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EQUILIBRIUM STUDIES ON ADSORPTION OF MALACHITE GREEN DYE BY ZINC OXIDE NANOPARTICLE

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ABSTRACT: In this work, zinc oxide nanoparticle prepared by the precipitation method were employed as a potential adsorbent for the removal of Malachite Green dye from aqueous solutions. The prepared zinc oxide nanoparticle was characterized using X-ray diffraction, scanning electron microscopy, and Brunauer-Emmett-Teller (BET) surface area analysis. Various parameters affecting the removal efficiency, such as solution pH, shaking time, adsorbent amount, Temperature and the dye concentration, were studied and optimized. The effect of various zinc oxide nanoparticle amounts and initial Malachite Green dye concentration were tested. The experimental data were analysed by different Equilibrium isothermal model. The Langmuir and the Freundlich isotherm models were used to fit the adsorption isotherms of the zinc oxide nanoparticle. This study suggests zinc oxide nanoparticle as an effective adsorbent for the removal of the dyes from polluted water.

KEYWORDS: Zinc oxide Nanoparticle, Malachite Green dye, Adsorption, Batch Equilibrium and Kinetic Studies.

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1.INTRODUCTION

Zinc oxide is an inorganic compound with the formula ZnO. ZnO is a white powder that is insoluble in water, which is widely used as an additive in numerous materials and products including plastics, ceramics, glass, cement, lubricants [1] paints, ointments, adhesives, sealants, pigments, foods, batteries, ferrites, fire retardants, and first aid tapes. It occurs naturally as the mineral zincite but most zinc oxide is produced synthetically [2]. ZnO occurs as a white powder. The mineral zincite usually contains manganese and other impurities that confer a yellow to red color [3-4]. Crystalline zinc oxide is thermochromic, changing from white to yellow when heated and in air reverting to white on cooling [5]. Synthetic ZnO crystals red and green colours are associated with different concentrations of oxygen vacancies. A large number of specialized methods exist for producing ZnO for scientific studies and niche applications. These methods can be classified by the resulting ZnO form (bulk, thin film, nanowire), temperature (low or high), process type and other parameters Nanophase ZnO can be synthesized into a variety of morphologies including nanowires, nanorods, tetrapods, nanobelts, nanoflowers, nanoparticles etc. Nanostructures can be obtained with most above-mentioned techniques, at certain conditions, and also with the vapor-liquid-solid method [6]. Rod like nanostructures of ZnO can be produced via aqueous methods, which are attractive for the following reasons: They are low cost, less hazardous and thus capable of easy scaling up; the growth occurs at a relatively low temperature, compatible with flexible organic substrates; there is no need for the use of metal catalysts, and thus it can be integrated with well-developed silicon technologies. The applications of zinc oxide powder are numerous, and the principal ones are summarized below. Most applications exploit the reactivity of the oxide as a precursor to other zinc compounds. Zinc oxide as a mixture with about 0.5% iron (III) oxide (Fe_2O_3) is called calamine and is used in calamine lotion. There are also two minerals, zincite and hemimorphite, which have been historically called calamine. When mixed with eugenol, a ligand, zinc oxide eugenol is formed, which has applications as a restorative and prosthodontics in dentistry [7]. In this study, ZnO nanoparticles are synthesized by the precipitation method using zinc nitrate hexahydrate and sodium alginate as reducing agent. The synthesized ZnO nanoparticles are characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The specific surface area and particle size distribution are investigated by the Brunauer– Emmett–Teller (BET) technique. In this study, we have focused on preparation of Zinc oxide nanoparticle and their efficiency in removal of dye from dye solution.

2. MATERIALS AND METHODS

Preparation of Zinc Oxide Nanopaticles

Zinc nitrate hexahydrate $Zn(NO_3)_2.6H_2O$ and low-viscosity of alginic acid sodium salt (analytical grade) were purchased from Sigma-Aldrich, USA.

Preparation of zinc–alginate beads

Zinc solution was prepared either from Zinc Nitrate by dissolving the appropriate amounts of the respective salts in ultrapure water. Alginate solutions at a concentration of 1% w/w were prepared by dissolving the appropriate amounts of sodium alginate in ultra pure hot water under magnetic stirring. The zinc alginate beads were produced by drop wise addition of 10 ml of alginate solution into 20 ml of zinc solution through a 0.49 mm inner diameter stainless steel needle. The formed gel beads were maintained in the gelling medium for 30 min under gentle stirring and then separated from the solution through a stainless steel grid placed in a porcelain crucible and heated at 450 or 800°C for 24 h with a heating rate of 10 °C/min.

Characterization of adsorbent Samples

Synthesized zinc oxide nanoparticle were analysed using XDL 3000 powder X-ray diffractometer (XRD), FTIR analysis and Philips Scanning Electron Microscope (SEM) and Brunauer– Emmett–Teller (BET) technique.

Dye Adsorption studies

Preparation of Dye

Malachite Green dye was commercial product supplied by CDH Chemicals India. Dye determinations were performed on a UV spectrophotometer at different dyestuff (nm). Replicate measurements yielded a relative standard deviation of about 3%. The detection limit for all dyestuffs was 0.1 mgL^{-1}. The absorbance at the optimum wavelengths was plotted against the corresponding concentrations of each dyestuff to generate standard curves for use in the determination of dyestuff concentrations after treatment.

Batch Equilibrium Studies

In experiments of equilibrium adsorption isotherm, the mixture of ZnO Nanomaterial (containing 0.1 g dry basis of Malachite Green dye solution) and acetic acid buffer solution with desired pH value were shaken for 24 hrs using a water bath to control the temperature at 30 $\pm 1^0$C. The effect of the adsorption isotherm was determined by examining the series of isotherms at Malachite Green dye: adsorbent dosages (1.0, 2.0, 3.0), pH (3.2, 6.8, 9.0), Temperature (30, 40, 60^0 C) 0.1 g of adsorbent of (ZnO Nanomaterial). The concentrations of dyes were measured with an UV/Visible spectrometer (JASCOV-530). Each experiment was at least duplicated under identical conditions.

3. RESULTS AND DISCUSSION

Characterization studies

XRD analysis

The ZnO nanoparticle XRD spectrum shows the synthesized particles are crystalline in nature was shown in Fig. 1. Whereas, the ZnO nanoparticles from zinc nitrate are amorphous in nature. The presence of unassigned peaks in the XRD spectra shows the presence of impurity associated with the synthesized nanoparticles. But in ZnO from zinc nitrate XRD spectrum, the presence of unassigned peaks indicates the association of impurities with the crystalline ZnO nanoparticles. The reported XRD spectra were compared with the standard XRD spectrum which was released by Joint Committee on Powder Diffraction Standards (JCPDS file no. 89-4921). The SEM images also confirmed the result of XRD analysis. Our XRD analysis was well coincided with the report of [8-9].

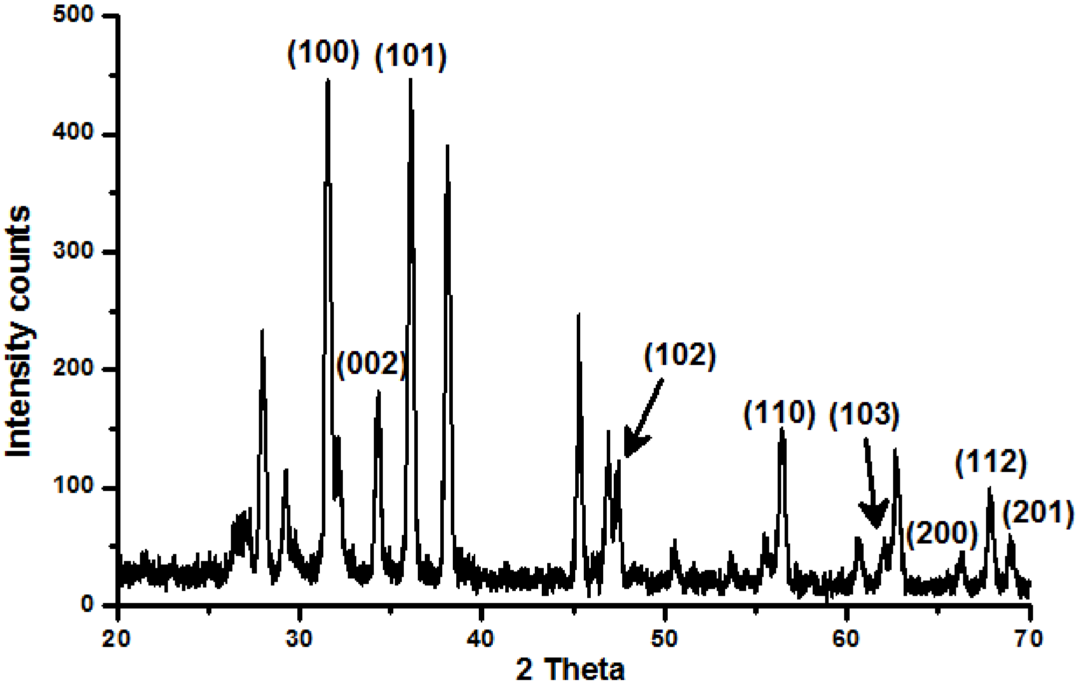

Fig.1 XRD analysis of ZnO ZnO nanoparticle from zinc nitrate

SEM analysis

The scanning electron microscope uses a beam of high-energy electrons to produce a variety of signals at the surface of specimens used. The signals show information about the sample including chemical composition, and crystalline structure, external morphology and orientation of materials which make up the sample. Fig.2. shows the SEM images of ZnO, ZnO from zinc nitrate. The morphology of the ZnO was entirely different from the ZnO nanoparticles from zinc nitrate. The ZnO nanoparticle could increases or enhances the dye adsorption were investigated.

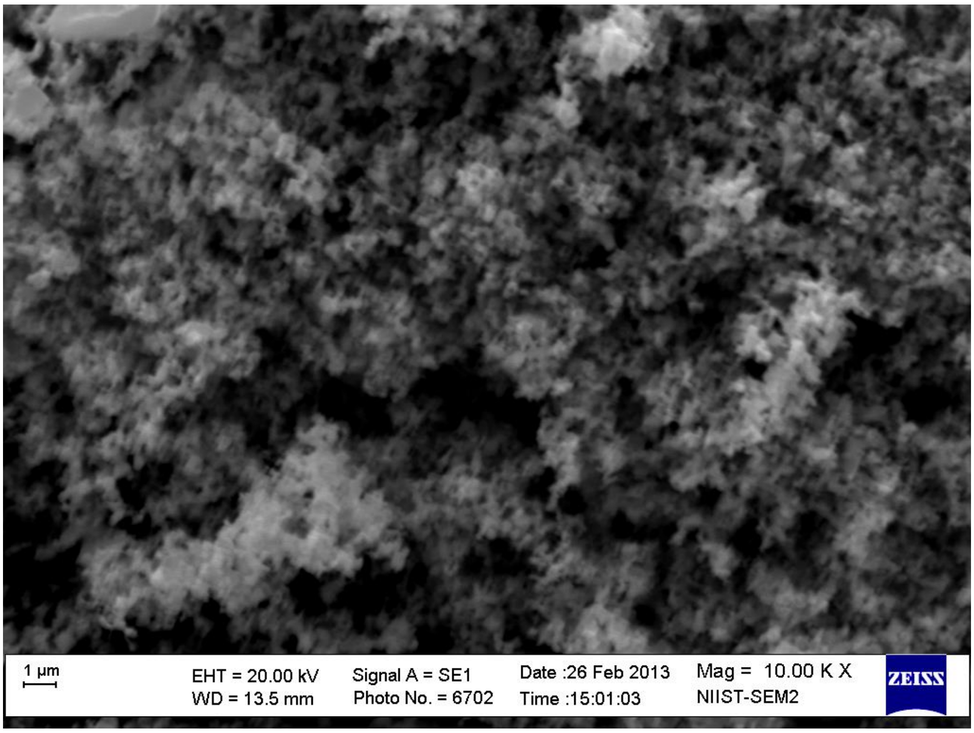

Fig.2 SEM image of ZnO, ZnO nanoparticle from zinc nitrate

FTIR analysis

To identify the surface nature, FTIR spectra was recorded for the ZnO Fig 3. ZnO nanoparticle were appear at 3368 cm^{-1} and 3369 cm^{-1} correspond to H-O-H stretching of alcohols. The peak observed at 1633 cm^{-1} in both ZnO nanoparticle represents the C=O stretching of aldehydes. The 1426 cm^{-1} and 1416 cm^{-1} band for ZnO nanoparticle respectively corresponds to N=O beding of nitro groups. The peak at 1107 cm^{-1} in ZnO nanoparticle represents the C-O stretching of ether.

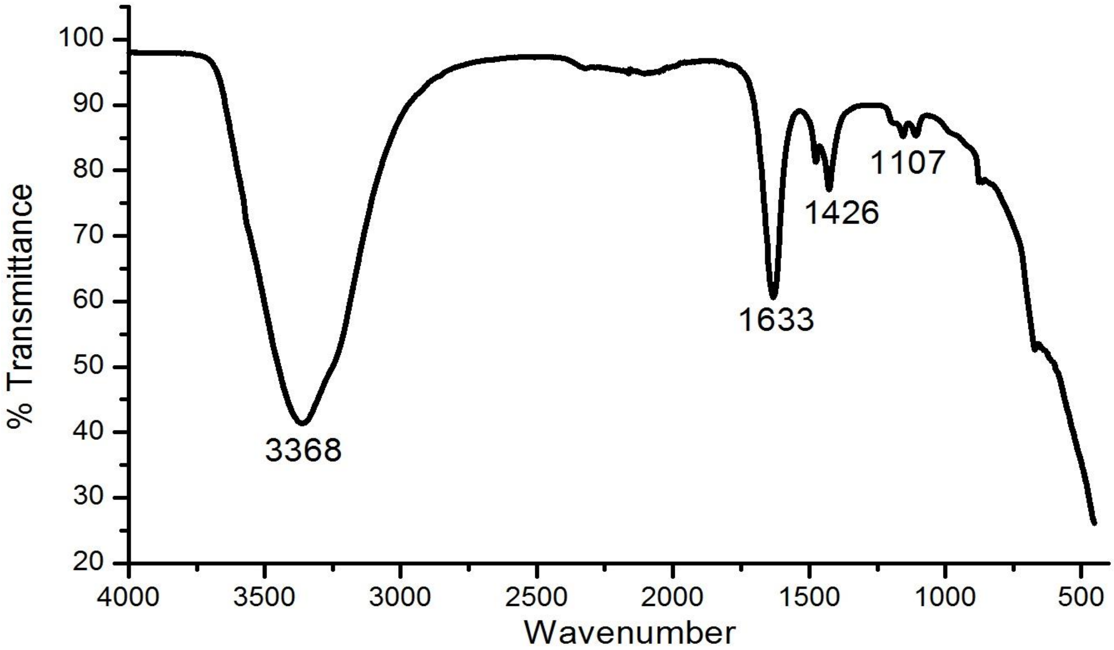

Fig. 3 FTIR spectrum of ZnO nanoparticle

BET Surface area analysis

From Table.1 shows the ZnO nanoparticle, the Langmuir surface area also high when compare to other nanoparticle. Similarly, the microspore and external surface area are also high. Due to the presence of enormous number of microspore on the surface of ZnO with the combination of other nanoparticles, it could acts as fine dye degradation agent and adsorb the dye actively.

Table 1: BET Surface area of ZnO nanoparticle

	ZnO nanoparticle
Single point surface area at P/Po 0.27230297	1.12952 m^2/g
BET surface area	1.1257 m^2/g
Langmuir Surface Area	1.6255 m^2/g
Micropore Area	0.3882 m^2/g
External Surface Area	0.7394 m^2/g
BJH Adsorption Cumulative Surface Area of pores between 17.000000 and 3000.000000 A Diameter	1.7255 m^2/g
Micropore Volume	0.000175 cm^3/g
BJH Adsorption Cumulative Pore Volume of pores between 17.000000 and 3000.000000 A Diameter	0.002530 cm^3/g
BJH Adsorption Average Pore Diameter (4V/A)	64.1025 A

Adsorption of Malachite Green

Effect of dosage, temperature and pH

The Langmuir isotherm has found successful application for many other real sorption processes and it can be used to explain the sorption of dyes into Zinc oxide nanoparticle. A basic assumption of the Langmuir theory is that sorption takes place at specific sites within the adsorbent. The data obtained from the adsorption experiment conducted in the present investigation was fitted in different dye concentrations, sorbent dosages, pH and temperature in isotherm equation as shown in Fig. 4-6. Fig. 4-6 had shown the adsorption of dye at different adsorbent dosage, temperature and pH by using Zinc oxide nanoparticle. The adsorbent rate variation may be due to the number of positive charges on the sorbent surface which leads to the no rejection of negatively charged dye molecule, and thereby increasing the adsorption. The adsorption of dye increased with the increase in adsorbent dosage (Fig. 4). The maximum percentage removal of about 37.1 g/L was obtained for adsorbent dosage of 3.0 g/L for Malachite green dye at 100 mg/L concentration. The increase in adsorption of dye with adsorbent dosage was due to the availability of more surface area of the adsorbent for adsorption [10]. The dye uptakes are much higher in acidic solutions than those in neutral and alkaline conditions. This explanation is conflict with our data on pH effect (Fig 5). It can be seen that the pH of aqueous solution plays an important role in the adsorption of (MG) dye onto Zinc oxide nanoparticle. The present results conflict with the results parallel to the results of [11]. The maximum percentage removal of 26.1 g/L was obtained in pH of 6.8 for (MG) at 100 mg/L concentration. Temperature is an important parameter for the adsorption process. A plot of the Malachite green dye uptake as a function of temperature (30, 40 and 60 ºC) is shown in Fig 6. The maximum percentage removal of 33.1 g/L was obtained for the temperature of 60ºC for (MG) dye at 100 mg/L concentration. The adsorption of dye at higher temperature was found to be greater compared to that at a lower temperature. The curves indicate the strong tendency of the process for monolayer formation [12-19]. The increase in temperature would increase the mobility of the large dye ion and also produces a swelling effect within the internal structure of the Zinc oxide nanoparticle, thus enabling the large dye molecule to penetrate further [19]. Therefore, the adsorption capacity should largely depend on the chemical interaction between the functional groups on the adsorbent surface and the adsorbate and should increase with temperature rising.

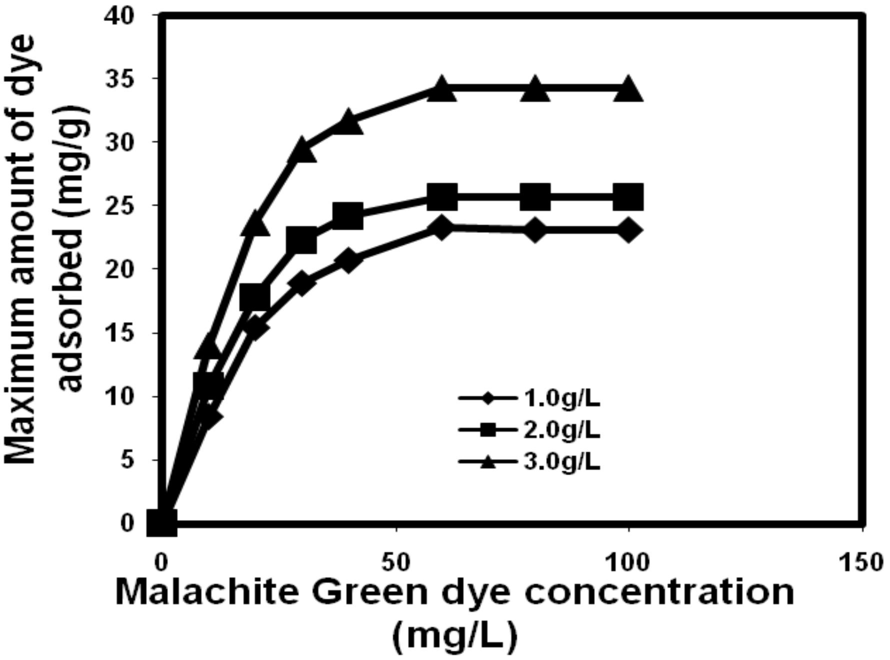

Fig. 4 Effect of specific dye (MG) uptake at different adsorbent dosages

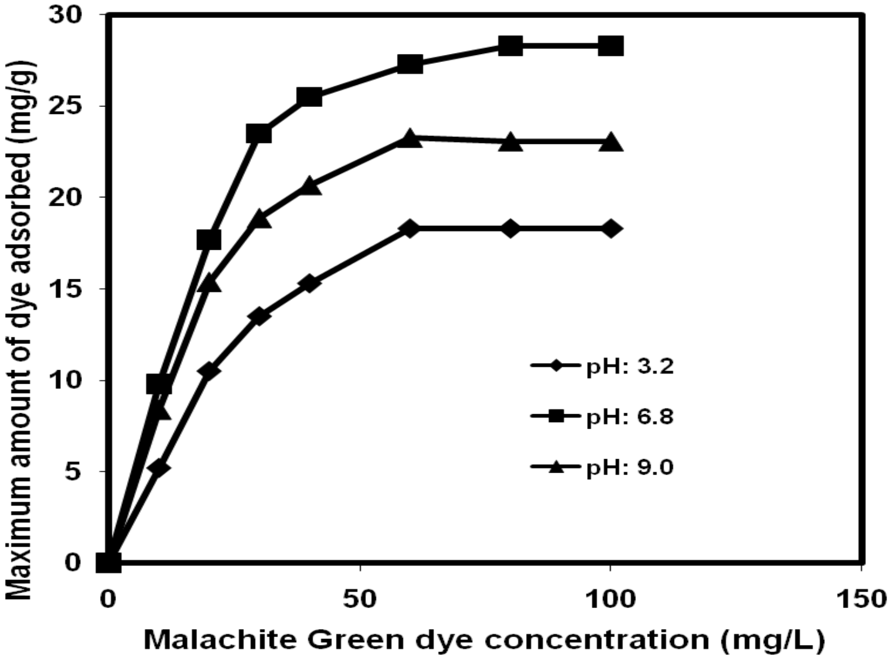

Fig. 5 Effect of specific dye (MG) uptake at different pH

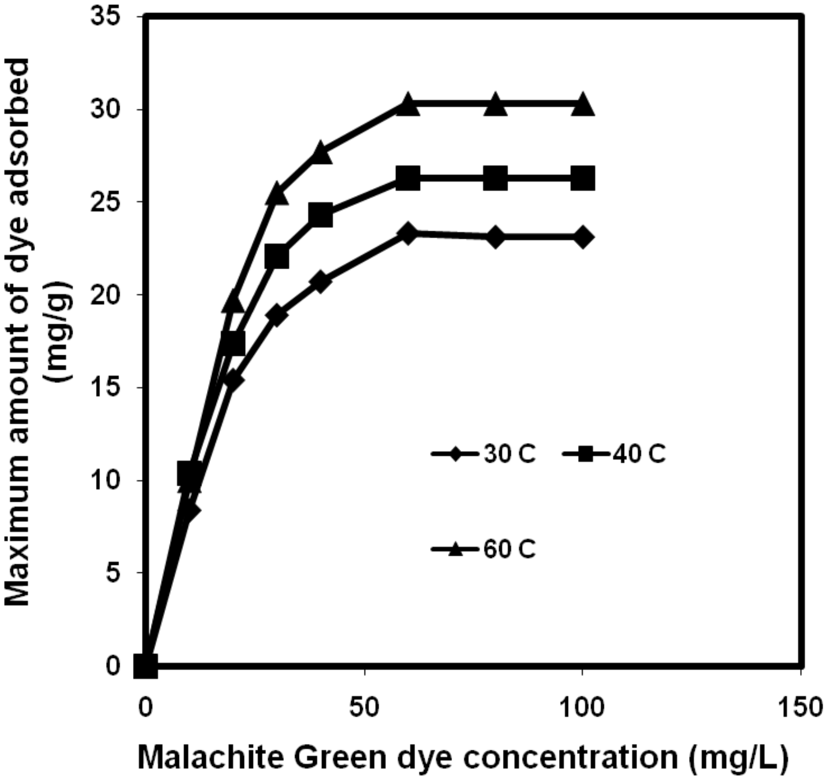

Fig. 6 Effect of specific dye (MG) uptake at different Temperatures

Langmuir isotherm

The equilibrium adsorption isotherm is of fundamental importance in the design of adsorption systems. The isotherm expresses the relation between the mass of dye adsorbed at a particular dosage, temperature and pH and liquid phase of dye concentration. For any adsorption investigation one of the most important parameters required to understand the behaviour of the adsorption process in the adsorption isotherm. The shape of an isotherm not only provides information about the affinity of the dye molecule for adsorption, but it also reflects the possible mode of adsorbing dye molecule. The most common way of obtaining an adsorption isotherm, is to determine the concentration of dye solution before and after the adsorption experiments, although several attempts have been made to find the adsorbed amount. A basic assumption of the Langmuir theory [20] at sorption takes place at specific sites within the adsorbent [21-23]. The data obtained from the adsorption experiment conducted in the present investigation was fitted in different adsorbent dosage, pH and temperature in isotherm equation as shown in Fig. 7-9. The saturation monolayer can be represented by the expression. A plot of ($1/q_e$ vs $1/C_e$) resulted in a linear graphical relation indicating the applicability of the above model as shown in (Fig.7-9). The values are calculated from the slope and intercept of different straight line representing the different sorbent dosages, pH and temperature (b) energy of adsorption and (k) adsorption capacity and Q_0 is represented by (K). The Langmuir isotherm constant (Q_0) in eqn (3) is a measure of the amount of dye adsorbed, when the monolayer is completed. Monolayer capacity (Q_0) of the adsorbent for the dye is comparable as obtained from adsorption isotherm. The observed statistically significant (at the 95% confidence level) linear relationship as evidenced of these by the R^2 values (close to unity) indicate the applicability of the isotherm (Langmuir isotherm) and surface. The Langmuir isotherm constants along with correction coefficients are reported on (Table 2). It is also clear from the shape of the adsorption isotherm, that it belongs to the L_2 category of isotherm, which indicates the normal (or) Langmuir type of adsorption. Such isotherms are often encountered when the adsorbate has a strong intermolecular attraction for the surface of the adsorbent.

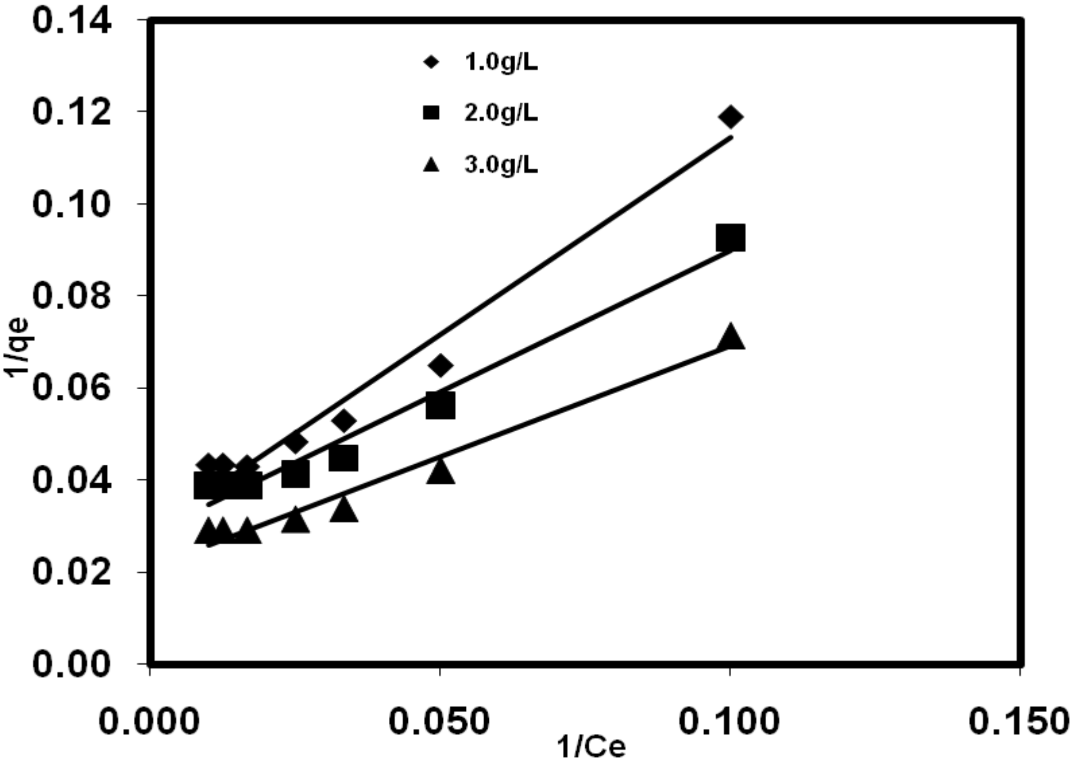

Fig. 7 Langmuir isotherm for the adsorption of Malachite Green dye using Zinc oxide Nanoparticle at different adsorbent dosages

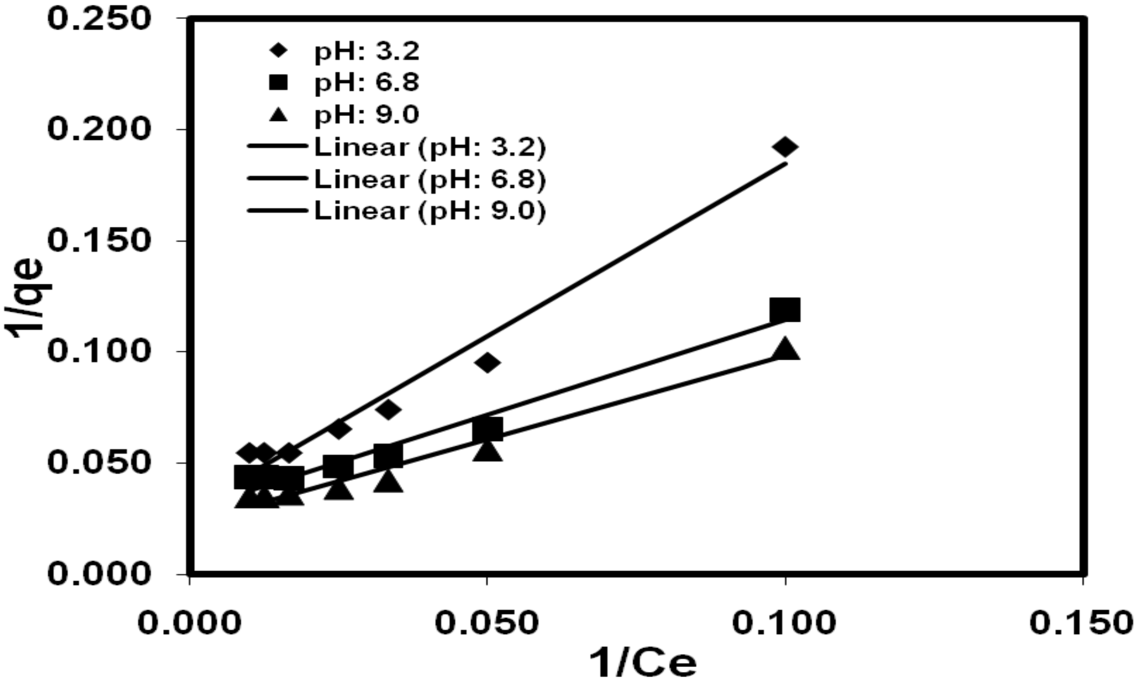

Fig. 8 Langmuir isotherm for the adsorption of Malachite Green dye using Zinc oxide Nanoparticle at different pH

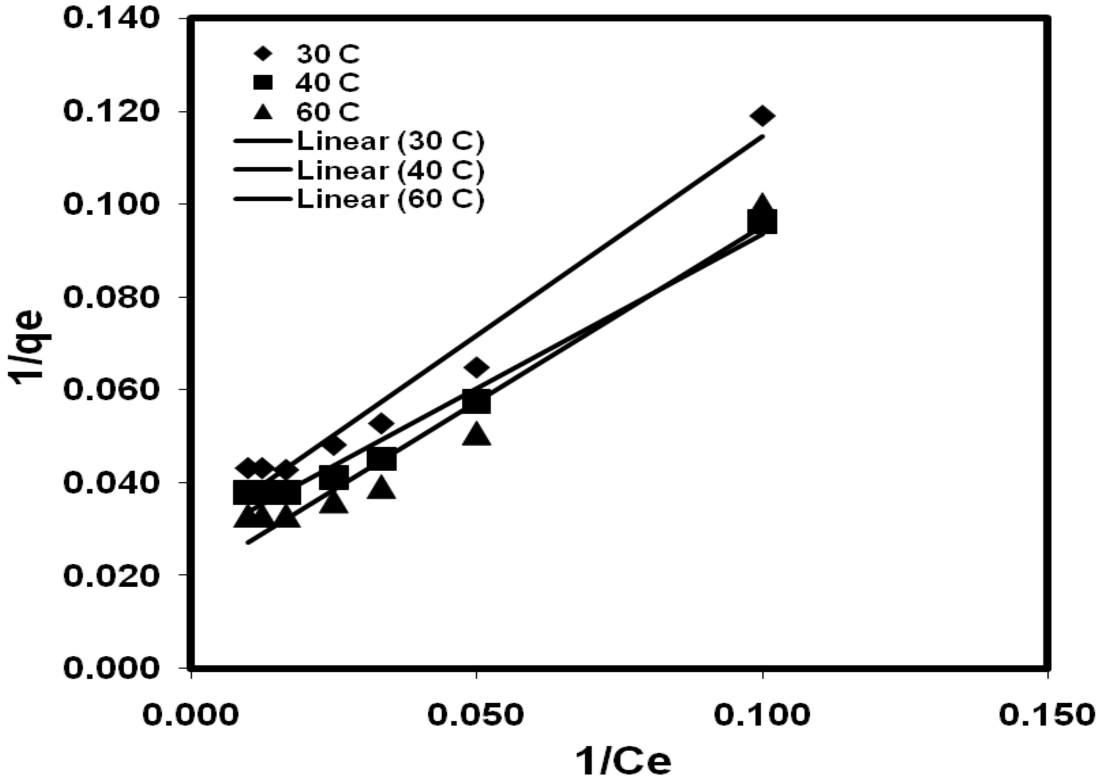

Fig. 9 Langmuir isotherm for the adsorption of Malachite Green dye using Zinc oxide Nanoparticle at different Temperatures

Freundlich isotherm

Freundlich isotherm [24] is used for heterogeneous surface energies system. The sorption isotherm is the most convenient form of representing the experimental data at different adsorbent dosage, temperature and pH as shown in Fig. 10-12. Moreover the figures show the batch isothermal data fitted to the linear form of the Freundlich isotherm. The various constants, associated with the isotherm are the intercept, which is roughly an indicator of sorption capacity (k_f) and the slope (1/n) sorption intensity values are recorded in Fig. 10-12. Freundlich isotherm has been illustrated to be a special case of heterogeneous surface energies and it can be easily extended to this case [25-26]. It has been stated by that magnitude of the exponent 1/n gives an indication of the favorability and capacity of the adsorbent system. The values n>1 represents favorable adsorption conditions. In most of the cases the exponent between 1<n<10 shows the beneficial adsorption as shown in Table.2. The adsorption of malachite green dye from aqueous solution using zinc oxide nanoparticle has been investigated under different reaction conditions in batch and equilibrium mode. The fitness of Langmuir model in the present system shows the formation of monolayer coverage of the adsorbate at the outer space of the adsorbent. Freundlich model isotherm was analysed [27]. The monolayer adsorption capacity determined was reasonably high (g/L) at adsorbent dosage 1.501 (g/L), Temperature 1.367 (g/L) and pH 0.644 (g/L) for adsorption of (MG) dye respectively. The monolayer adsorption capacity was determined to be 22.86 to 53.82 mg/g. The values of dimensionless equilibrium parameter like separation factor (R_L) at different dosages, pH and temperature indicates the favorability of the process described in the present study.

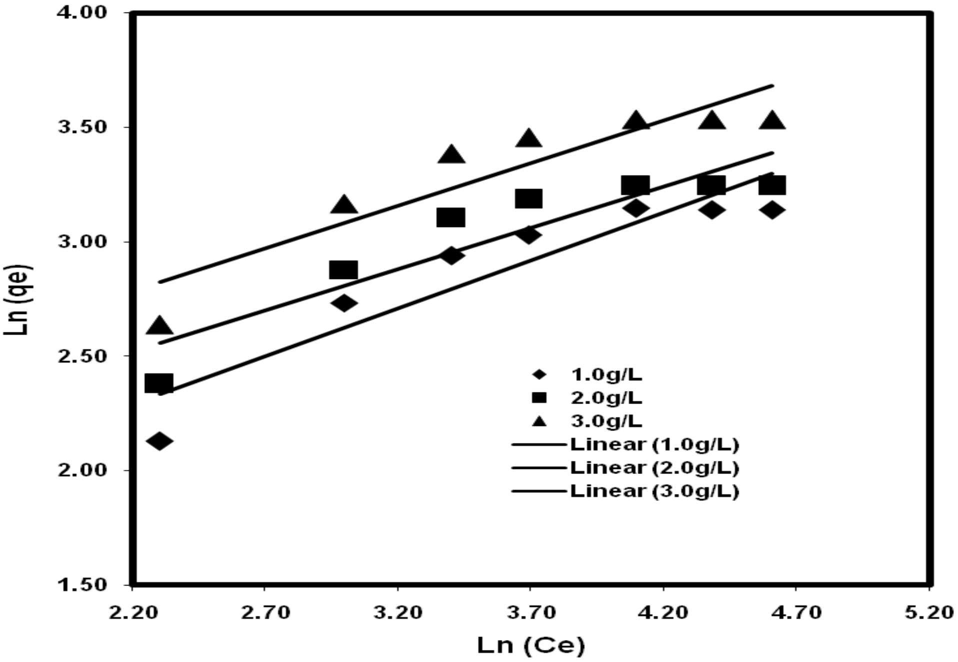

Fig. 10 Freundlich isotherm for the adsorption of Malachite Green dye using Zinc oxide nanoparticle at different adsorbent dosages

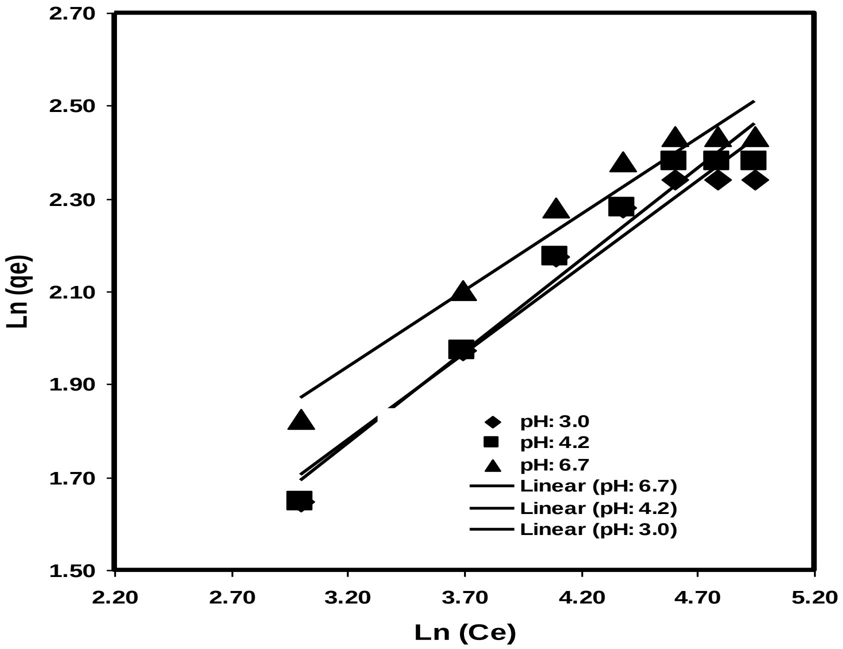

Fig. 11 Freundlich isotherm for the adsorption of Malachite Green dye using Zinc oxide nanoparticle at different pH

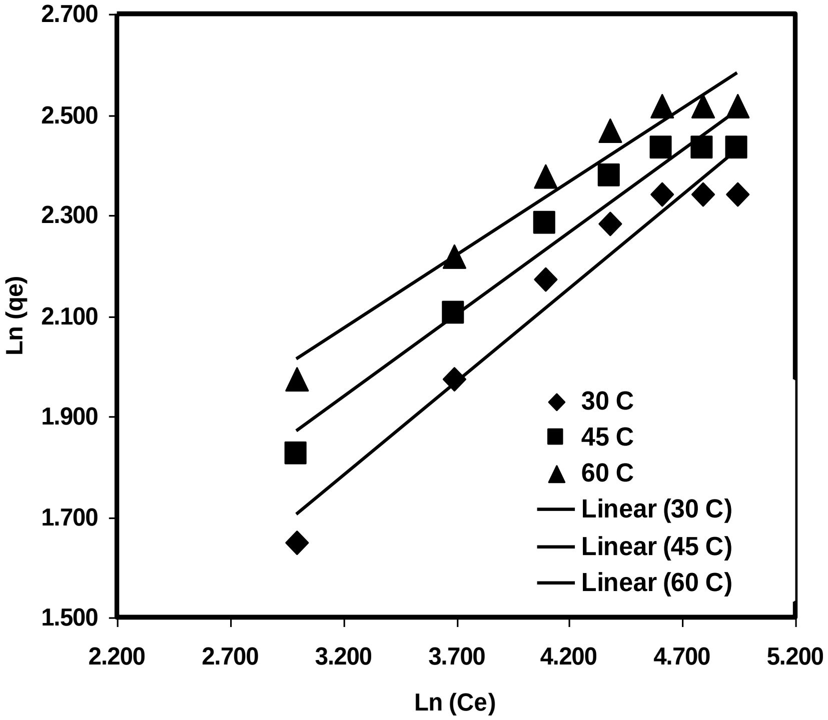

Fig. 12 Freundlich isotherm for the adsorption of Malachite Green dye using Zinc oxide nanoparticle at different temperatures

Table 3 Langmuir and Freundlich isotherm constants at different adsorbent dosages, pH and Temperatures (MG)

Adsorbent Dosage (g/L)	**Langmuir Isotherm -model parameters**	**Freundlich Isotherm -model parameters**
1.0	K= 29.48; b= 1.17; R^2= 0.9929	K_F=1.971; n= 0.371; R^2= 0.9727
2.0	K=21.86; b= 1.63; R^2= 0.9883	K_F= 1.729; n= 0.36;R^2= 0.9494
3.0	K= 22.86; b=2.08;R^2= 0.9565	K_F=1.367; n= 0.419; R^2= 0.9353
pH	**Langmuir Isotherm -model parameters**	**Freundlich Isotherm -model parameters**
3.2	K= 53.52; b= 0.64; R^2= 0.9926	K_F=1.474; n= 0.44; R^2= 0.9929
6.8	K= 29.48; b=1.17; R^2= 0.9929	K_F=1.367; n= 0.419; R^2= 0.9926
9.0	K= 32.78.; b= 1.33;R^2= 0.991	K_F= 0.644;n= 0.734; R^2= 0.991
Temperature (^{0}C)	**Langmuir Isotherm -model parameters**	**Freundlich Isotherm -model parameters**
30	K= 29.48; b= 1.17; R^2= 0.9929	K_F=1.501; n= 0.44; R^2= 0.9929
45	K= 22.86; b= 1.51; R^2= 0.9889	K_F = 1.621; n= 0.412; R^2= 0.991
60	K= 39.76.0;b= 1.32; R^2= 0.991	K_F = 1.367; n= 0.74; R^2= 0.9889

4. CONCLUSION

Conclusion In summary, ZnO nanoparticle prepared using the precipitation method. A little amount of prepared ZnO was employed for the elimination of Malachite Green dye from aqueous solutions in high concentrations. The precipitate obtained as calcined at to different temperature 400 and 800^{O}C to get powdered form on ZnO. That proved that the particles obtained were pure nanoparticles. SEM images gave clear indication that the flake like morphology. The nanoparticles calcined at 800^{O}Cwere chosen for batch adsorption studies. The effect of adsorbent dosage, adsorbate concentration, Temperature and pH were varied. It found that at 24hrs contact time equilibrium was achieved, 0.1 gm of ZnO loading and 100 ppm dye concentration and 6.8 pH conditions showed highest removal efficiency. Langmuir and Freundlich Isotherm Model fitted well to the data obtained. These results indicate that his type of adsorbent with nanoporous structure is reasonable and affordable in the wastewater treatment studies.

studies.

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CONFLICT OF INTEREST

Author has no conflict of interest.

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