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RESEARCH ARTICLE

Comparative Study for Photocatalytic Degradation of Bromo Phenol Blue by Some Nanoparticales Semiconductors

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Abstract

In this study, a comparison of different types of nanocatalyst such as zinc oxide nanoparticles, copper oxide nanoparticles and magnesium oxide nanoparticles on the photocatalytic activity efficiency of Bromo Phenol blue dye. Heterogeneous photocatalytic method was utilized; it was approved out by using UV (A) as light source. Some factors influence on the rate of the photocatalytic degradation of each catalyst were studied and compared and selected the most efficient nanocatalyst. The results of many factors, (such as weight of catalyst, primary dye concentration, pH of aqueous solution, and temperature) , shows that the photodecolorization and degradation is a pseudo-first order reaction giving to the Langmuir-Hinshelwood relationship. The experiments were carried out by varying weight of catalyst (0.02–0.07 g), initial concentration of dye (50–30ppm) , pH solution (1-11), and temperature range(298-313)K. The optimum conditions were approximated as: pH 3 when use ZnO NPs and pH = 5 when using both of CuO NPs and MgO NPs, catalyst amount of 0.06 g,0.05, and 0.03g for ZnO NPs, CuO NPs and MgO NPs respectively. The degradation extents of 92.85%, 65.16% and 74.18% with ZnO NPs, CuO NPs and MgO, respectively obtained for BPB during 20 min irradiation and 30ppm dye concentration. The degradation extent was monitored by UV–vis spectroscopy. The Photocdecolorazation and degradation extent was observed increase with high temperature. Arrhenius plot shows that the E_a is equal to (29.7±1, and 18.54±1, 13.9±1) kJ mol^{-1} by using ZnO, CuO and MgO NPs respectively. The thermodynamic parameters of the photocatalytic degradation of BPB, like E_a, ΔH^*, $\Delta S^*$and ΔG^*showed the efficiency of the process. The most efficient nanocatalyst ZnO NPs>MgO NPs>CuO NPs

Introduction

Water contamination is one of the major problems which the world is facing today[1]. The treatments of industrial wastewater for aqueous waste effluents include different techniques such as biological treatment, reverse osmosis and activated carbon adsorption. These techniques often utilize potentially hazardous or polluting materials and even most of them are non-biodegradable[2].

Therefore, the development of an effective treatment technique that can convert pollutants into non-toxic or less harmful materials is highly required. Advanced oxidation processes (AOPs) were first proposed in the 1980s for drinking water treatment and later were widely studied for treatment of different wastewaters[3]. AOP have been developed, such as photochemical degradation reactions using photodecomposition of hydrogen peroxide (H2O2/UV), ozone photolysis (O3/UV), photocatalysis by semiconductors (TiO2/UV) and photoredox reactions of transition metal complexes[4]. Although these processes use different reacting systems, all are characterized by similar chemical feature of utilizing highly reactive oxidizing agent such as hydroxyl radical (HO*) with redox potential of 2.80 eV[5]. A photocatalyst is defined as a substance which is activated by adsorbing a photon and is capable of accelerating a reaction without being consumed.

These substances are invariably semiconductors. Semiconducting oxide photo catalysts have been increasingly focused in recent years due to their potential applications in solar energy conversion and environmental purification. Semiconductor heterogeneous photocatalysis has enormous potential to treat organic contaminants in water and air [6].

Heterogeneous photocatalysis using metal oxides owing to its potential applications to both environmental applications and organic synthesis. Many attempts have been made to study photocatalytic activity of different metal oxides such as SnO_2, ZnO, TiO_2[7].Generally, there are four essential key steps in the mechanism of heterogeneous photocatalysis on the surface of semiconductor, as follows:(1) charge carriers generation, (2) charge carriers trapping, (3) charge carriers recombination and (4) photo catalytic degradation of organic pollutants[8].

Semiconductor compounds have drawn much attention during the last few years because of their novel optical and transport properties which have great potential for many optoelectronic application[2].When the size of semiconductor materials is reduced to nanoscale, their physical and chemical properties change drastically, resulting in unique properties due to their large surface area or quantum size effect.

Currently, semiconductor nanomaterials and devices are still in the research stage, but they are promising for applications in many fields, such as solar cells, nanoscale electronic devices, light-emitting nano devices, laser technology, waveguide, chemicals and biosensors [9].

Nano zinc oxide (ZnO), as a n-type semiconductor material with a band gap of 3.37eV at room temperature, has high chemical stability, strong photosensitivity and non-toxicity property. ZnO nanoparticles have a large specific surface area and small size effect, and show wide application potential in microbial inhibition and mildew removal[10]. Nano copper oxide CuOis a p-type semiconductor with a narrow band gap (Eg = 1.2eV)[11]. It has been applied to the catalyst, superconducting materials, thermoelectric materials, sensing materials, glass, ceramics and other fields.

In addition, the nano-copper oxide can be used as rocket propellant combustion catalyst. Magnesium oxide (MgO) The band gap energy of MgO is 7.8 eV[12]normally, but for MgO nanoparticles this value is deceased to 4.2 eV. which make it possible to use in photocatalysis[13]. Magnesium oxide (MgO) nanoparticles can be applied in electronics, catalysis, ceramics, petrochemical products, coatings and many other fields.

MgO is also chosen as an adsorbent with strong adsorption capacity[14]. Organic dyes are a well-known source of environmental pollution and therefore their removal from waste waters receives increasing attention. One major source of these wastes comes from the industrial process effluents, such as these provided by paper, plastic, textile, natural and artificial fibers industries. Bromophenol blue (BPB) is a good example of industrial dye deriving from triphenylmethane[15].

Experimental

A homemade photo reactor (Fig.1) equipped with a Philips 250W, medium pressure mercury lamp as a source for UV radiation, was used to determine Photo degradation efficiency (P.D.E).In all experiments, the required amount of the catalyst was suspended in 100 cm3 of aqueous solutions of BPB, using a magnetic stirrer. At predetermined times; 5 cm3 of reaction mixture was collected and centrifuged (3000 rpm, 15 min) in centrifuge.

The supernatant was carefully removed by a syringe with a long pliable needle and centrifuged again at same speed and for the same period of time. This second centrifugation was found necessary to remove fine particles of catalysts. After the second centrifugation the absorbance at (591) nm of the supernatants was determined using ultraviolet-visible spectrophotometer, type UV-1650pc.

First experiment dark reaction, in this part a series of experimental has been done as blank experimental. In each onebromo phenol blue (BPB) solution in concentration 50ppm at temperature 293 K was stirred to 60 min in the presence of the catalysts (ZnO NPs, CuO NPs and MgO NPs) and the absence of the irradiation. Second experiment photolysis. In this part, a series of experiments were performed.

50 ppm dye concentration was irradiation with ultraviolet with the absence of catalyst, and continuous stirring for 120 min at 298K. P.D.E. of BPB was followed spectrophotometrically by a comparison of the absorbance, at specified interval times, with a calibration curve accomplished by measuring the absorbance, at λ max (591) nm, with different concentrations of the dye solution.

$$\% \ Decolorization = 100 \times (C_0 - C)/C_0$$

Where C_0 = initial concentration of dye solution, C = concentration of dye solution after photo irradiation. In order to determine the effect of catalyst loading, the experiments were performed by varying catalyst weights from 0.02 to 0.07 g for dye solutions of 50ppm at natural pH (7). Similar experiments were carried out by varying the pH of the solution pH (1–11) and concentration of dye (30,40,50)ppm. The reaction temperatures amounted to (298- 313) K.

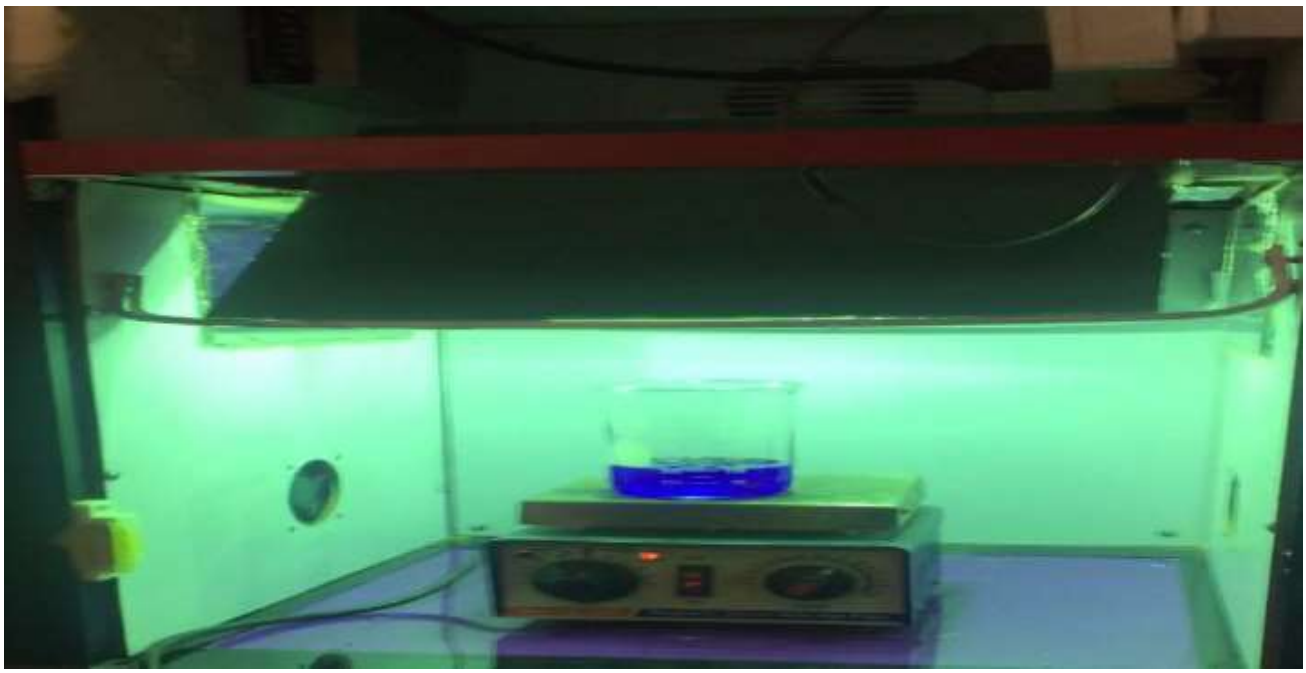

Fig.1: homemade photo reactor

Results and Discussion

Spectra of dye

As shown in the Fig.2 below the absorption spectra of the raw BPB solution shows the peaks in the UV and visible region and maximum absorbance at visible region (591nm) indicates that the BPB dye is highly toxic and needs the degradation to overcome the toxic effect[15].

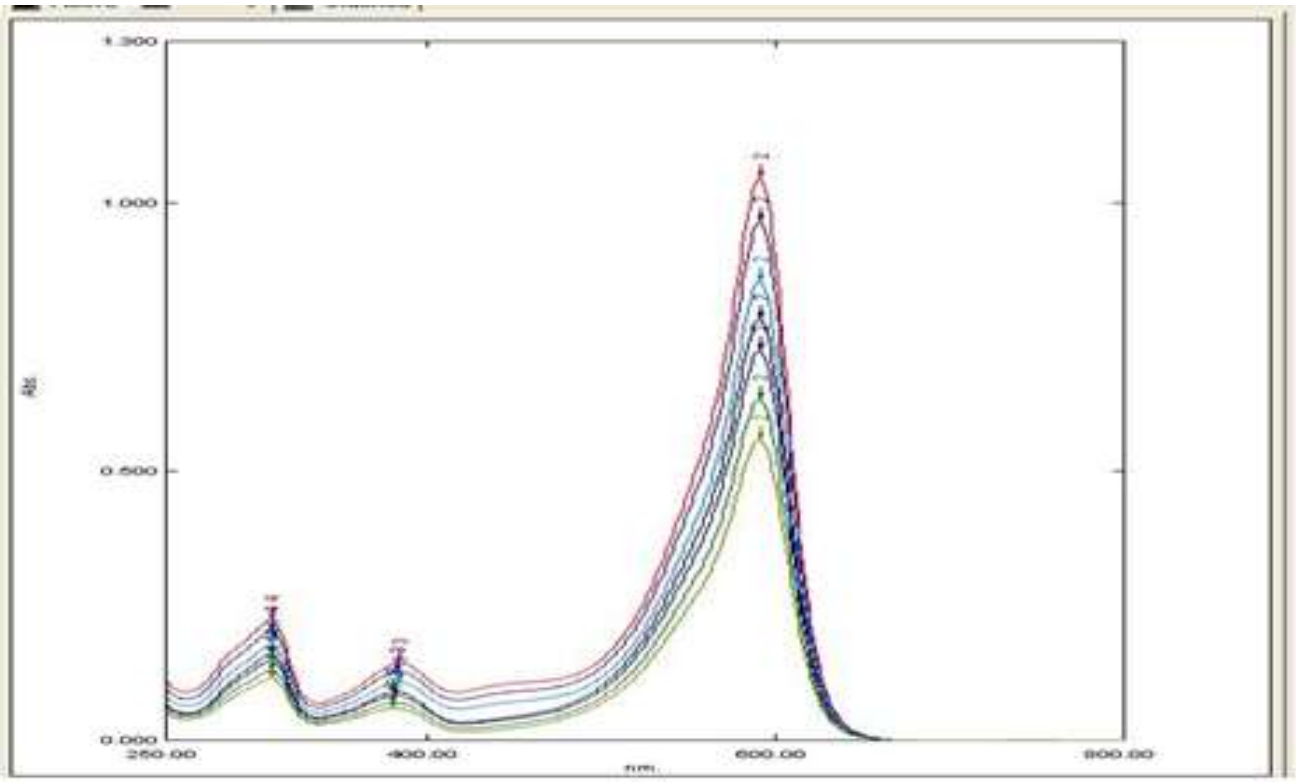

Fig. 2: Absorption spectra of BPB solution at different concentration.

Degradation of BPB solution Under Different Experimental Conditions

Degradation of BPB solution was investigated under seven different experimental conditions through UV alone, UV+ ZnO, UV+ CuO, UV+ MgO, Dark+ ZnO, Dark+ CuO and Dark+ MgO. Fig.3 depicts the photo catalytic degradation of BPB solution under these experimental conditions. Initially blank experiments were performed under UV irradiation without addition of any catalyst (UV alone) and only 10.02% degradation was observed after 20 min.

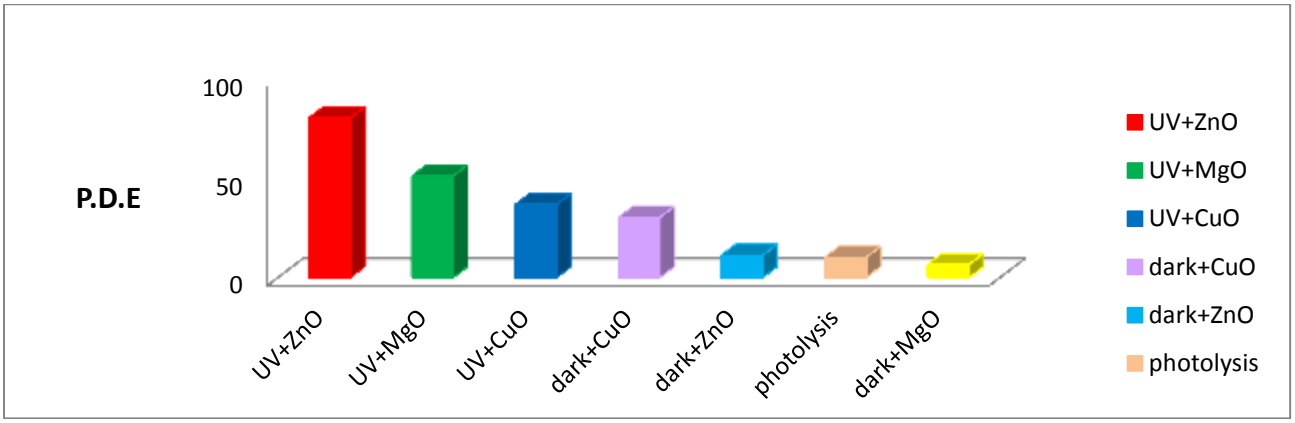

Fig. 3: Photo catalytic degradation of BPB dye (dye initial concentration—50ppm, (0.06g)ZnO,(0.05g)CuO ,(0.03g) MgO NPS after 20min

Thereafter the adsorption of the dye was observed with both catalysts, i.e., Dark + ZnO, Dark+ CuO and Dark + MgO only 11.17%, 30.18% and 6.56 % respectively adsorption of the dye was seen in the same time with both catalysts under dark conditions. Then photo catalytic experiments were carried out using all catalysts at fixed dye concentration (50 ppm) and catalyst amount of 0.06g of ZnO, 0.05g of CuO and 0.03g of MgO.

When experiments were performed under UV irradiation with ZnO as photo catalyst (UV + ZnO), the complete degradation of dye was achieved after40 min, whereas with CuO as a photo catalyst (UV + CuO), only 61.17%decolorization of BPB solution was observed and only 72.4% by using MgO in the same duration. It indicates that ZnO exhibits higher photo catalytic activity than other semiconductors for the decolorization of BPB dye.

Photodecolorization Studies

The experiments were carried out to study the degradation of BPB solution employing (ZnO, CuO and MgO) NPs as catalysts under UV light. Various parameters which affect the degradation efficiency such as catalyst loading (0.02–0.07) g, pH (1-11), initial concentration of dye (30–50) ppm, and temperature (298-313) K of degradation were assessed under UV light.

Influence of the Weight of Semiconductors

As reported, the efficiency of the photo catalytic processes depends on the amount of semiconductor[16].Fig. 4 shows the effect of the ZnO, CuO and MgO nanocatalyst amount on the decolorization of BPB aqueous solution at natural pH. As shown, the catalyst weight of ZnO, MgO and CuO was 0.06, 0.03 and 0.05 respectively showed the best efficiency toward the decolorization of dye and thereafter a sharp decrease was happened in the decolorization efficiency.

Increasing in the photocatalytic efficiency with increase in the catalyst weight until a definite level can be explained by the optical properties of the photocatalyst. Indeed, the total active surface area increased with increasing catalyst dosage. In this case more photons can be absorbed by the available catalyst particles which in turn increases the number of hydroxyl and superoxide radicals.

The decrease in the efficiency of the process at higher catalyst concentration can be considered as the fact that when the concentration of the catalyst rises, the solid particles increasingly block the penetration of the photons due to aggregation of catalyst particles[17,18].Hence, less catalyst particles available, due to decrease in the effective surface area, for receiving photons, so fewer OH radicals produces[18,19].

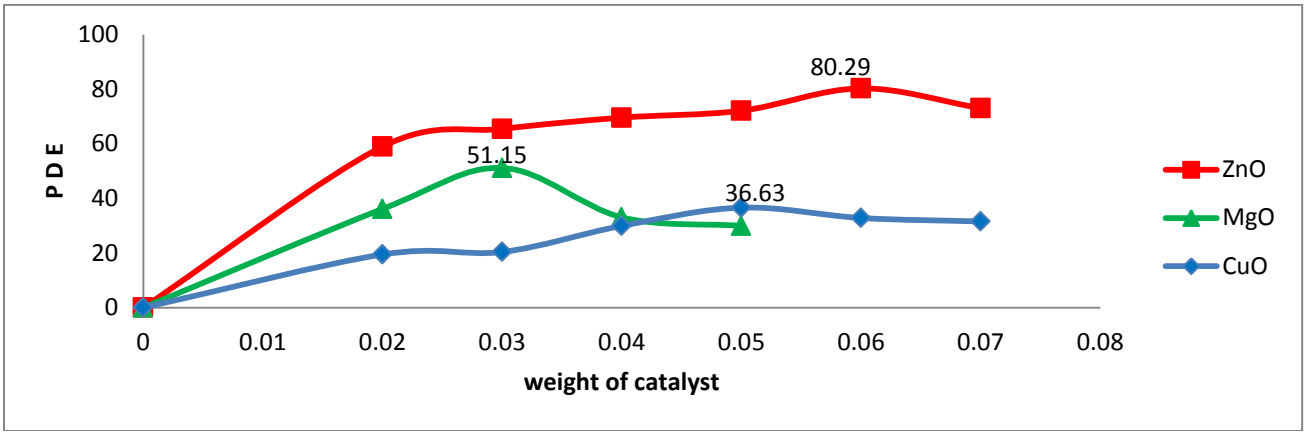

Fig. 4: Effect of ZnO , CuO and MgO nanocatalysts on degradation efficient of BPB dye (at natural pH(7), and initial concentration of dye 50ppm),after (20min)

Influence of Dyes Concentration

The effect of initial dye concentration in the BPB aqueous solution (30, 40and 50 ppm) on the photodecolorization processes was investigated, due to its important role on process efficiency[20]. Fig.5 show the decolorization extent of dye as a function of their concentration using ZnO, CuO and MgO nanocatalystat the solution natural pH = 7.

As shown the concentration 30 ppm of dye is the optimum concentration to reach efficient decolorization of dyes. At high concentrations, the dye starts acting as a filter for the incident light and it does not permit the desired light intensity to reach the semiconductor surface in a limited time domain; thus, photodecolorization percent decreases and in low concentration the reverse effect is observed, thereby increasing the number of photon absorption by the catalyst in lower concentration[21]. In these conditions, more of dye molecules will also be adsorbed on the surface of the photocatalyst and the active sites of the catalyst will be reduced.

The lifetimes of hydroxyl radicals are very short (only a few nanoseconds) and thus they can only react where they formed [22,23,24]. Thus, increase in the number of substrate ions accommodating in inter layer spacing inhibit the action of catalyst which thereby decreases the reactive $OH^{\cdot}$ and $O2^{\cdot}$ free radicals attacking the dye molecules and photodecolorization efficiency [23,24].

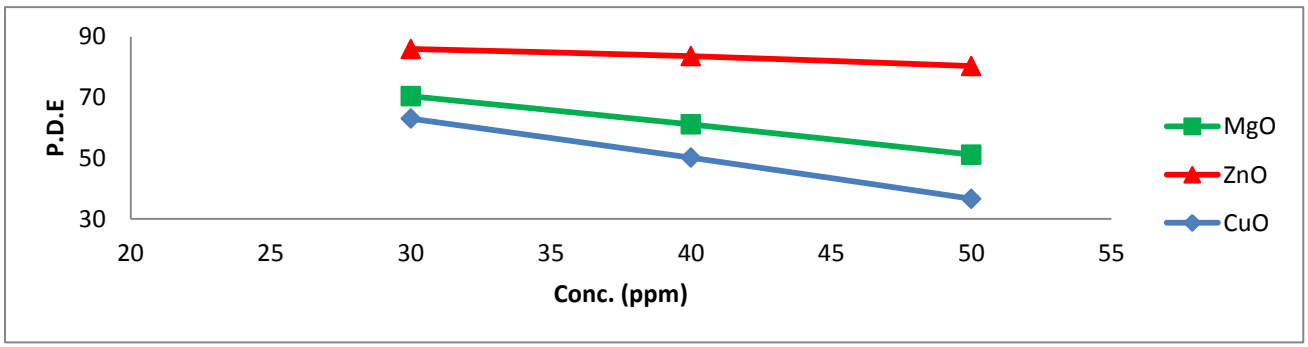

Fig. 5: Effect of initial concentration of BPB dye on photo degradation efficiency when using (ZnO dose0.06g, CuO dose0.05g and0.03g MgO after 20 min

Influence of PH

The effect of solution pH was investigated by performing the experiments at various pH covering the range from 1 to 11. The pH is one of the most important factors controlling the photocatalysis processes of pollutants especially due to its effects on the charge of the catalyst surfaces [18]. The maximum photo decolorization of Bromophenol Blue was observed at pH 3 by using ZnONPs and pH = 5 by using CuO NPs and MgO NPs (Figs.6). Changes to protonation-deprotonation characteristics of the mineral surface due to structural transformation will alter the pHpzc and therefore the equilibrium pH of the suspension. The pHpzc is a point at which the surface acidic (or basic) functional groups no longer contribute to the pH value of the solution[25,18].

The pH pzc for the used ZnO, CuO and MgO was 9.3,6.9 and 12.4 respectively[8,18,26]. The surface of the catalyst in pHs lower than

pHpzc due to the adsorption of protons has a net positive charge [2]. As mentioned above the catalysts has positive charges at pHs smaller than its pHpzc . Hence it is desirable that more anionic BPB molecules degrade at acidic pHs due to the electrostatic attractive forces between BPB molecules and positively charged catalyst surface [18].

Maximum decolorization extent for BPB in presence ZnO nanoparticles was observed at pH = 3, shows maximum attractive forces between rather positive charged surface and anionic dye molecules. But, at pH = 1 less decolorization extent was observed because in the strong acidic pHs, contamination of the solution by chloride anions (due to adding of HCl), produces OCl radicals by reacting with OH radicals which are less reactive than the OH radicals [22]. In the strong acidic pHs, protonation of BPB molecules also increases the repulsive forces between BPB molecules and positive charges present at the catalyst surface. This in turn reduces the decolorizationefficiency[18]. At pH = 11, decrease in the photodecolorization extent is due the repulsive forces between the negatively charged surface and anionic BPB molecules [2]. The highest decolorization efficiency by using CuO and MgO was observed at solution pH=5. Above pH= 5, the photocatalytic degradation of BPB rapidly decreases.

This can be explained in terms that BPB molecule has a negative charge in a wide range of pH and the point of zero charge (PZC) for CuO and MgO are a pH of 6.9 and 12.4 respectively. Below the PZC the surface of CuO NPs and MgO NPs catalyst particle is positively charged[27] and hence bromo phenol blue anions are readily adsorbed onto catalyst surface via coulombic interactions. But above pH= 5, the photo catalytic drgradation of BPB may decrease due to the decrease of positive charge at CuO and MgO photocatalyst due to the adsorbed OH^- ions at its surface and the repulsive forces between the negatively charged surface and anionic BPB molecules [18].

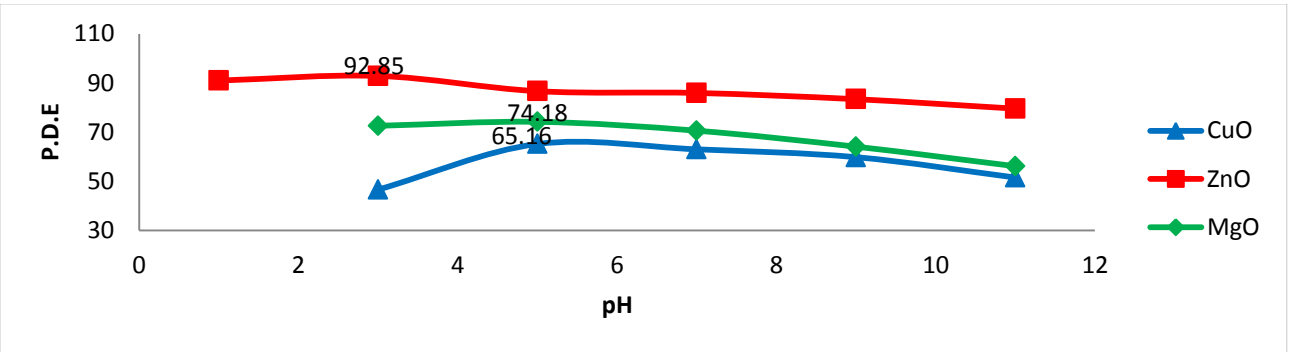

Fig.6: Effect of pH on degradation rate of BPB dye (ZnO dose0.06g, CuO dose0.05g and0.03g MgO,dye initial concentration 30ppm) after 20 min

Kinetic Study

Figure 7 show the kinetics of disappearance of BPB for an initial concentration of 30ppm under optimized conditions. The results show that the photo catalytic degradation of dye in aqueous ZnO NPs, CuO NPs and MgO NPs can be described by the first-order kinetic according to the Langmuir–Hinshelwood model[28]ln (C/C_0) =- kt, where C_0 is the initial concentration and C is the concentration at any time, t. The semi-logarithmic plots of the concentration data gave a straight line. The rate constants were calculated to be (0.1314, 0.0582 and 0.0723) min^{-1} for ZnO , CuO, and MgO NPs respectively.

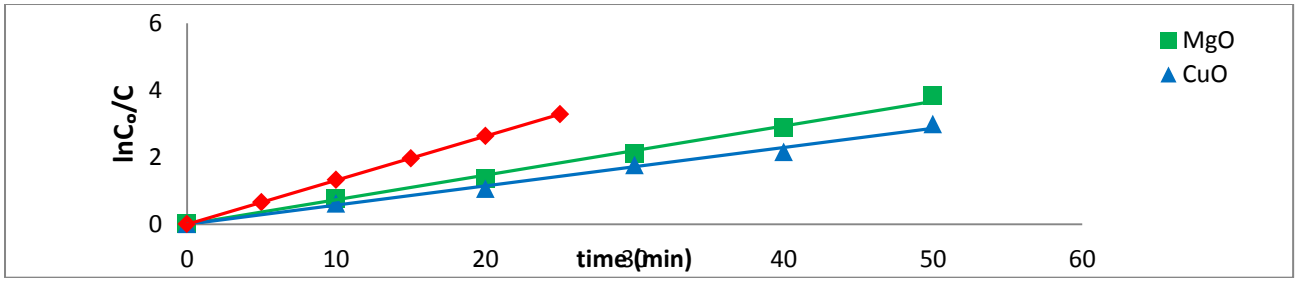

Fig.7. Kinetics analysis for BPB dye (dye initial concentration 30 ppm), (0.06g ZnONPs,pH = 3), (0.05g CuO NPs, pH =5) , and (0.03g MgO NPs, pH=5)

Effect of Temperature

The photocatalytic degradation was studied at various temperatures in the range (298–313) K and rate constant, *k*, was determined from the first-order plots. An increase in temperature helps the reaction to compete more efficiently with *e*–/*H*+ recombination[22].

The energy of activation, *E*a, was calculated from the Arrhenius plot of ln*k* vs. 1/*T* (figure 8). Arrhenius plot shows that the activation energy for photocatalytic degradation of BPB solution is equal to (29.7±1 kJ.mol^{-1}, and 18.54±1, 13.9±1) kJ mol^{-1} by using ZnO, CuO and MgO NPs respectively. The other thermodynamic parameters such as Enthalpy of activation *ΔH**, entropy of activation *ΔS**and free energy of activation *ΔG**.The positive Δ*H** refer to endothermic reaction, the positive Δ*G** obtained indicate that the reaction is non-spontaneous.

Fairly high positive Δ*H** and Δ*G** this could be because the activated state is a well solvated structure formed between the dye molecules and the reaction intermediates that is hydroxyl radicals which is also supported by negative entropy of activation. In the present case the value of *ΔS** is negative as in Tables 1, 2 and 3, so that the complex formed is more ordered than the reactants.

Initially the complex formed is unstable and degradation of the reactants into products is not very slow, but takes place rapidly under present experimental conditions. The temperature is the factor that has the smallest effect on the photocatalytic degradation of BPB solution ,*Ea*, which was found to be smaller than 40 kJ mol^{-1} .The results illustrate the decoloration of BPB dye is mainly physical interaction[29].

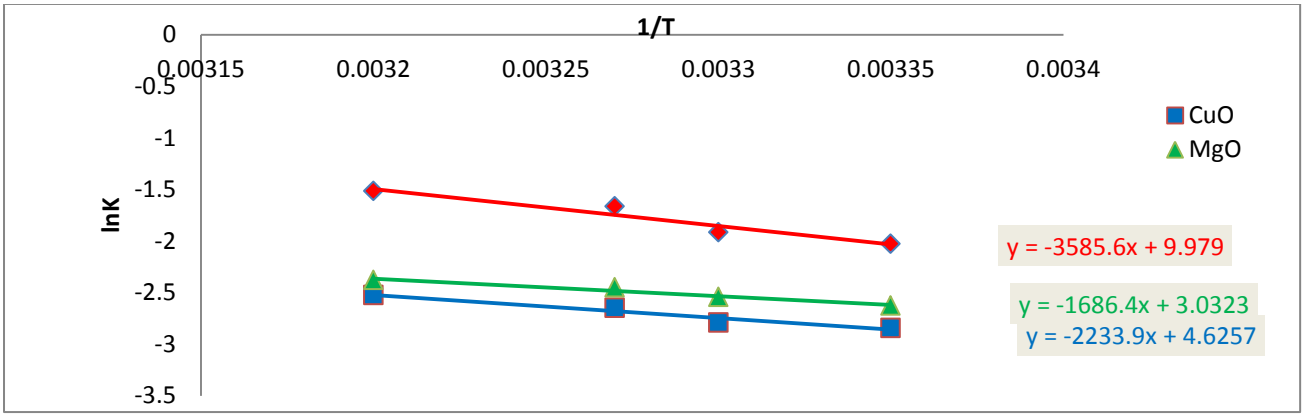

Fig. 8: Arrhenius plot for photocatalytic degradation of BPB on ZnO , CuO and MgOnanocatalysts.

Table I: values of kinetics and thermodynamic parameters for the photocatalytic degradation of BPB solution by using ZnO NPs

T(k)	K(min^{-1})	Ea(KJ mol^{-1})	ΔH(KJ mol^{-1})	ΔS(KJ mol^{-1}.K^{-1})	ΔG(KJ mol^{-1})
298	0.1314	29.76048	27.28	-0.256	105.95
303	0.1472		27.24		107.23
308	0.1889		27.22		108.54
313	0.2193		27.16		109.79

Table II: Values of kinetics and thermodynamic parameters for the photocatalytic degradation of BPB solution by using CuO

T(k)	K(min^{-1})	Ea(KJ mol^{-1})	ΔH(KJ mol^{-1})	ΔS(KJ mol^{-1}.K^{-1})	ΔG(KJ mol^{-1})
298	0.0582	18.54137	16.06	-0.264	94.73
303	0.0613		16.02		96.01
308	0.0708		15.98		97.29
313	0.0800		15.94		98.57

Table III: Values of kinetics and thermodynamic parameters for the photocatalytic degradation of BPB solution by using MgO

T(k)	K(min^{-1})	Ea(KJ mol^{-1})	ΔH(KJ mol^{-1})	ΔS(KJ mol^{-1}.K^{-1})	ΔG(KJ mol^{-1})
298	0.0723	13.99	11.52	-0.264	90.19
303	0.0785		11.48		91.47
308	0.0864		11.44		92.75
313	0.0926		11.39		94.03

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