Photochemical Degradation of an Environmental Pollutant by Pure ZnO and MgO Doped ZnO Nanocatalysts

Giahi, Masoud*[+]

Department of Chemistry, South Tehran Branch, Islamic Azad University, Tehran, I.R. IRAN

Rahbar, Ali

Department of Chemistry, Lahijan Branch, Islamic Azad University, Lahijan, I.R. IRAN

Mehdizadeh, Khorshid

Department of Chemistry, Roudsar and Amlash Branch, Islamic Azad University, Roudsar, I.R. IRAN

ABSTRACT: *MgO doped ZnO and pure ZnO nanoparticles were successfully synthesized by the sedimentary method. The products were characterized by XRD, TEM, and EDX. XRD patterns showed that the doped nanoparticles had the same crystal structures as the pure ZnO nanoparticles. Pure ZnO nanoparticles had a larger lattice volume than MgO doped ZnO nanoparticles. The photochemical degradation of indole 3- butyric acid as a pollutant in aqueous solutions was investigated by both pure and MgO doped ZnO under UV light irradiation. The effect of different parameters such as indole 3- butyric acid concentration, photocatalyst amount, PH, oxidant concentration on degradation of I-3BA, and optimum condition was obtained.*

KEYWORDS: *MgO doped ZnO; Nanoparticles; Photocatalytic degradation; Indole 3-butyric acid.*

INTRODUCTION

Zinc oxide nanopowder is a good semiconductor and it has been applied in electronics, optics, optoelectronics, photonics, lasers, acoustics and sensing [1-4]. The photocatalytic properties of ZnO nanopowder make it as good candidate for photochemical degradation of various pollutants [5-13]. This is while, zinc oxide can only absorb a small section of solar spectrum in the ultraviolet (UV) region, the result causing in the low-photocatalytic yield [14]. In the survey was showed that, zinc oxide is a promising substance for future high quantum yield light evicting / detecting devices operating in the blue and UV regions, owing to its wide and direct band gap of 3.37 ev at room temperature and a large excitation bonding energy of 60 meV. [15]. Newly, some metal ions like magnesium(II) [16], cadmium (II) [17], iron (II) [18], manganese (II), copper (II) and cobalt (II) [19] and some non-metal like nitrogen [20], nitrogen and phosphorus [21] and carbon, nitrogen, sulfur [22], was incorporated as doping ions to adjust the band gap of ZnO nanopowders cadmium (II) ions with cytotoxicity could result in serious environmental problems [16].

The characteristic of zinc oxide nanopowders strongly appertain on its crystallite size and surface morphology and dopant concentrations which in turn rely on various

* *To whom correspondence should be addressed.*
+ E-mail: m_giahi@azad.ac.ir
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preparation methods [23]. However, some various methods have been used to preparation zinc oxcide nanopowders, it still needs some simple method and new approach with low cost to preparation zinc oxide nanopowders. Various chemical or physical synthesize approaches have been applied to produce nano-sized zinc oxide nanopowders [231, 24-26]. Electrochemical method is a cost effective and versatile process for controlling the production of nanoparticle materials.

In this research, we synthesized pure zinc oxide and MgO doped zinc oxide nanopowder by "sedimentary method" and then photochemical degradation of Indole 3-butyric acid in the presence of pure and MgO doped zinc oxides nanopowder under illumination of the ultraviolet (UV) light was studied.

EXPERIMENTAL SECTION

Chemicals

Sodium hydroxide (NaOH), zinc sulfate ($ZnSO_4$), Magnesium sulfate ($MgSO_4$), cetyltrimethylammonium bromide (CTAB), Hydrogen peroxide (H_2O_2), potassium peroxodisulfate ($K_2S_2O_8$), Hydrochloric acid (HCl), Sodium chloride (NaCl). All reagents used were purchased from Merck and Fluka chemical companies and all of them were of the highest purity available and used without any further purification.

Preparation of pure Zinc oxide

Pure ZnO nanopowders were prepared using100ml NaOH 0.2 M and 100ml $ZnSO_4$ 0.1 M in deionized water by sedimentation method. For complete dissolution, NaOH solution was added slowly to zinc sulfate solution with magnetic stirring at 90°C. The obtained mixture was placed in vacuum oven for 5 h at 80 °C to receive a bright and homogeneous solution. Then this solution was slowly cooled in air down to room temperature for 24 h. The nanopowders were calcined at 400 °C in electric furnace for 2 h.

Preparation of MgO doped Zinc oxide nanopowders

MgO/ZnO nanopowders were synthesized by sedimentation method. At the first step for preparation of MgO/ZnO needed 100ml NaOH 0.2 M, 100 ml $ZnSO_4$ 0.1 M and 100 ml $MgSO_4$ 0.1 M. Then three prepared solutions were mixed with magnetic stirring, after than CTAB added to mix solutions for 3 h. The solution was filtered and then the produce precipitate was placed in vacuum oven for 5 h at 80 °C. At last, the dry precipitates were calcined at 400 °C in Electric furnace for 2 h.

Photocatalytic activities measurement

The experiments were done in a quartz cell with capacity of 50 ml into a reactor. The light source was two 18 W lamp UV-C. The experiment was performed by mixing 9 mg/L pure ZnO or Mg-doped ZnO and 3 mM of $K_2S_2O_8$, in 25 mL of the Indole 3- butyric acid solution with an initial concentration range of 10-50 mg/L. The pH was chemically controlled at 6. The mixtures were mixed by stirring at 80 rpm for 2.5 h under UV irradiation. The aqueous suspension was stirred throughout the experiment. Then, 5 mL samples were withdrawn on orderly time distance and centrifuged. Absorbance solutions were determined and returned to the reactor. The quantitative estimation of the environment pollutant was carried out using a UV –Vis spectrophotometer (Jenway, Model 6405) at λ_{max}=223 nm the degree of photochemical degradation as a function of time is given by the following equation:

$X= (C_0-C)/C_0$

Where C_0 and C are the concentration of indole 3-butyric acid at t = 0 and t time, respectively.

RESULTS AND DISCUSSION

Characterization of ZnO doped Mg

The result of XRD pattern for pure zinc oxide and MgO doped zinc oxcid are seen in Figs. 1a and b. Fig. b shows that there are not characteristic peaks of the impurities observed. However, in this research, it was showed that the peaks location and shape did not change with incorporation of Mg dopant. This is dependent to the proximity of ionic radius of magnesium ion (r = 0.57 Å) and zinc ion (r = 0.60 Å). Therefore, replacement of zinc ion by magnesium ion should not reason a significant variation in lattice constants.

By using the Debye–Scherrer equation, the crystallite sizes of pure zinc oxide and MgO doped zinc oxcid were calculated to be 20.15 and 16.45 nm [27].

Fig. 2 shows that the Transmission Electron Microscope (TEM) image of the pure zinc oxide and MgO–doped zinc oxide nanoparticles. As shown in the image, most of the particles are quasi spherical and the mean crystallite sizes are found to decrease with adding Mg from 18.8 nm

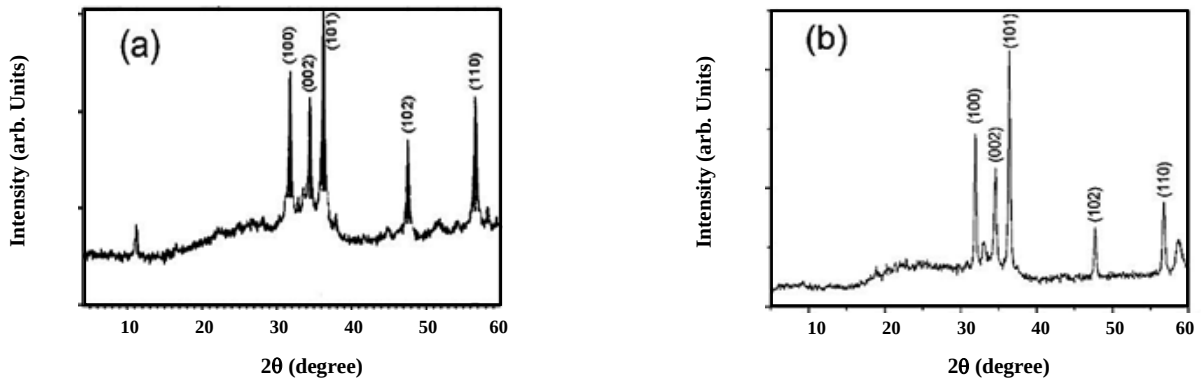

Fig. 1: XRD patterns of (a) Pure ZnO and (b) MgO doped ZnO nanoparticles.

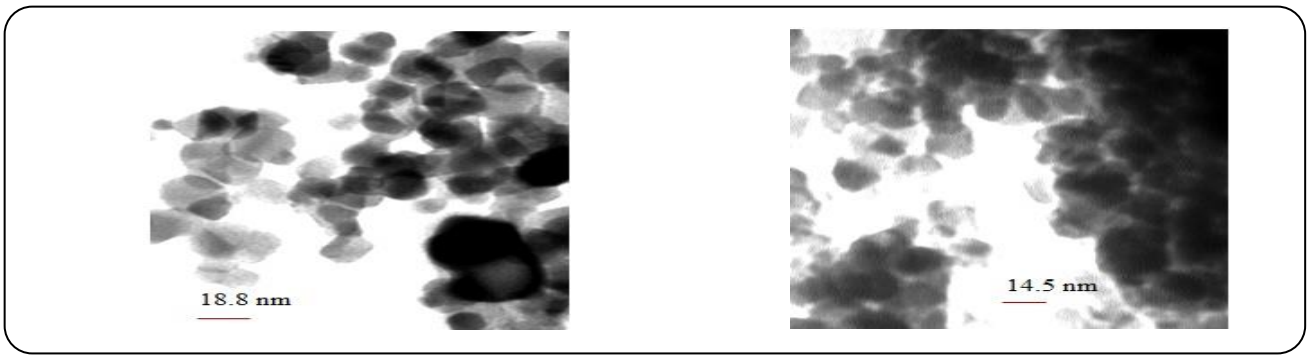

Fig. 2: TEM images for (a) Pure ZnO and (b) Mg doped ZnO nanoparticles.

for pure zinc oxide to 14.5 nm for MgO–doped zinc oxide nanoparticles. Since, TEM scans the population of the particles directly. Therefore, the difference between the particle size obtained from XRD and TEM is expected and the particle mean size is obtained by TEM more accurate than XRD method [28].

The related energy-dispersive X-ray (EDX) spectroscopy results show that the surface composition of Zn: O: Mg was 50.18: 8.29: 1.76, which implying that the doping amount of Mg was lower than that of nominal value (see Fig. 3).

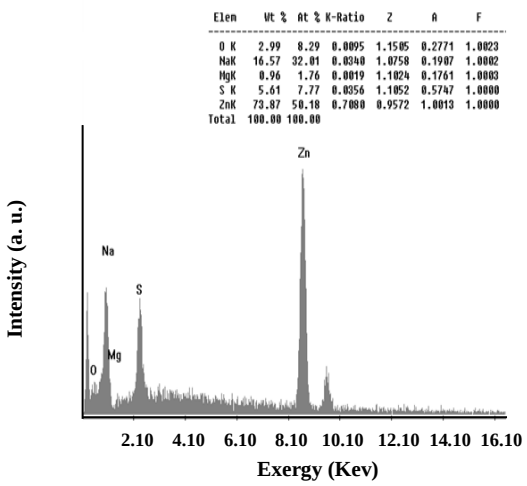

Fig. 3: Typical EDX spectrum for MgO–doped ZnO nanoparticles.

Mechanism degradation of indole 3- butyric acid by nanophotocatalysts

It was shown that the photochemical degradation of indole 3- butyric acid in solution is started by photochemical excitation of the semiconductor, followed by the formation of an electron– hole pair on the surface of MgO-doped ZnO nanophotocatalyst (Eq. (1)). The high oxidative potential of the hole (h_{VB}^{+}) in the catalyst cause direct oxidation of indole 3- butyric acid to reactive intermediates (Eq2). Highly reactive hydroxyl radicals can also be formed either by the dissociation of water (Eq3) or through reaction of the hole with hydroxide ion (OH^-) (Eq4). The hydroxyl radicals are an extremely strong,

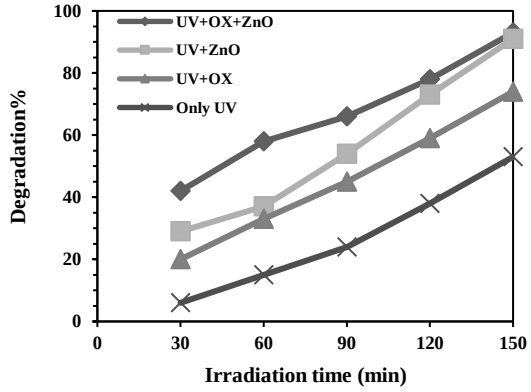

Fig. 4: Optimized degradation of indole 3- butyric acid by MgO doped ZnO nanoparticles. Conditions: Indole 3- butyric acid= 20 ppm, MgO/ZnO = 9 mg, $K_2S_2O_8$ = 3 mM, PH=6, Irradiation time = 150 min, V=25 ml.

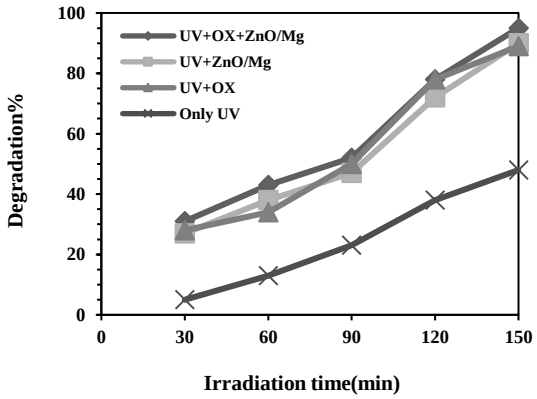

Fig. 5: Optimized degradation of indole 3- butyric acid by pure ZnO nanoparticles. Conditions: Indole 3- butyric acid= 30 ppm, Pure ZnO = 9 mg, $K_2S_2O_8$ = 1 mM, PH=6, Irradiation time = 150 min, V=25 ml.

non–selective oxidant which leads to the partial or complete mineralization of several organic chemicals [29-31].

$$MgO-doped\ ZnO + h\nu \rightarrow \quad (1)$$

$$MgO-doped\ ZnO\ (e^{-}_{CB} + h^{+}_{VB})$$

$$h^{+}_{VB} + Organic\ substance \rightarrow Organic\ substance^{\bullet+} \rightarrow \quad (2)$$

$$Oxidation\ of\ organic\ substance$$

$$h^{+}_{VB} + OH^{-} \rightarrow OH^{\bullet} \quad (3)$$

$$h^{+}_{VB} + H_2O \rightarrow H^{+} + OH^{\bullet} \quad (4)$$

Optimum condition of photochemical degradation of indole 3- butyric acid by pure and MgO-doped ZnO nanophotocatalys

In this work, we were obtained the optimum condition for degradation of indole 3- butyric acid by pure zinc oxide and MgO-doped zinc oxide in presence of UV light in aqueous solution. The experiments were carried out employing different concentrations of MgO-doped zinc oxide varying from 0.04 to 0.44 g/L, the effect of initial concentration of some environmental pollutants varying from 10 to 50 ppm and the primary concentration of oxidant such as potassium peroxydisulfate and hydrogen peroxide varying from 1 to 7 mM in pH range of 2.0- 11.0 in the presence of UV light.

The results indicate that photodegradation efficiency increases in the same condition by MgO-doped ZnO (Fig. 4) related to pure ZnO (Fig. 5).

Taguchi design

For gathering logical conclusion, some documentary clues may be needed. The method which supports these goals is called DOE (Design of Experiment) [32-33]. Six factors contain: type of nanocatalyst (2 level), concentration of pollutant, pH, amount of nanocatalyst, dosage of $K_2S_2O_8$ and irradiation time (each one is 4 level) were investigated on degradation of indole 3-butyric acid as shown in Table 1. The factors and levels were used to design an orthogonal L-32 array for experimentation as shown in Table 2.

The Taguchi analysis results are shown in Table 3. According to the analysis time and type of nanocatalyst are the most and the little effective factors, respectively. Based on the results of Table 3, it seems possible that the amount of contributing factors in the degradation process of indole 3-butyric acid included: time (h), amount of nanocatalyst, $K_2S_2O_8$ (mM), pH and type of nanocatalyst, respectively in Fig. 6.

Fig. 7 shows that there is some interaction between factors on degradation of indole 3-butyric acid. There is the least interaction between pH and time with type of nanocatalyst. Also, there is the most interaction between $K_2S_2O_8$ with amount of nanocatalyst, pH and pollutant.

Table 1: Description of experiment levels and factors in taguchi method.

Factor \ Level	1	2	3	4
Type of nanocatalyst	1	2		
Concentration of pollutant (mg/L)	20	30	40	50
pH	4	5	6	7
Amount of nanocatalyst (mg)	3	5	7	9
Dosage of $K_2S_2O_8$ (mM)	1	3	5	7
Irradiation time (min)	30	60	90	120

Table 2: Optimization of the oxidation ingredients by taguchi method.

Number	Type of nanocatalyst	Pollutant (mg/L)	pH	Nanocatalyst (mg)	$K_2S_2O_8$ (mM)	Time (min)	%Degradation
1	1	10	4	3	1	30	29
2	1	10	5	5	3	60	42
3	1	10	6	7	5	90	53
4	1	10	7	9	7	120	62
5	1	20	4	3	3	60	38
6	1	20	5	5	1	30	22
7	1	20	6	7	7	120	27
8	1	20	7	9	5	90	47
9	1	30	5	3	5	120	80
10	1	30	4	5	7	90	48
11	1	30	7	7	1	60	38
12	1	30	6	9	1	120	93
13	1	40	5	3	7	90	56
14	1	40	4	5	5	120	72
15	1	40	7	7	3	30	33
16	1	40	6	9	1	60	45
17	2	10	7	3	1	120	62
18	2	10	6	5	3	90	47
19	2	10	5	7	5	60	33
20	2	10	4	9	7	30	20
21	2	20	7	3	1	90	41
22	2	20	6	9	3	120	96
23	2	20	5	7	7	30	25
24	2	20	4	9	5	60	38
25	2	30	6	3	5	30	27
26	2	30	7	5	7	60	39
27	2	30	4	7	1	90	45
28	2	30	5	9	3	120	58
29	2	40	7	3	7	60	29
30	2	40	6	5	5	30	23
31	2	40	5	7	3	120	47
32	2	40	4	9	1	90	32

1= Pure ZnO, 2= MgO doped ZnO

Table 3: Order of variables influencing the parameters in degradation of Indole 3-butyric acid.

Level	Type of nanocatalyst	Pollutant (mg/L)	pH	Nanocatalyst (mg)	$K_2S_2O_8$ (mM)	Time (min)
1	49.06	43.50	40.25	45.25	45.22	25.57
2	41.38	41.75	45.38	41.86	51.57	37.75
3		53.50	51.38	37.63	46.63	46.13
4		42.13	43.88	54.56	38.25	66.33
Delta	7.69	11.75	11.13	16.93	13.32	40.76
Rank	6	4	5	2	3	1

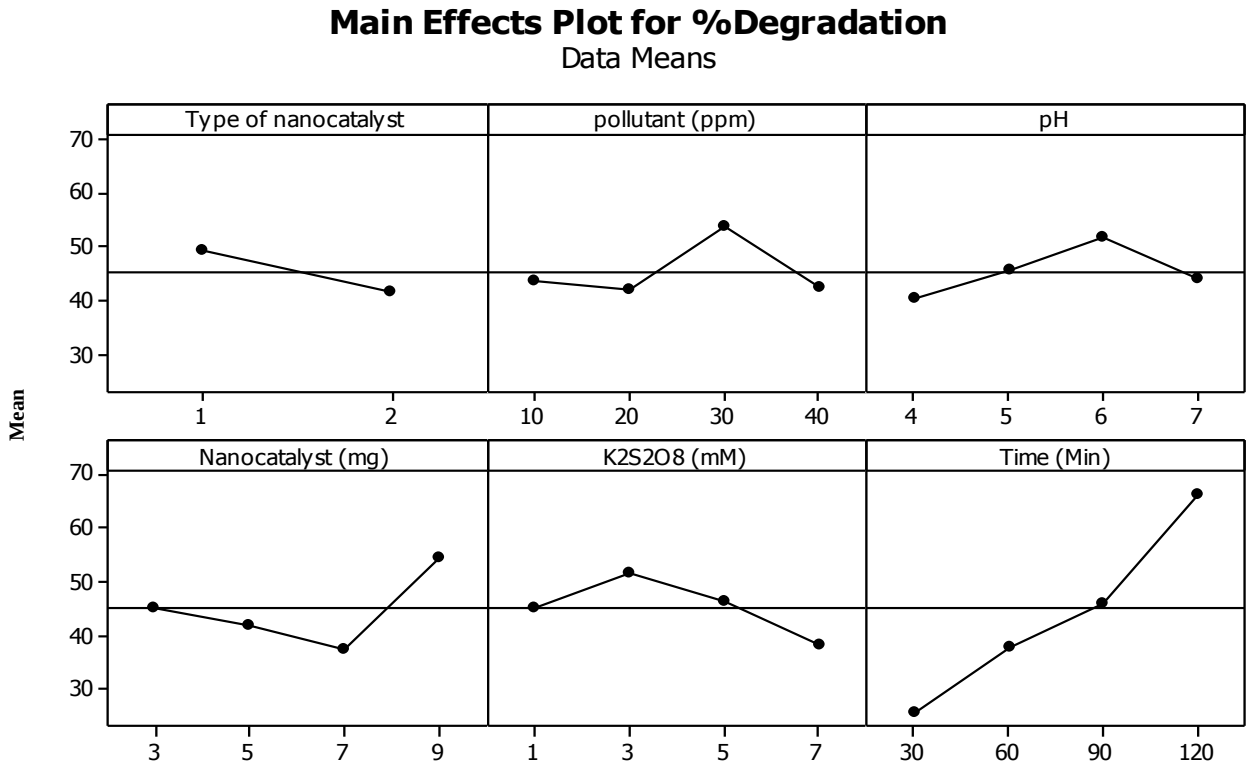

Fig. 6: Average level of factors in photodegradation of indole 3- butyric acid by pure ZnO and MgO doped ZnO nanoparticles.

CONCLUSIONS

Based on the results, MgO-doped zinc oxide nanopowders were synthesized and characterized by sedimentation modified method. The obtained samples have similar crystal structure to zinc oxide nanopowders.The present synthesized nanopowders (MgO/ZnO) good properties in photochemical degradation compared by pure zinc oxide nanopowders due to the changing of band gap. The optimum condition of degradation Indole 3-butyric acid by trial and error and Taguchi method was investigated as shown in Table 4. The result shows that there is good agreement between two methods. Finally, present work compare with other work the same area in literature [34-36].

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Table 4: The comparison of this work (by Trial-error and Taguchi method) with some other work the same area in literature.

Method	Type of Nanocatalyst	Type of pollutant	UV or Visible light	Irradiation time(min)	Degradation %	Reference
Trial-error	MgO/ZnO Pure ZnO	Indole 3-butyric acid	UV	150 150	95% 93%	This work
Taguchi	MgO/ZnO Pure ZnO	Indole 3-butyric acid	UV	120 120	96% 93%	This work
Trial-error	Nb-doped ZnO	Indigo carmine dye	UV	300	97.4	34
Trial-error	CuO-doped ZnO	Methyl orange (MO)	UV-vis	60	83	35
Trial-error	Cr, N-doped ZnO	Thymol blue(TB)	UV Visible	180 180	78.5 98.9	36

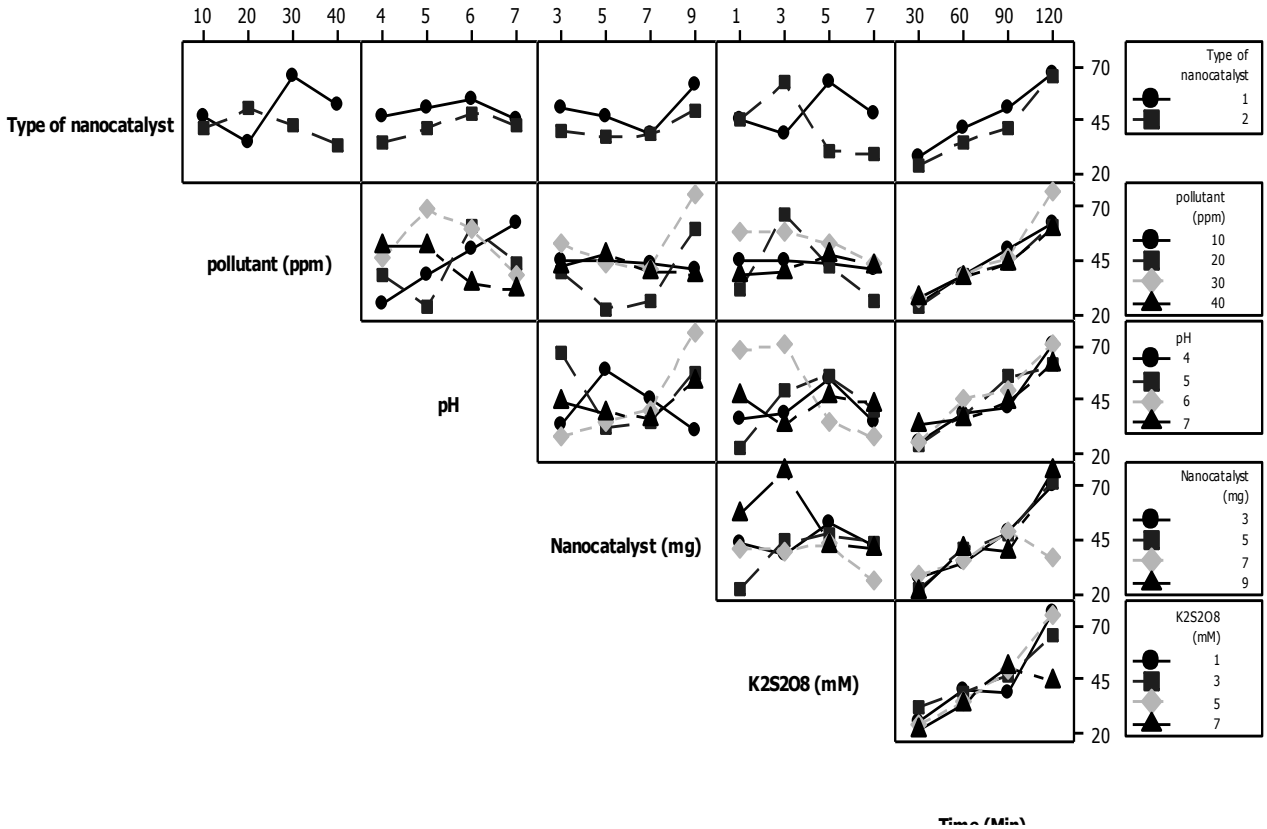

Fig. 7: The effect of interaction factors in photodegradation of indole 3- butyric acid by pure ZnO and MgO doped ZnO nanoparticles.

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