Kinetic and isothermal study of effect of transition metal doping on adsorptive property of zinc oxide nanoparticles synthesized via green route using *Moringa oleifera* leaf extract

Vartika Srivastava and Abhay Kumar Choubey
Division of Sciences & Humanities, Rajiv Gandhi Institute of Petroleum Technology, Bahadurpur, Mukhetia More, Post: Harbanshganj, Jais, Amethi - 229304, Uttar Pradesh, India
E-mail: achoubey@rgipt.ac.in

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Abstract
In this study, a green route has been adopted to successfully synthesize pure zinc oxide nanoparticles (ZnONPs) as well as Cu doped zinc oxide nanoparticles (Cu-ZnONPs) which is quite a novel work. The synthesized nanoparticles (NPs) were used as adsorbent for removal of Congo red (CR) dye from aqueous solution and efficiency of both doped and undoped ZnONPs was investigated and evaluated. The synthesized products were further characterized and confirmed by UV–visible (UV–vis), Fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), Thermo gravimetric Analysis (TGA), Transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Cu-ZnONPs were found to be more efficient adsorbent as compared to undoped ZnONPs. The adsorption process of CR on both the synthesized NPs were scrutinized using kinetics and isothermal parameter respectively, which depicted that the adsorption process in case of doped ZnONPs was faster (adsorption reached equilibrium in 120 min) as compared to undoped ZnONPs (which took 180 min) and followed a pseudo-second-order kinetics in both the cases. When pure ZnONPs was used as adsorbent, it correlated more with the Freundlich isotherm and Temkin isotherm as compared to Langmuir isotherm, however, when Cu–ZnONPs was used as adsorbent, the data fitted well to Langmuir and Freundlich models.

1. Introduction
Nanotechnology is one of the most dynamic fields which has got applications in diverse areas such as electronics, agriculture, energy, pharmaceutical, waste water treatment, etc. Variety of organic compounds and synthetic dyes are used in various industries like food, pulp & paper, leather, textile, printing and cosmetic industries. The bright colored dyes, which are very useful in these industries, are toxic and carcinogenic in nature. These are released into the water bodies as effluent from those industries. Therefore, these dyes are considered as undesirable from environmental point of view [1]. These dyes are posing serious health hazards to living organisms. The efficient removal of CR dye has always been challenging for researchers [2–4]. CR dye is mainly discharged into the water bodies from paper, plastic and textile industries [5, 6]. After usage, the dye is directly released into the water bodies. For reducing developed to degrade such toxic dyes into non-toxic compounds [7–10]. Among all the developed methods, adsorption is one such method which is used to remove dyes and various heavy metal ions from the waste water. This method is advantageous because it is not only economical but is also easy to operate. It has simple design and is effective against toxic pollutants and harmful substances [11]. While working on adsorption, researchers have used different adsorbents such as sawdust [12], activated carbon [13], carbon nanotubes [14], swelling clays [15] etc to remove dyes from aqueous solution. Although these adsorbents have been proved to be useful for the removal of dyes but there are many disadvantages associated with those materials such as these adsorbents are costly, have long adsorption time and also inconvenient to separate, which creates a need to find other alternatives. Nanomaterials possess specific
chemical properties which are completely dependent on their composition, shape and size. The unique physical and chemical properties of nano-materials make it suitable to be used as adsorbent. The nano-metre size of particles enables it to disperse easily in the solution and provides high surface contact with the pollutants. The present work concerns green route synthesis of nanoparticles using plant extract (PE) derived from *Moringa oleifera*. Although different methods have been reported for the synthesis of ZnONPs, which includes solvothermal and hydrothermal synthesis [6], sol gel methods [16], polymerization method, and precipitation method. These methods have several issues associated with it such as stability of nanoparticles, heterogeneity, aggregation which results in broadening of particle size distribution [17]. Green route synthesis is the easiest, cost effective, ecofriendly method for the synthesis of nanoparticles [18, 19]. Natural products such as plant extract and microbial surfactants have been used as reductants and as capping agents during synthesis [20, 21]. According to Raveendran *et al* nanoparticles synthesized using biosynthetic routes have better defined sizes as well as morphology as compared to other methods [22]. The natural compounds present in biological system plays a vital role not only in the synthesis of nanoparticles but also acts as reducing and capping agent. The literature survey exhibits that as compared to other biological systems plant extract offers additive advantages. Plants are easily accessible, safe to handle and also produces highly stable nanoparticles [21, 17]. ZnONPs and Cu-ZnONPs were synthesized using plant extract and then used as adsorbent for degradation of CR dye in aqueous solution. Most of the literature have reported the degradation of dyes using nanoparticles as photocatalyst [7, 23, 9, 24]. The aim of this study is to depollute the water from dye using synthesized nanomaterial as adsorbent. As per our literature survey, no study has been carried out which uses Cu-ZnONPs as adsorbent for dye removal. The objective of this work is also to compare the efficiency of adsorption of the pure and doped ZnONPs. The process of adsorption was studied as a function of pH, contact time, adsorbent dose, and concentration of dye for maximum adsorption. The adsorption data obtained for different time and concentration was fitted to kinetics and isotherm models in order to analyse the adsorption process.

2. Materials and methods

2.1. Materials

Zinc acetate dehydrate, Zinc sulphate heptahydrate and Copper sulphate pentahydrate were procured from S D Fine-Chemicals Ltd, India. Sodium hydroxide pellets and CR dye were procured from Molychem, India. All chemicals used in this study were of LR grade.

2.2. Synthesis of plant extract (PE)

The extract was prepared by using leaves of a plant called *Moringa oleifera*. The leaves of the plant were collected from the fields in Jais, Amethi, Uttar Pradesh. Leaves were properly washed by using tap water and then twice using double distilled water. They were then kept in sunlight, dried for 2–3 days and finally crushed into powdered form. Crushed leaves were used to prepare plant extract by heating 10 g of leaves powder with 200 ml of distilled water at 100 °C for around 2 h. The resulting solution was then cooled at room temperature. After cooling, the solution was filtered using Whatmann filter paper no. 1. The filtrate was then stored at 4 °C in an amber bottle for further experimentations.

2.3. Biosynthesis of pure ZnO and Cu doped ZnO

15 ml of leaf extract was added to 35 ml of 200 mM zinc acetate dihydrate (prepared by dissolving 1.536 g of zinc acetate dihydrate in 35 ml of distilled water). The reaction mixture was thoroughly stirred on magnetic stirrer for about 6 h. After 6 h, the pH of the solution was adjusted at 12 (pH of the solution was maintained using 0.1 M NaOH) to make it basic and the reaction mixture was heated at a temperature of 90 °C overnight with magnetic stirring. After heating the solution overnight, the white powder dispersed in solution was centrifuged at 13 500 rpm for 15 min. The powder obtained was washed three times using distilled water and then thric with ethanol. It was eventually dried overnight at 90 °C and was crushed into fine powder using mortar and pestle. For Cu-ZnONPs, 5 g of zinc sulphate heptahydrate was added to 50 ml of plant extract and 50 mg of copper sulphate pentahydrate. The solution was stirred for an hour. The final solution was then treated in the same way as that of undoped ZnONPs. The possible mechanism for the synthesis of these nanoparticles is possibly similar to the one reported in Sigh *et al* [25]. The synthesized powders were characterized using different analytical tools such as UV–vis, DLS, XRD, FESEM-EDX, FTIR and TGA. The plant extract obtained from *Moringa oleifera* consists of various organic compounds such as polyphenols, flavonoids, carotenoids, fatty acids etc [26]. The synthesis reaction follows the similar mechanism as mentioned in [27, 28].
3. Adsorption experiments

The adsorption experiments were carried out for the removal of CR dye. The reaction was carried out using 50 ml of CR dye (20 mg l\(^{-1}\)) and 0.1 g of synthesized material solution was added to it. The temperature of the reaction was maintained at 28 °C and the stirring speed was kept 200 rpm under dark condition. The pH of the dye solution was analysed using pH tutor (Eutech Instruments, Singapore). The concentration of the dye was recorded using UV–vis spectrophotometer (Lab India UV–vis 3200).

The adsorption experiments were conducted to optimize process parameters viz., pH, time, temperature, etc. Dye removal \( (D) \) in percent was calculated using following equation (3.1):

\[
D = \frac{C_0 - C_e}{C_0} \times 100
\]  

In the above equation 1, \( C_0 \) represents the initial concentration and \( C_e \) is the equilibrium dye concentration in mg l\(^{-1}\). The amount of dye adsorbed per unit of the adsorbent at equilibrium was calculated in terms of \( q_e \) (mg g\(^{-1}\)) using equation (3.2) given below:

\[
q_e = \frac{C_0 - C_e}{m} V
\]  

Where, \( q_e \) is adsorption capacity, \( V \) is the volume of dye solution (L) and \( m \) is the mass of the adsorbent (g).

4. Characterization of biosynthesized ZnONPs

4.1. UV–vis spectroscopy

The synthesis of NPs and the adsorption study was carried out using Lab India UV–vis 3200 spectrophotometer. The spectrum was recorded in the range of 300–800 nm with a 10 mm path length quartz cuvette.

4.2. XRD analysis

The purity of the phase was studied by using PANalyticalX'pertpro MPD diffractometer. X-ray diffraction spectrometry technique helps to investigate the formation and quality of synthesized NPs. Scanning of the samples was done in the range of 2\( \theta \) from 20 to 80° with monochromatic radiation (CuK\( \alpha \)).

4.3. FESEM analysis with EDX

Scanning Electron Microscopy was carried out using JSM-7100F, Jeol FESEM. The SEM analysis was used to determine surface morphology of the synthesized NPs. The synthesized powders were dispersed in ethanol and ultra sonicated for 15 min. The solution was then drop casted on Al foil and was air dried and finally put on copper grid for analysis. To prevent samples charging, a thin gold coating was sputtered onto the samples prior to the analysis.

FESEM was coupled with EDX and the sample used for FESEM was used as such for this analysis as well. EDX analysis gave an idea about the elemental composition and the chemical purity of the synthesized NPs.

4.4. FTIR analysis

The FTIR spectra of the samples was recorded using Perkin Elmer Spectrum Two FT-IR spectrometer. The samples were used either in solid form or thin film. ‘Attenuated total reflectance’ (ATR) mode was used for recording the data. The PIKE MIRacle single reflection horizontal ATR accessory equipped with a ZnSe ATR crystal was used for the analysis.

4.5. TGA analysis

TGA analytical technique was used to detect the response of particles against rise in temperature. The basic principle of the technique is to raise the temperature of the sample below its melting point, a reduction in the weight of the sample is observed due to evaporation of water and biochemicals present in the plant extract [29]. TGA analysis (TGA, Linseis PT 1000) of the synthesized materials was carried out in air by maintaining the heating rate of 10 °C min\(^{-1}\) from room temperature to 600 °C.

4.6. TEM analysis

Transmission electron microscopy was carried out using Jeol JEM 1400 (Jeol Ltd, Tokyo, Japan). Sample for carrying out electron microscopy observations was prepared by dispersing the NP powder in distilled water using ultra sonication. The solution was then drop casted on a carbon film supported on a Cu grid and was then evaporated under ambience conditions.
5. Results and discussion

5.1. UV–vis spectral analysis
The UV–vis spectrum revealed a characteristic absorption peak of ZnONP at wavelength of 358 nm [figure 1] and the peak for Cu-ZnONP was obtained at 366 nm.

5.2. XRD analysis
XRD technique was used for identification of crystal structure and for getting various lattice parameters. The XRD spectra of pure and Cu-ZnONPs are shown in the figure 2 below. The data revealed a series of characteristic peaks with $2\theta$ values of 31.774°, 34.4268°, 47.5965°, 56.6433° and 62.9327° (figure 2). These peaks were indexed to (1 0 0), (0 0 2), (1 0 2), (1 1 0) and (1 0 3) planes of ZnONPs hexagonal phase structure respectively. The peaks and Miller Indices obtained are related to the standard hexagonal wurtzite crystal structure. The data is in accordance with the standard JCPDS card (36-1451). The data not only confirms the synthesis of ZnONPs but also the absence of other impurities.

When the Cu is doped into the ZnO lattice, much significant shift in the peaks was not observed. Small intensity peaks were observed for copper which indicates that copper has been incorporated well inside the crystal lattice of zinc oxide nanoparticles.

5.3. FESEM and EDX analyses
The structure of the nanoparticles synthesized was analysed using FESEM. The image in figure 3(a) shows individual ZnONPs as well as aggregates and exhibits that the ZnONPs synthesized are irregular in shape. The SEM images of Cu-ZnONPs are shown in figure 3(c). These images depicts that the incorporation of Cu into the crystal lattice of ZnO changes the shape and morphology of ZnONPs. In Cu-ZnONP samples, particles seems to
be even more agglomerated, and therefore it is difficult to determine the average grain size from the less-
resolved SEM images.

EDX analysis was conducted for looking at the elemental composition of the synthesized samples and for the
confirmation of the successful doping and the formation of ZnONPs [represented in figures 3(b) and (d)]. EDX
signals and their percentage composition of the samples are shown in the figure 3 given below. Figure 3(b) shows
strong signals of zinc and oxygen, which represents the purity of the synthesized material. For doped ZnONPs,
copper signals were also found along with zinc and oxygen, which signify copper has been successfully doped.
The EDX spectra confirmed the presence of chemical constituents (Zn = 79.52 wt % and O = 20.48 wt % in
undoped ZnO; Cu = 8.1 wt %, O = 15.6 wt % and Zn = 76.2 wt % in doped ZnO).

5.4. FT-IR analysis
FTIR spectrum was observed to investigate the chemical composition of the samples synthesized as ZnONPs and
Cu doped ZnONPs and for the study of functional groups present in the plant extract used as stabilizer. The
phytochemicals, which act as capping agent for synthesis and stabilization of ZnONPs are revealed by FT-IR
spectroscopic technique. FT-IR graphs of pure and Cu-ZnONPs are shown in figure 4. The spectrum range was
from 500 cm$^{-1}$ to 4000 cm$^{-1}$. Different peaks were observed at different wave number values. Strong bands
were obtained at 3368, 2934, 1569, 1406 cm$^{-1}$ corresponding to OH stretching vibration of phenol group, CH
stretching, C=C stretching of alkyl ether group and N=O bond of secondary amine [30, 31]. The origin of band
at 543 cm$^{-1}$ is due to metal oxygen bond which confirms the synthesis of Zn-O [8, 32]. The phytochemicals
present in the plant extract such as alcohols, phenols, amines and others interact with the surface of zinc and
provides stability to the synthesized nanoparticles [33].

5.5. TGA analysis
For ascertaining heat stability and temperature response of the synthesized NPs, TGA technique was used. Here
in TGA study (shown in figure 5), TGA data depicts the reduction of mass over a range of temperature. In both
the samples (Pure and doped ZnONPs), reduction of mass was first observed below 100 °C. The reduction of
mass occurred due to the evaporation of moisture present on the outer surface of the materials. The second
degradation occurred at around 250 °C, which was due to the water present internally as well as biomolecules,
which acts as stabilizer. The last peak was obtained at 421 °C which might be due to degradation of various other
biomolecules as depicted in FTIR spectrum. Hence, from the thermal analysis, it may be concluded that all the
prepared samples are thermally stable at higher temperature and also that Cu doping increases the thermal
stability of ZnO and hence the weight loss of pure ZnONP is more compared to that for Cu-ZnONP samples [34].

5.6. TEM analysis

Figures 6(a) and (b) shows the TEM micrograph of synthesized ZnONPs and Cu-ZnONPs respectively, which reveals that particles are very much aggregated and particles of size as small as 10 nm are visible.

6. Optimization of adsorption parameters

All the optimization study was carried out using 100 ml of 20 mg l⁻¹ of dye and 0.1 g of adsorbent added to it. The adsorption process was allowed to run for 180 min.

6.1. Optimization of pH

The percent removal of CR by pure ZnO and Cu-ZnONPs was studied by varying pH in the range from 2 to 10 (figure 7(a)). It was observed that removal efficiency of CR by both ZnONPs and Cu-ZnONPs was in the range of 90%–93% for entire pH range (2–10) using both the adsorbents synthesized. Thus from the above mentioned result it can be concluded that both the NPs work efficiently in the wide pH range for the removal of CR dye. It
has also been observed that on addition of any of the synthesized nanoparticles, the pH of dye solution automatically comes in the 6.5–7.5 pH range.

6.2. Optimization of contact time

Contact time was optimized by varying it from 0 to 180 min at adsorbent dose 0.10 g for 100 ml CR dye (20 mg l\(^{-1}\)) as shown in figure 7(b). It was observed that with increase in the time of contact the percent removal of CR by ZnONPs increased. The reason for increase in adsorption with time is, more time allows sufficient contact period for interaction of dye with the adsorbent. The time taken for the removal of dye using ZnONPs
was observed to be 180 min while for the process in which Cu-ZnONPs was used as adsorbent, approximately 95% of dye was removed in 120 min. The result shows that both the nanoparticles act as good adsorbent and remove more than 90% of the dye but the time taken by Cu-ZnONPs was comparatively less than that of ZnONPs.

6.3. Optimization of adsorbent dose
The efficiency of pure ZnONPs and Cu-ZnONPs was examined by determining the percent removal of CR by varying the concentration of adsorbent in the range of 0.02 to 0.1 g for 100 ml of 20 mg l\(^{-1}\) of CR dye solution. Figure 7(c) exhibits the percent removal of CR on increasing adsorbent dose. On increasing the concentration of ZnONPs, there is an increase in the percentage of removal of CR dye within an optimized time.

6.4. Optimization of Congo red dye concentration
Maximum adsorption capacity of CR dye was obtained by optimizing the concentration of dye. The concentration of CR dye was varied in the range of 20–100 mg l\(^{-1}\) at optimized adsorbent dose and time. The result is depicted in Figure 7(d). It was found that percent removal of CR dye decreases with increase in dye concentration. The active sites on adsorbents get saturated after adsorption of certain concentration of dye and therefore, further adsorption does not take place.

7. Kinetic study
The mechanism of adsorption of CR on the surface of synthesized NPs can be explained by various kinetic models such as Pseudo first order and Pseudo second order.

Pseudo first order can be represented by the equation (7.1) given below:

\[
\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t
\]

Where, \(q_t\) (mg g\(^{-1}\)) is the adsorption capacity at time \(t\) and \(k_1\) (min\(^{-1}\)) is the kinetic rate constant. The value of constant \(k_1\) and \(q_e\) was calculated from linear plot between log \((q_e - q_t)\) versus \(t\) (figures 8(a), (b)). The dye adsorption process using both the synthesized NPs (ZnONPs and Cu-ZnONPs) did not follow pseudo first order kinetics as the calculated value of \(q_e\) is not in agreement with experimental value and value of \(R^2\) is smaller as compared to second order kinetics (given in table 1).

A linear form of pseudo second order kinetics is represented in the equation (7.2) below:

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]

Where \(k_2\) (gmg\(^{-1}\) min\(^{-1}\)) is the rate constant of the pseudo-second order. The value of \(k_2\) and \(q_e\) was determined from the graph plotted between \(t/q_t\) versus \(t\) (figures 8(c), (d)). The pseudo-second order model is in good agreement with the experimental data.
agreement with adsorption process as the calculated value of \( q_e \) is in agreement with experimental value and value of \( R^2 \) is also very high.

### 8. Isotherm study

The interaction between the liquid and solid phase of the system is justified by the isotherm study. The adsorption equilibrium of CR dye onto ZnONPs and Cu-ZnONPs was studied by carrying out various experiments and the data obtained was explained by mainly three adsorption isotherm models i.e., Langmuir, Freundlich and Temkin. Langmuir adsorption model assumes monolayer distribution of dye considering the surface of adsorbent to be homogenous. Langmuir adsorption model can be represented in a linear form and is given by the equation (8.1) below:

\[
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}}b} + \frac{C_e}{q_{\text{max}}} \quad (8.1)
\]

Where \( q_{\text{max}} (\text{mg} \text{ g}^{-1}) \) is the maximum monolayer adsorption capacity, \( b (\text{l mg}^{-1}) \) is the Langmuir constant. The graph was plotted between \( C_e \) versus \( q_e \) (figure 9(a)) which gives the value of adsorption model parameters and correlation coefficient (\( R^2 \)) given in table 2. The feasibility of Langmuir adsorption isotherm was determined by the value of separation factor \( R_L \) [35], which is given by equation (8.2) shown below:

\[
R_L = \frac{1}{1 + bC_0} \quad (8.2)
\]

\( C_0 \) represents the initial concentration of CR.
RL < 1 indicates the adsorption to be feasible while RL > 1 indicates non-feasible reaction and RL = 1 represents linear adsorption process.

The value of RL in case of CR being adsorbed on ZnONPs was found to be 0.129, which exhibits the feasibility of adsorption. In case of Cu-ZnONPs, on comparing the data to Langmuir isotherm mode, the value of separation factor was found to be 1 which exhibits that linear adsorption is taking place.

Freundlich isotherm model is based on the assumption that adsorption of the molecules takes place in multilayer over a heterogeneous surface of adsorbate. The linear form of this model is represented in equation (8.3):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$  \hspace{1cm} (8.3)

Where $K_f$ (mg g$^{-1}$) is Freundlich constant, which defines the adsorption capacity and $n$ is the heterogeneity factor depicting the intensity of adsorption. The linear plot between $\log q_e$ versus $\log C_e$ determines the value of $K_f$ and $n$ (figure 9(b)). The value of $n$ represents whether the reaction is favourable or not. The value of $n$ in the range of 1 to 10 represents favorable adsorption [36]. The adsorption of dye on both ZnONPs and Cu-ZnONPs is a favorable adsorption.

Temkin & Pyzhev isotherm model follows the assumption that (a) adsorption of the molecules occurs in monolayer over heterogeneous active sites on the adsorbent surface or (b) binding energy is uniformly distributed due to adsorbent-adsorbate interaction, the heat of adsorption of adsorbed dye molecule decreases linearly with coverage. A linear form of model is expressed by equation (8.4):

$$q_e = B \ln K_T + B \ln C_e$$  \hspace{1cm} (8.4)

Where $B = RT/b$, $b$ is the Temkin constant related to heat of adsorption (J mol$^{-1}$), $R$ is universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$) and $K_T$ is equilibrium binding constant (l g$^{-1}$). The linear plot between $q_e$ versus $\ln C_e$ gives the value of $K_T$ and $B$ (figure 9(c)).

By comparing the above mentioned isotherm models, it was found that the data obtained in case of ZnONPs fitted well to Freundlich and Temkin models. The value of correlation coefficient was found to be high for these two models as compared to Langmuir model having lower value of correlation coefficient.

While in case of Cu-ZnONPs the data does not fit to Temkin isotherm as the value of correlation coefficient is very low but fits well to Langmuir and Freundlich isotherm.

9. Conclusions

Both ZnONPs and Cu–ZnONPs were successfully synthesized using Moringa oleifera leaf extract and their identity was characterized using various analytical techniques such as UV–vis, XRD, FESEM, TEM etc. All the techniques used in the characterization revealed that Cu was successfully doped into the lattice of ZnO. Kinetic study of both the NPs showed that the adsorption process on CR dye using both the undoped and doped ZnONPs follows pseudo second order kinetics. On calculating the percent removal of dye using both the NPs within an optimized time, it was found that both the nanoparticles act as good and potential adsorbent. The time taken by Cu-ZnONPs to achieve maximum adsorption was comparatively less than that of ZnONPs. The adsorption data obtained for ZnONPs fitted well to both Freundlich and Temkin model, while for Cu-ZnONPs, the data fitted well with Langmuir and Freundlich model.
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Conflict of interest

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ORCID iDs

Abhay Kumar Choubey © https://orcid.org/0000-0002-3251-9013

References

[1] Lachheb H, Puzenata E, Houraie A, Kebib M, Elaloui E and Guillaud C 2002 Photocatalytic degradation of various types of dyes (Alizarin S) in water by UV-irradiated titania Appl. Catal. B 39 75–90
[2] Tanwar R, Kumar S and Kumar U 2017 Photocatalytic activity of PANI/Fe3O4 doped BiOCl under visible light - degradation of Congo red dye J. Photochem. & Photobiol. A: Chem. 335 105–16
[3] Rekha P, Muhammad R and Mohanty P 2015 Sonochemical synthesis of cyclophosphazene bridged mesoporous organosilicas and their application in methyl orange, congo red and Cr (VI) removal RSC Adv. 5 67690–9
[4] Yagub M T, Sen T K, Afroz S and Ang H M 2014 Dye and its removal from aqueous solution by adsorption : a review Adv. Colloid Interface Sci. 209 172–84
[5] Zare K, Sadehg H, Gholshakandi R S, Mazazinejad B, Ali V, Tyagi J, Agarwal S and Gupta V K 2015 Enhanced removal of toxic Congo red dye using multi walled carbon nanotubes : kinetic, equilibrium studies and its comparison with other adsorbents J. Mol. Liq. 212 266–71
[6] Chen M, Ding W, Wang J and Diao G 2013 Removal of azo dyes from water by combined techniques of adsorption, desorption, and electrolysis based on a supramolecular sorbent Ind. Eng. Chem. Res. 52 2403–11
[7] Chamjangali M A, Bagherian G, Bahramian B and Fahimi Rad B 2015 Synthesis and application of multiple rods gold–zinc oxide nanoparticles in the photocatalytic degradation of methyl orange Intl. J. Environ. Sci. Technol. 12 151–60
[8] Kumar R, Kumar G and Umar A 2013 ZnO nano-mushrooms for photocatalytic degradation of methyl orange Mater. Lett. 97 100–3
[9] Tripathy N, Ahmad R, Song J E, Ko H A, Hahn Y B and Khang G 2014 Photocatalytic degradation of methyl orange dye by ZnO nanorod under UV irradiation Mater. Lett. 136 171–4
[10] Tian F, Wu Z, Chen Q, Yan Y, Cravotto G and Wu Z 2015 Microwave-induced crystallization of AC/TiO2 for improving the performance of rhodamine B dye degradation Appl. Surf. Sci. 351 104–12
[11] Sharma Y C, Sinha A S K and Upadhyay S N 2010 Characterization and adsorption studies of Cocos nucifera L. activated carbon for the removal of methylene blue from aqueous solutions J. Chem. Eng. Data 55 2662–7
[12] Malik P K 2004 Dye removal from wastewater using activated carbon developed from saw dust: adsorption equilibrium and kinetics J. Hazardous Material 113 81–8
[13] Rodriguez A, Garcia J, Ovejerio G and Mestanza M 2009 Adsorption of anionic and cationic dyes on activated carbon from aqueous solutions: equilibrium and kinetics J. Hazard. Mater. 172 1311–20
[14] Gupta V K, Kumar R, Nayak A, Saleh T A and Barakat M A 2013 Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: a review Adv. Colloid Interface Sci. 193 24–34
[15] Li Z, Zhang P, Jiang W, Jean J and Hong H 2011 Mechanism of methylene blue removal from water by swelling clays Chem. Eng. J. 168 1193–200
[16] Ba-Abbad M M, Kadhum A A H, Mohamad A B, Takriff M S and Sopian K 2013 The effect of process parameters on the size of ZnO nanoparticles synthesized via the sol-gel technique J. Alloys Compd. 550 63–70
[17] Chand A, Patel D, Kumari P, Jangwan J S and Yadav S 2019 Phytomediately synthesized zinc oxide nanoparticles of Berberis aristata characterization, antioxidant activity and antibacterial activity with special reference to urinary tract pathogens Materials Science & Engineering C 102 212–20
[18] Hussain I, Singh N B, Singh A, Singh H and Singh S C 2013 Greensynthesis of nanoparticles and its potential application Biotechnology Letters 38 345–360
[19] Bansal V, Poddar P, Ahmad A and Sastry M 2006 Room-temperature biosynthesis of ferroelectric Barium titanate nanoparticles J. American Chemical Society 10 11958–63
[20] Singh B R, Singh B N, Khan W, Singh H B and Naqvi A H 2012 Biomaterials ROS-mediated apoptotic cell death in prostate cancer J. Nanomater. cells induced by biosurfactant stabilized CdS quantum dots Biomater. 33 5753–67
[21] Agarwal H, Meeron S, Kumar S V, kumar S R, Sheba B D, Lakshmi T and Nallawasamy V D 2019 Phytosynthesized zinc oxide nanoparticles using Cusia alata and its antibacterial activity against Escherichia coli Biochemistry and Biophysics Reports 17 208–11
[22] Ravendran P, Fan J, Wallen S L, Hill C and Carolina N 2003 Completely ‘Green’ synthesis and stabilization of metal nanoparticles J. American Chemical Society 125 13940–1
[23] Chidambaram S, Pari B, Kasi N and Muthusamy S 2016 ZnO/Ag heterostructures embedded in Fe3O4 nanoparticles for magnetically recoverable photocatalysis J. Alloys Compd. 665 404–10
[24] Huang N, Shu J, Wang Z, Chen M, Ren C and Zhang W 2015 One-step pyrolytic synthesis of ZnO nanorods with enhanced photocatalytic activity and high photostability under visible light and UV light irradiation J. Alloys Compd. 648 919–29

[25] Singh B N, Kumar A, Rawat S, Khan W, Naqvi A H and Singh B R 2014 Biosynthesis of stable antioxidant zno nanoparticles by Pseudomonas aeruginosa rhamnolipids PLoS One 9

[26] Saini R K, Sivanesan I and Keum Y S 2016 Phytochemicals of Moringa oleifera: a review of their nutritional, therapeutic and industrial significance 3 Biotech 6 203

[27] Ahmed S, Annu, Chaudhry S A and Ikram S 2017 A review on biogenic synthesis of ZnO nanoparticles using plant extracts and microbes: a prospect towards green chemistry J. Photochem. & Photobio. B: Biology 166 272–84

[28] Khalafi T, Buzar F and Ghanemi K 2019 Phycosynthesis and enhanced photocatalytic activity of zinc oxide nanoparticles toward organosulfur pollutants Sci. Rep. 9 1–10

[29] Suman T Y, Rajasree S R R, Kanchana A and Elizabeth S B 2013 Biosynthesis, characterization and cytotoxic effect of plant mediated silver nanoparticles using Morinda citrifolia root extract Colloids and Surfaces B: Bio interfaces 106 74–8

[30] Roshmi T, Jishma P and Radhakrishnan E K 2016 Photocatalytic and antibacterial effects of silver nanoparticles fabricated by Bacillus subtilis SJ 15 Inorganic and Nanometal Chemistry 3174 901–8

[31] Pulipati S, Parveen S H, Babu R K, Vagdevi G and Babu S 2013 Pharmacognostical and physicochemical standardization of leaves of Spathodea campanulata P. Beauv J. Pharmacognosy and Phytochemistry 2 189–92

[32] Prasad A R, Garvass I, Oruvil S K and Joseph A 2018 Bio-inspired green synthesis of zinc oxide nanoparticles using Abelmoschus esculentus mucilage and selective degradation of cationic dye pollutants J. Physical and Chemistry of Solids 127 265–74

[33] Kulkarni S, Jadhav M, Raikar P, Barretto D A, Vootla S K and Raikar U S 2017 Green synthesized multifunctional Ag@Fe2O3 nanocomposites for effective antibacterial, antifungal and anticancer properties New J. Chem. 41 9513–20

[34] Chithra M J, Pushpanathan K and Nadu T 2016 Thermal, structural and optical investigation of Cu-doped ZnO nanoparticles Modern Physics Letters B 30 1–13

[35] Sivaraj K K R and Namasivayam C 2001 Orange peel as an adsorbent in the removal of acid violet 17 (acid dye) from aqueous solutions Waste Manage. (Oxford) 21 105–10

[36] Freundlich H M F 1905 Over the adsorption in solution J. Phys. Chem. 57 385–471