Research Article

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Studies on Adsorption of Congo red (Acid Red 28) Azodye by Nano Copperoxide

Madiha Batool[1], Farwa Hashmi[2], Nida Mehboob[2], Zahid Qureshi[1] and Walid M. Daoush[3, 4*]

[1]*Department of Chemistry, Government College University, Lahore, Pakistan*

[2]*Lahore College for Women University, Lahore, Pakistan*

[3]*Department of Production Technology, Faculty of Industrial Education, Helwan University, Cairo, Egypt*

[4]*Department of Chemistry, College of Science, Al Imam Mohammad Ibn Saud Islamic University (IMSIU), Al Riyadh, KSA*

[*]Corresponding author
Madiha Batool, Department of Chemistry, Government College University, Lahore, Pakistan, E-mail: tweetchem56@gmail.com

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Abstract
In this study, stable copper nanoparticles were synthesized by using Aloe barbadensis leaf extracts. The present study tracing of an object is a green synthesis of copper nanoparticles by the interaction of leaf extract and copper salt and its azo dye (congored) degradation efficiency. The characterization of copper oxide nanoparticles were performed by XRD, SEM, FTIR, UV spectroscopy. The XRD analysis showed that average particle size was between 5-30nm by scherrer equation. The shape of the copper nanoparticles was spherical and cubic. The EDX of synthesized nanoparticles confirmed copper content 68%. UV spectrophotometer analysis confirms peak of the copper nanoparticles between 200-400nm. The effect of variables like concentration, time, PH, adsorbent dosage also examined in this present study on % degradation of dye. It was noted that maximum dye removal occured at PH= 4, maximum concentration of adsorbent 1mg/l, maximum time for dye degradation 120 mint. The nanoparticles removed 70% of congored dye from solution at optimum condition of reaction parameters.The kinetics of pseudo second order is followed by adsorption process.The calculated sum of square .012 and r2 =.980 were analyzed. Langmuir isotherm model fit best and straight line graph drawned with r2 value .991 and probability 1.6E-5. This showed that copper oxide nanoparticles have efficient capacity of azo dye degradation.

Keywords: Aloe barbedensis, SEM, copper oxide nanoparticles, cogo red, XRD

Introduction
Nanotechnology deals with the manipulation of matter at low size normally less than 100nm [1]. Recent development in the field of science and nanotechnologyhas lead to a new concept of synthesizing nano-sized particles of desired size and shape. wastewatercharacteristics, such as dyes, detergents, [2] etc. 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 copper oxide nanoparticles [3].

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 [4]. copper oxidenanoparticles have attracted much attention of researchers due to its application degradation and biomedicalproperties[5]. Metallic nanoparticles can be prepared bythechemical and physicalmethod.These methods have certain flaws like toxic chemicals and also dangerous to the environment [6]. Developing research in green chemistry employed prominent part in nanotechnology to gain benefit to the society [7]. 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 [8]. Green synthesis has been engaged in synthesis of highly stabilized nanoparticles [9]. Copper nanoparticles were synthesized by leaf extract of Aloe vera plant. Phenolic content in plant extracts dissolved in water, degradable and used tocatalyzed synthesis ofthenanoparticle as capping andreducing agent [10].

Nanoparticles show unusual structural, electrical, optical and magnetic properties [11]. Several clinical trials are being conducted to further evaluate the use of aloe vera gel for a variety of disorders [12]. Aloe vera juiceis commonly used as an ointmentand skin abrasions Functional groups in aloe veracontain,Carboxymethyl -O-CH2-COO- and Sulphoxy -O-CH2-CHOH-CH2-O-CH2-CH2SO3- [13]. This ancient plant may offer deeper healing abilities. Aloevera keep antioxidant vitamins A, C and plus vitamin B12, folic acid, and choline. It contains eight enzymes [14]. These chemicals salicylic acid and anthraquinones (aloin, emodin, aloetic acid, anthranol, cinnamic acid, anthracene) are responsible for the reduction of copper [15,27].

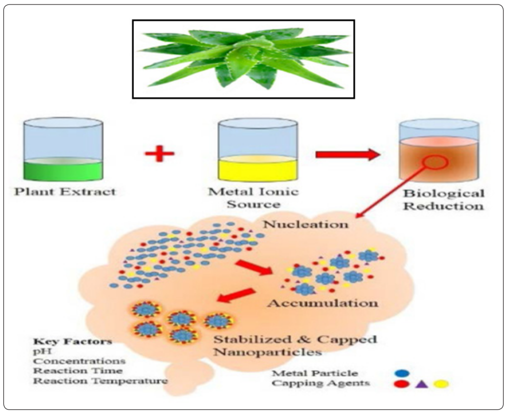


Figure 1: Mechanism of green synthesis

Polyphenols in alovera plants leaves extract like aloin can act as chelating, capping and also reducing agents for nanopartical formulation [16]. This is One-step processes in which no surfactants and other capping agents used [26].

Experimental

Material

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.

Preparation of Plant Leaf Extract

To prepare the leaf extract of Aloe vera plant, leaves (25g) were thoroughly washed, dried and finely chopped. The finely chopped material was allowed to boil for 5 min at 80°C with 100 mL of de-ionized water in a 250-mL Erlenmeyer flask and then cooled down to room temperature. The resulting solution is passed through a filter paper to remove any solid particles and then again filtered through a Whatman filter paper of pore size 0.2µm. The filtrate is stored at 4°C as a stock for the synthesis of CuO NPs [17].

Green Synthesis of Cuo Nps

Fifty millilitres of 10 mM aqueous solution of copper sulphate (99.99 % purity, Aldrich) Was added to 25-mL A. Vera extract in a 100-mL Erlenmeyer flask with constant stirring on a stirrer at 100–120°C [18-20]. Color change of the reaction mixture was observed fromdeep blue to green and then dark greenish on stirring for 24 h.Then the resultant solution is centrifuged at 10,000 rpm for 10min, at room temperature (using Beckman centrifuge with a Beckman JA-17 rotor), and the mixture is collected after discarding the supernatant [21]. The collected CuO NPs are allowed to dry in a watch glass. The formed black precipitate is grinded for further characterization

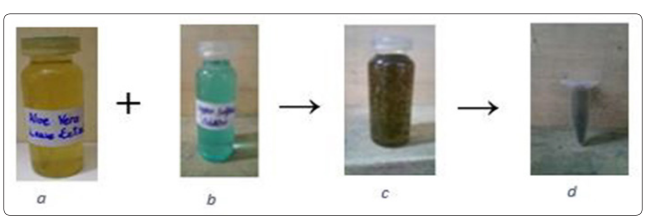


Figure 1: synthesis of CuOnanoparticles

Characterization of Copper Oxide Nanoparticles

Structural, chemical composition, size and shape of copper oxide nanoparticles were analyzed by SEM (JSM-6480), XRD (XPERT-PRO), EDX, TEM, and UV
Spectrophotometer (DB-20).

Result and discussion

Solution color change observation

Color changes indicate the formation of nanoparticles of copper oxide [22]. The greencolor solution was turned into dark brown, indicated fortheformation of copper nanoparticles synthesis.

X-Rays Diffraction Studies

Copper oxide nanoparticles were examined by XRD (expert pro), put in the cubes of the machine for calculation of intensity [16]. The resultant pattern of synthesized copper oxide nanoparticles was analyzed. The peaks at 2θ intensity 32.4, 35.6, 38.8, 48.9, 53.3, 58.2, 61,66 and have 110,200,202,020,202,113and022 pattern compare to JCPDS card no (01-071-0251). XRD pattern confirmed that CuO nanoparticles are highly crystalline with tetragonal crystal structure which analyzed through search match analysis. The average size of the particle calculated by Scherrer equation was between 5nm-30nm.

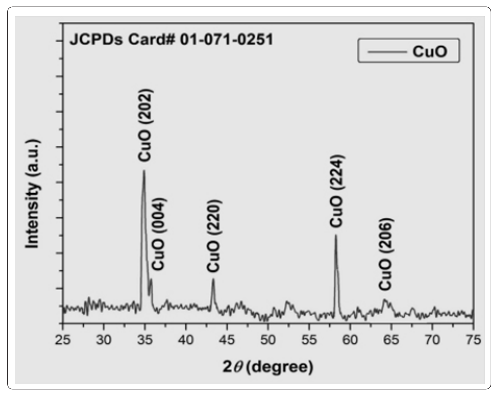


Figure 2: XRD pattern of cu oxide nanoparticle prepared By alovera

Scanning Electron Microscope (Sem)

The average particle size of copper nanoparticle wasanalyzed by SEM model (JSM-6480) was an 80-120 nm range. It was observed that particles were smooth with a spherical shape [23]. EDX result showed strong copper signal with other elements like S, P etc.

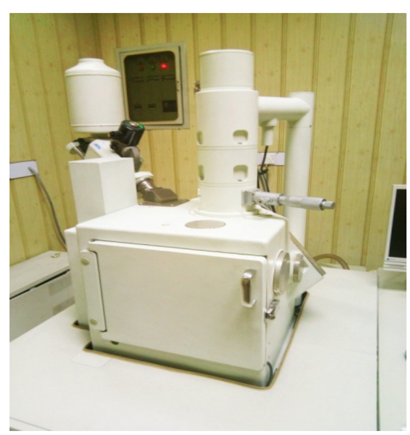


Figure 3: SEM model (Jsm-6480)

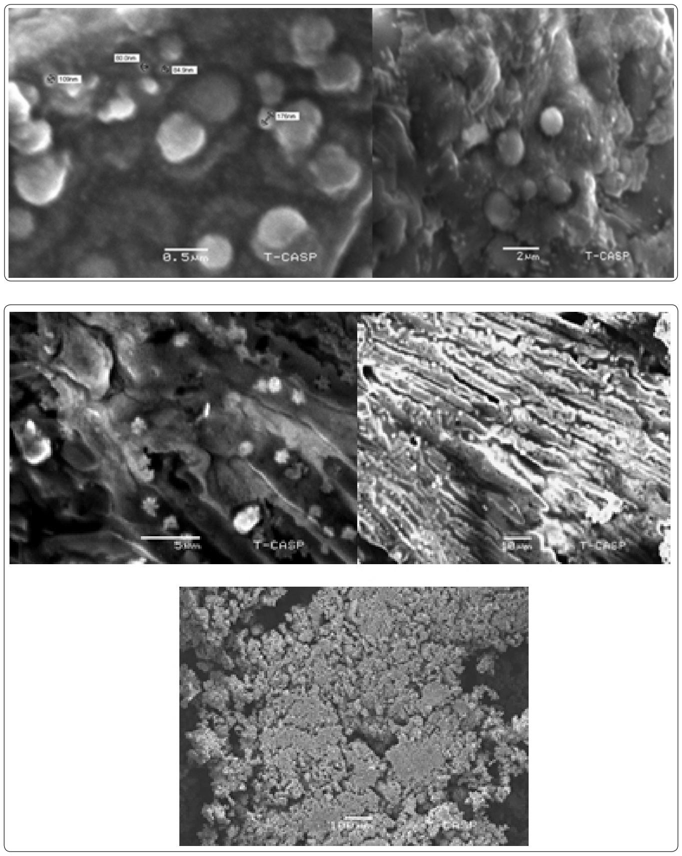


Figure 6: Sem micrographs of copper oxide nanoparticals at different magnification 0.5, 2, 5, 10, 100 micrometers

Edx Analysis

EDX image of copper nanoparticles showed about the composition of nanoparticles. The Image confirms the presence of 68% copper and 35% oxygen.

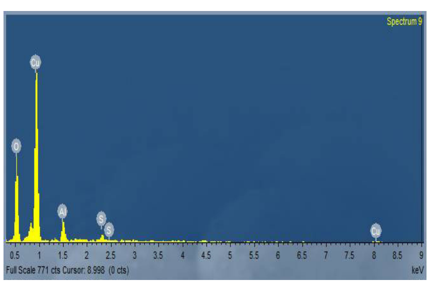


Figure 7: EDX of copper oxide nanoparticles

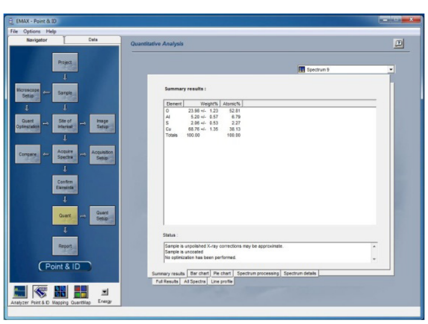


Figure 8: EDX DATA OF CuO NPS

FTIR analysis

In this study, FTIR spectrum was analyzed to confirm copper nanoparticles. The Peak observed at 1100cm^{-1}, indicatedthe formation of copper oxide NPS. The peak was observed in the range of 400-4000cm^{-1}. The peaks at 3450, 1600 and 2250 indicate the presence of alcohol, alkene, and CH bond.

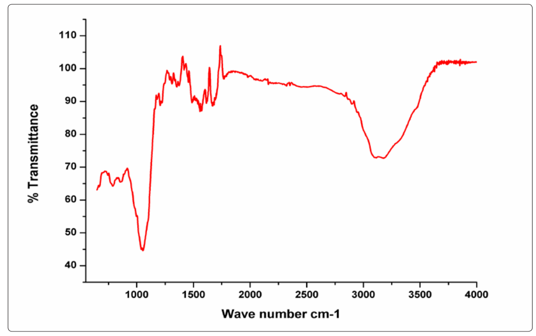


Figure 9: FTIR analysis

Different functional groups in FTIR SPECTRA
OH-stretch stretching 3250.8cm^{-1}
C-H stretching 2860.1cm^{-1}
C=C Aromatic bending 1650.7cm^{-1}
C=O stretching 2250.1cm^{-1}
CuO stretch stretching 1100cm^{-1}

Uv Visible Spectra

Peaks of UV spectrometer atarange of 200-300nm confirm the formation of copper oxidenanoparticles.

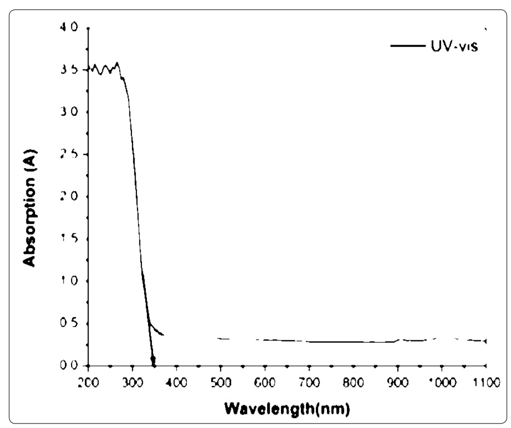


Figure 4: UV spectrum of copper oxide nanoparticles

Removal of Congo Red Dye by Cuo Nanoparticles

Preparation of 1000mg/l dye S.S

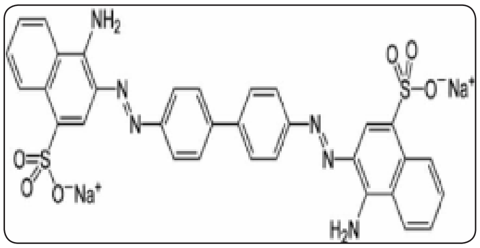
1000 ppm solution of Congo red CR was prepared by dissolving dye in 1 liter distilled water. Different concentration of dyes was prepared from stock solution. 100 ppm solution was prepared from 1000 ppm solution after dilution [25]. After that 150, 200, 250 ppm solution was prepared.The catalytic activity of CuO nanoparticles were examined by the degradation of congo red. 10 mg of the compound was added into 50 ml of congored dye solution. 50 µliter of hydrogen peroxide (oxidizing agent) was also added into the mixture solution to obtain adsorption equilibrium. The solution was stirred for 50 minutes. Mixture of 3ml was taken out after intervals of 10min time. Color removal efficiency was calculated by % decolorization =A-B/A×100

Where A and B are absorbance of dye solution with outnanoparticles and with particles respectively.

Mechanism of CRdye removal

50 microliter of the hydrogen peroxide H2O2 was added as the oxidizing agent to yield hydroxyl radical. Catalytic activity proocess mainly depends on the formation of super oxide anion radical and hydroxyl radicals .[24]Congo Red (CR) (Direct Red 28) having a chemical formula $C_{32}H_{22}N_6Na_2O_6S_2$: and molecular mass: 696.66 g/mol. The concentration of CR in each aqueous solution measured by UV–vis spectrophotometer) at λmax = 500 nm.copper

Equation of congored degradation:



congored structure

Congored $\xrightarrow{CuO/H_2O_2}$ biphenyl+biphenyl4, 4diammine+naphthalein+ammonia products [27]

Parameters affect studies on de-colorization

1-Time effect on dye removal

Decolorization of dye Congo red at room temperature was studied. Amount initially taken was 50 ml dye solution and 1mg of copper nanoparticles [26]. The time interval was noted gradually during reaction .the removal % removal was calculated and draw graphically. The maximum time was 120 min with 75% color removal. This confirms the rapid reaction of copper oxide nanoparticles (CuONPs).

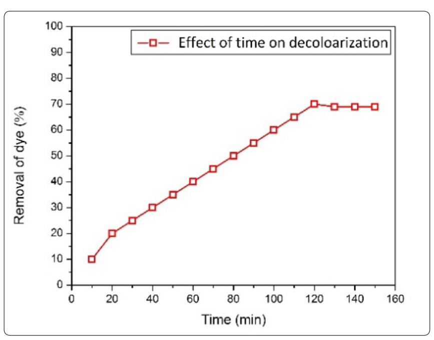


Figure 10: Effect of time on % removal of Congo red

PH effect on dye removal

De-colorization also strongly affected by PH of the solution. PH effect on the decolorization of copper oxide nanoparticles was studied in this research. Aloevera synthesized copper oxide nanoparticles showed maximum % age de-colorization as PH=4 was increased at a certain limit after more increase has a negative effect. This effect may be due to the formationof morepositive ion competition. maximum de-colorization 75% was at PH 4.

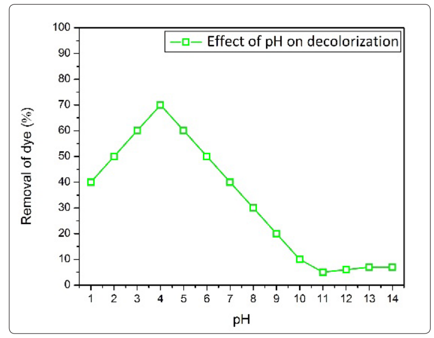


Figure 11: Effect of PHon % removal of Congo red dye PH 4 observed maximum removal

Concentration of dye effect on decolorization of dye

The initial concentration of Congo red CR dye is also effective in decolorizationefficiency . The graph was drawn after experimenting different concentration of dyes.The maximum amount of dye was 20mg/l for maximum degradation. After increasing concentration no effect on75 %decolorization of dye was observed.

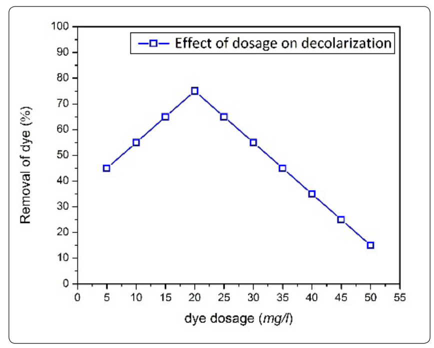


Figure 12: Effect of dosage effect of dye on %removal

Effect of copper oxide nanoparticles (CuONPS) amount on dye removal

The number of copper oxide nanoparticles depicted positive results on decolorization. The number of nanoparticles 1 mg/l was taken showed maximum de-colorization power. This confirmed from the graph that overdosage of nanoparticle showed no effect on de-colorization. This concentration of nanoparticles was used in further experimentation of research.

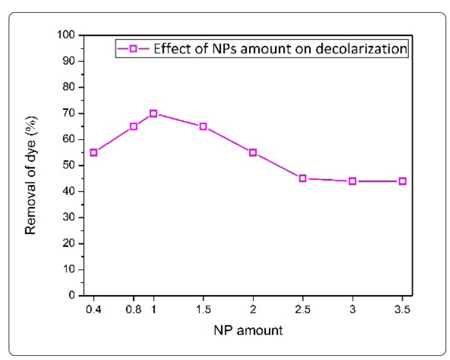


Figure 13: Effect of copper oxide NPs on %removal of Congo red dye

Kinetic study of degradtion

Removal of dye Congo red by copperoxide nanoparticals follow pseudo second order reaction rather then first order. The straight curve shown in (figure 14) below.

Table 1: parameters of second order kinetics of degradation of CR DYE at 25C°

parameter	values
K_2	0.689
qe	14.9
r^2	.980
Sum of square	.012
t/qt slope	.029
intercept	1.65
standarderror	.0013

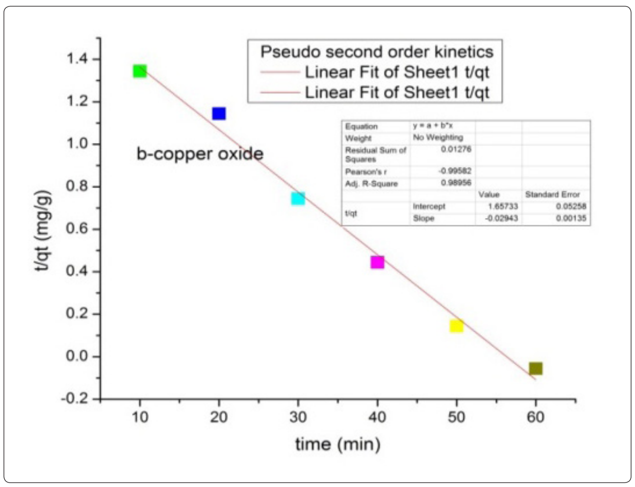


Figure 14: 5pseudo-second order kinetics of degradtion of CR. Equation $y=a+b^2X$

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. Reaction place on adsorbents is equally effective. The Langmuir equation is

$$C_e/q_e = 1/K_L q_m + (1/q_m)\, C_e$$

In the equation q_m is adsorption capacity in unit mg/g.Ce is concentration of adsorbent at equilibrium. qe is difference of initial and equilibrium concentration of copper oxide nanoparticals. Langmuir isotherm constant is K_L .Langmuir constant provide the binding affinity. The values of isotherm q_m and constant K_L can be calculated by plotting a graph between Ce /qe and Ce. The characteristics of a Langmuir isotherm can be examined in terms of equilibrium parameter. $K_{L\ can}$ be calculated by formula

$$RL = 1/1+bC_e$$

Plotting graph between (Ce/q_e) and C_e a straight line proves Langmuir isotherm model. Present data, when drawn for Langmuir isotherm, showed well linearity which indicates strong attraction of congo red dye degradation by adsorbent copper oxide nanoparticles.The parameters of Langmuir equation are listed in (table 2) below

Table 1: parameters of Langmuir isotherm at 30C°

parameters	values
KL	0.6
qm	80
RL	- .03
r2	0 .991

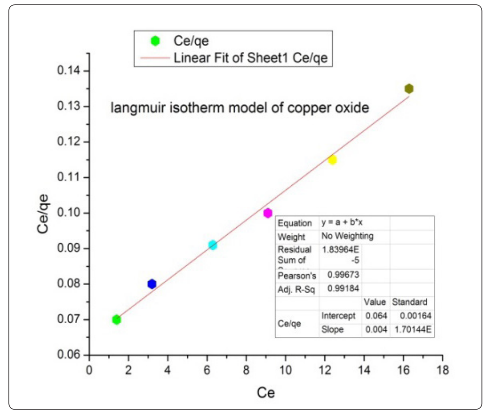


Figure 15: Langmuir isotherm model straight line between ce and ce/qe

Table 3: values of ce and ce/qe for langmuir isotherm with respect to concentration adsorbent and. qe=Co-Ce

Sr no	C_0 initial	C_e	qe	Ce/qe
1	20	1.4	18.6	.07
2	40	3.2	36.8	.08
3	80	6.3	70.7	.091
4	100	9.1	90.9	.12
5	120	12.4	107.6	.115
6	140	16.3	123.7	.134

ANOVA and statistics of Langmuir curve is listed below in table 4

Table 4: ANOVA of Langmuir isotherms Ce/qe

	DF	Sum of square	Mean square	F	pro≥F
Ce/qe	model	1	.002	608.6	1.6E-5
	error	4	1.83E-5		
	total	5	.002		

Table 5: Statistic calculations of Ce/qe Langmuir isotherm

parameters	values
Number of points	6
Degree of freedom	4
Residual sum of square	1.8394E-5
Pearsons r	.99673
Adj.R-square	.99184

Conclusion

In conclusion, here we reported an eco-friendly fabrication of CuO nanoparticles by leaf extract of aloe vera plant. Copper oxide nanoparticleshavethe ability to degrade azodye. SEM graphs confirmed spherical shape of copperoxide nano particals, XRD data predict range of nanopartical size b/w 5-30nm by scherrer equation. Copper oxide nanoparticleshave the ability to degrade azodye(congored). In the presentstudy, Congo red dye was removed 70-75% by nanoparticles and observed optimum condition werenoticed like (PH=4), contact time 120mint, adsorbent nanocopper dosage 1mg/l. The degradation of congored dye followed pseudo-second order kinetics rather than first order. Langmuir isotherm was drawn between Ce and Ce/qe which proved linear isotherm. The calculated sum of square of kinetic curve was .012 and observed r2 =.980 from graph. Langmuir isotherm model fit best and straight line graph drawn with r2 value .991 and probability 1.6E-5. It was concluded that copperoxidenanoparticles keep efficient degradation capacity of azodye (Congo red).

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