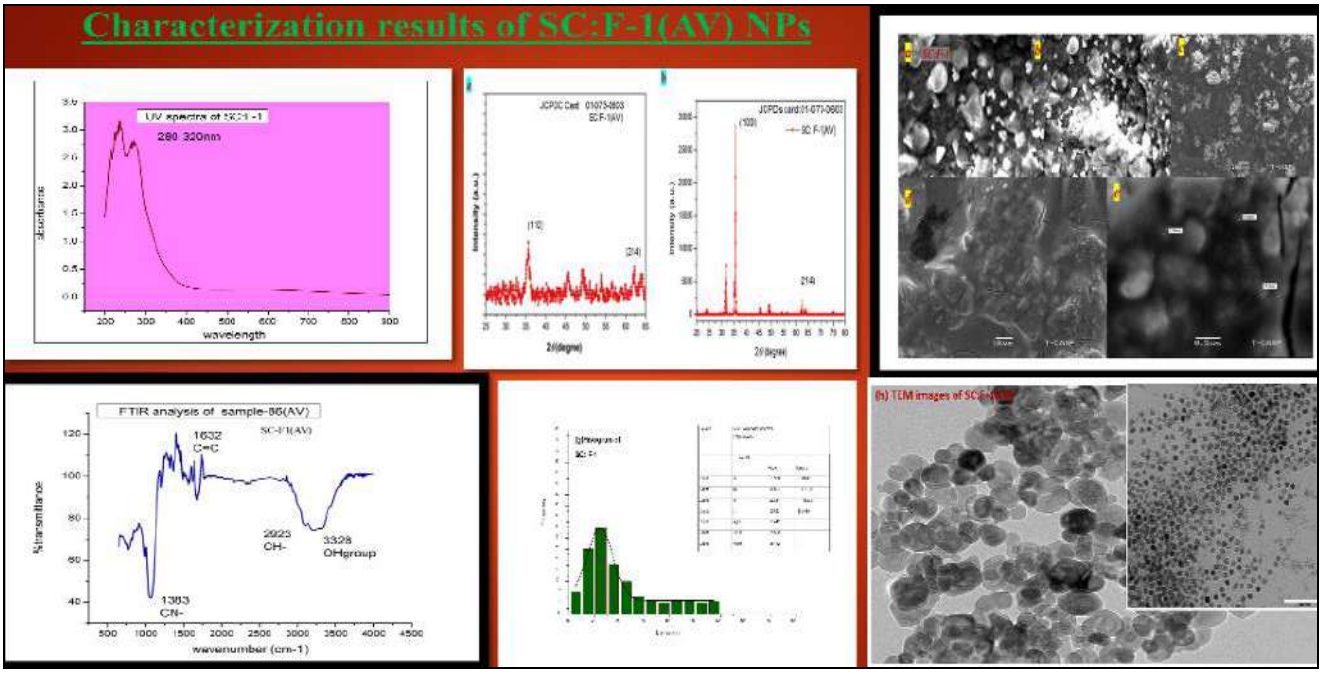

Fig 2: Characterization results of SC: F-1(AV)

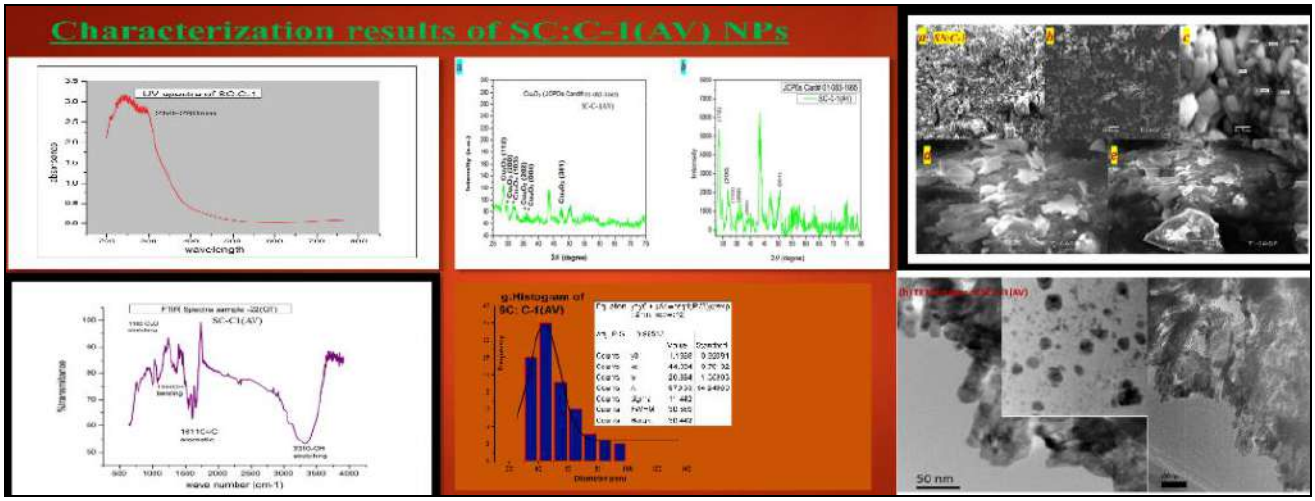

Fig 3: Characterization results of SC: C-1(AV)

Application of Congo red dye removal by MO-NPs

Preparation of AZO dyes stock solution

A 1000 mg/L stock solution of both AZO dye Congo red CR were prepared by dissolving 0.1g in 100mL flask. Up to mark dilution was completed by the addition of deionized water and volume adjusted to prepare the desired solution [14-16]. The standard solution of 2, 4, 6 and 8 mg/L of malachite green and Congo red azo dyes were prepared for calibration curves.

Adsorption equilibrium and batch kinetics studies

Equilibrium isotherms in experiments, the mixture of metals oxides nanoparticles (iron oxide, and copper oxide) with 0.1gram dry powder of azo dye and buffer solution were shacked in the water bath at specific temperature 27^0 C. the adsorption isotherms were analyzed by isotherm series examination of pH, time, adsorbent dose and adsorbate amount [17-19]. The dye concentrations were measured by UV-visible spectrophotometer at least duplicated under the same condition. The sorption batch experiment was performed in 100ml flasks (Erlenmeyer), in which 50ml of azo dyes CR solution with 5-30mg/l adsorbents sample were mixed with constant adjusted with PH value. 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 azo dyes was calculated by equation

% Removal of azo dye= Ci-Ct/Ct ×100

Adsorption parameters measurement

The maximum percentage removal of CR azo dye 88%, and 87% for adsorbent samples SC: F-1, and C-1 respectively were experimented at maximum adsorbate amount of 95mg/mL, 110mg/mL and 60mg/mL respectively .The highest percentage removal of CR azo dye by metal oxides samples SC: C-1and F-1 were analyzed at optimum PH values 4and 5. The maximum amount of adsorbents samples SC: C-1 and SC: F-1 were observed 0.81 and 0.08

respectively. The Congo red dye maximum time for percentage removal by metal oxides samples SC: F-1 (88% in 40min) and for SC: C-1(87% in 80min) were investigated. The graphical representation of time effect on adsorption shown in (Figure 4).

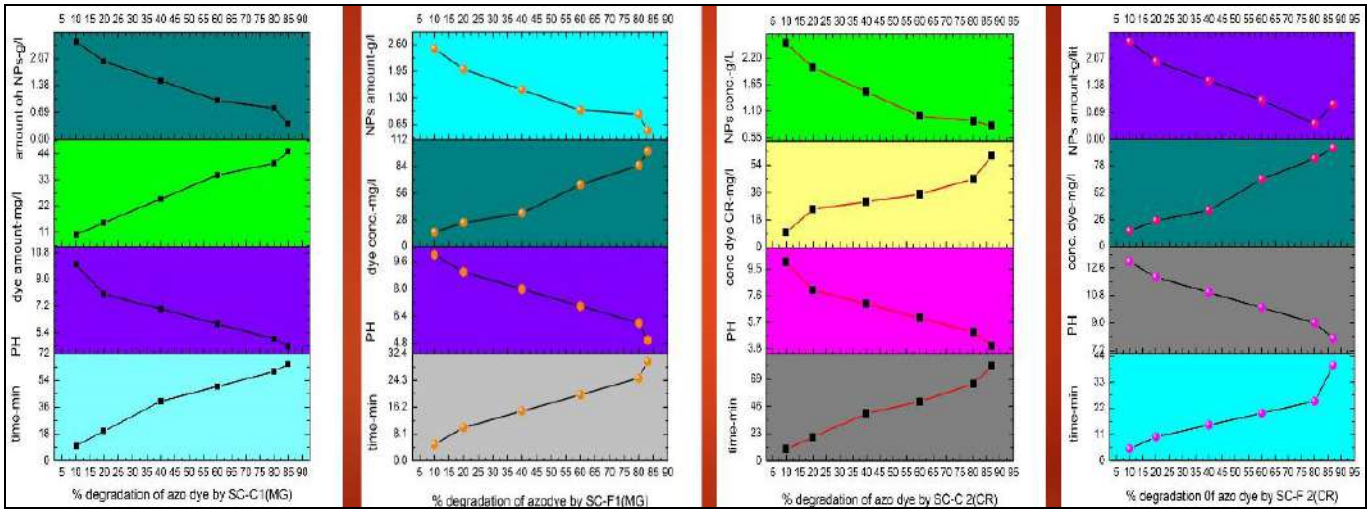

Fig 4: Effect of experimental parameter on MO- NPs for % removal of Congo red dye

Analysis Equilibrium isotherms

Adsorption equilibrium isotherms Elovich, Langmuir and Freundlich were investigated to determine the relationship of azo dyes and metal oxides nanoparticles. The mathematical relationship of targeted adsorbent (amount/gram) of adsorbent (mg/g) to solution concentration Ce (mg/L) at equilibrium point represents adsorption isotherms, which attributed to the removal of azo dyes mechanism and adsorbent properties knowledge [20-23]. Adsorption of azo dyes usually described by isotherm studies elaborated the adsorbate amount on the reacted adsorbent. The results of different equilibrium isotherms were experimentally calculated and consequently, favorable sorption of azo dyes malachite green and Congo red were investigated under observed selected equilibrium conditions.

Langmuir isotherm curve.

Langmuir equation is two-parameter equation study. Fixed number of sites available on surface. This study reveals that adsorbents are adsorbed efficiently at a fixed rate and only specified adsorbents are present at reaction place. The separation factor KL for Congo red dye for MO-NPs (SC: C-1, F-1) were observed 0.45 and 0.43 respectively (Figure 5). The strong monolayer maximum capacity and correlation coefficients between (0.990- 0.998) predicted the equilibrium data fitness of azo dyes CR by the Langmuir adsorption isotherm. The KL≤ 1 values confirmed the favorable and feasible reaction and adsorption capacity (Q_{max}) for samples F-1, C-1 were 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 azo 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 metal oxides. The data revealed that the Elovich model was better fitted than Freundlich equilibrium data (Figure 5).

Freundlich isotherm curve.

The Freundlich equilibrium isotherm 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 confirmed that Freundlich adsorption isotherm had least fitted then Langmuir model for all metal oxides samples SC: C-1 and F-1, for azo dyes CR.

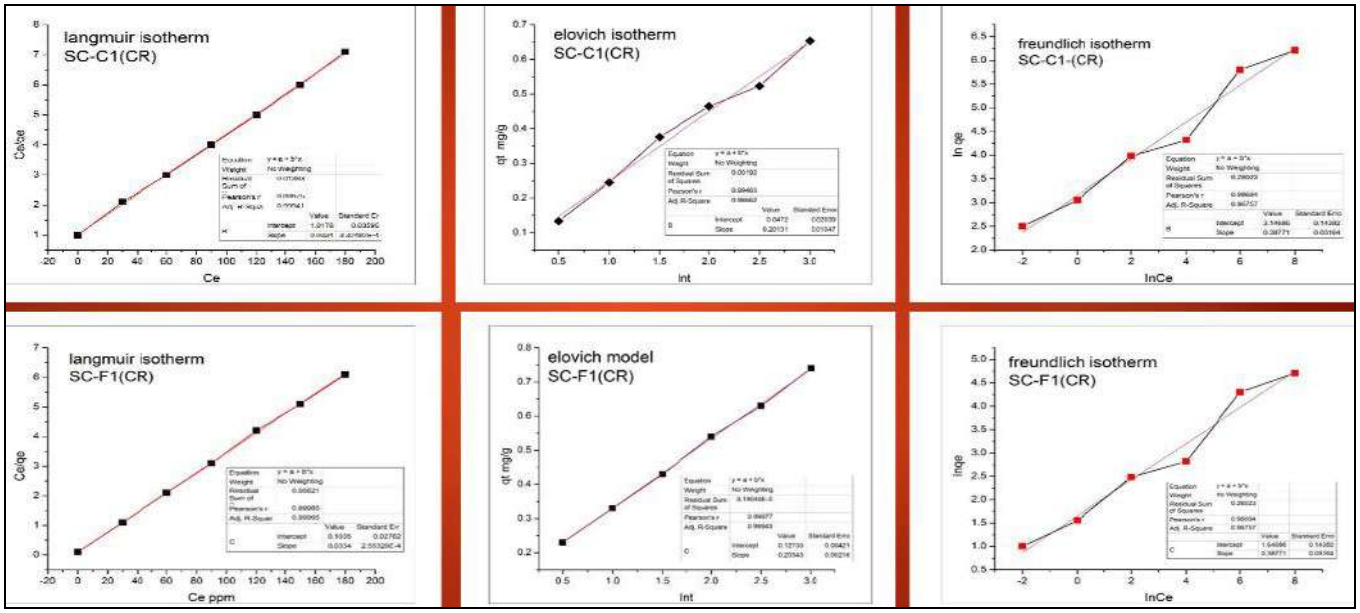

Fig 5: Equilibrium isotherm results of SC: C-1 and SC: F-1 for Congo red dye removal

6. Conclusion

In this study, biogenic fabrication had been used for iron oxide, copper oxide MO-NPs, with generally single-pot process, without application of additional capping agents and templates. Moreover, the predictable mechanism for biogenic synthesis required less time, low energy and easily available precursor which did not require pre-conditioning. So, the use of biogenic materials opened up opportunity for different metal oxides nanoparticles. The use of plants extract (*Aloe barbadensis*) in the fabrication of MO-NPs have encouraged the designing of stable, green, cheap and time effective approaches thereby, biomaterial based fabrication routes 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 azo toxic 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: Z-1 sample was observed highest percentage degradation of azo dyes malachite green and Congo red. 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 linear fit for all metal oxides. MO-NPs had expeditious kinetic data is in good agreement (R^2 >0.99) with pseudo-second order and Langmuir adsorption isotherm. Elovich model showed reasonably (R^2 ≤0.99) value which manifested nonfitting of model on calculated data in recent research for all MO-NPs. In conclusion, MO-NPs keep excellent azo dyes degradation potential at optimum conditions. The MO-NPs have greater adsorption capacity for malachite green (MG) than Congo red (CR) azodyes

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