Catalytic Photodegradation of Methyl orange using MgO nanoparticles prepared by molten salt method

Shahbaa F. Bdewi[*], Ayad M. Abdulrazaka[*] and Bakhtyar K. Aziz[**]
[*] *Chemistry dept., College of Science, University of Al-Anbar*
[**] *Clay and Environmental Chemistry Research Group, Chemistry dept., School of Science, Faculty of Science and Science Education, University of Sulamani*
[**]*bakhtyar.kamal@univsul.edu.iq*

Abstract— **MgO nanoparticles were prepared by molten salt method. The structure, particle size and surface morphology of MgO nanoparticles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM).**
The photocatalytic efficiency of the prepared MgO nanoparticles was evaluated by photocatalytic degradation of Methyl Orange in aqueous solution as a model pollutant under UV light irradiation. The particle sizes were ranging between 24 to 42 nm with an average particle size of 33.3 nm. The product exhibited good photocatalytic activity under UV irradiation. The influence of the operating parameters shows that 0.5 g.L-1 catalyst dose at an initial solution pH close to 7 are optimum conditions. The kinetics of the photodegradation of Methyl Orange was found to follow first order kinetics.

***Index Terms*—Cubic MgO, hexagonal $Mg(OH)_2$, nanoparticle, photodegradation.**

I. INTRODUCTION

Affairs associated with hazardous wastes and toxic water-pollutants are the major concern of environmental studies due to increasing demand on fresh water globally[1]. Rising of industrial activity awareness in the past several decades have focused on numerous damage on many ecosystems and the results shows threats on the human health and environment[2]. Dyeing and finishing industries are the major generators of waste water effluent. Fifteen percent of the total world production of dyes is lost during the dyeing process and is released in textile effluent[3]. The presence of dyes in natural streams can cause serious harm to aquatic life by increasing toxicity, chemical oxygen demand, and as well hindering photosynthetic phenomena through reduction of light penetration[4].

In attempts to de-contaminate dye effluents, several methods have been studied[5]. Some methods are in-effective, because dyes are generally stable and difficult to biodegrade due to their synthetic and complex aromatic structure[6] on one hand, and on the other hand, some other methods, e.g. adsorption on activated carbon, flocculation and electrocoagulation are not efficient methods because they generate solid wastes[7]. Another issue is that some destructive methods are cost-effective like advanced oxidation process[8]. Till now, photocatalytic process is been the most effective method for treatment of dye polluted waste water and titania has been the most efficient catalyst in solid-liquid systems[9] maybe due to its cheapness, good accessibility of treatment reagent and the simplicity in operating conditions and techniques[10]. Commercial titania has some disadvantages like low surface area and mixture of crystalline structures which may limit its use. Our objective was to explore another metal oxide as a photocatalyst, and we have selected methyl orange as a model in photocatalytic degradation experiments.

II. MATERIALS AND METHODS

All chemicals used in this research were of analytical reagent grade and were used without further purification. Methyl Orange ($C_{14}H_{14}N_3NaO_3S$) was obtained from Merck. Methyl orange solutions were prepared by dissolving requisite quantity of the dye without further purification in distilled water. The pH was adjusted to a given value in the range 3-10 by addition of HNO_3 (1N) or NaOH (1N). The pH was measured using a Schott titroline (TE96) pH meter. The aqueous solution concentrations of dye were determined using a Jenway 6405 UV/Visible spectrophotometer. The wavelength of maximum absorption was 485 nm. The determined absorption was converted to a concentration through the standard-curve method.

A. Synthesis of MgO nanoparticles

25 g bulk MgO was mixed with 100 g of NaCl powder in an agate mortar, the mixture was grounded for 15 min by motor. The mixture was heated in muffle furnace at 800ºC (melting point of NaCl) for 4h in air and then cooled gradually to room temperature. The product was washed several times with distilled water, filtered and then dried at 120 ºC 11.

B. XRD analysis

X-ray diffraction (XRD) analysis of the prepared nano-MgO was carried out on a ICDD Grant Germany instrument operating at 40 kV with a current of 30 mA using CuKα1 radiation (λ=1.5418 Å) in the range of 20.0-80.0º in steps of 0.05 (deg).

C. Morphology analysis

The morphology and particle size of the nanoparticles was analysed using VEGA3 TESCAN model (Scanning Electron Microscopy). The instrument was accelerated with a voltage of 30kV.

D. Photocatalytic reactor

A cylindrical opened top polyethylene batch reactor was used in the photocatalytic degradation experiments. The cell was 14 cm in diameter with a total height of 7 cm.
The cell was mounted on a heating magnetic stirrer inside the UV light cabinet (Chromato-Vue Cabinet , model C-75) (with UV sources of 365nm and 254 nm and a white source) (0.9 amp) placed in axial position inside the water jacket.

E. Catalytic Photodegradation

For all photocatalytic studies, the reactor was initially loaded with 200ml of 20mg.L^{-1} of MO aqueous solution (except for initial dye concentration study) and 0.1 g of photocatalyst (except in photocatalyst dose study) was introduced to the reactor and magnetically stirred under dark for 30 minutes to attain adsorption-desorption equilibrium between the adsorbent (nano-MgO) and the adorbate (MO solution). Irradiation under UV or visible light was done up to 100 minutes. 5 ml of the reaction mixture was collected at different time intervals, centrifuged at 3000 rpm for 10 minutes to separate the solution from catalyst and its absorbance at 490 nm was recorded using a UV-Visible spectrophotometer.

III. RESULTS AND DISCUSSION

A. Characterization of MgO nanoparticles

XRD analysis

The particle size and structural properties of the synthesized MgO nanoparticle was determined using powder XRD (Fig. 1).

The diffraction signals can be indexed to cubic MgO and hexagonal $Mg(OH)_2$ crystallites which are in good agreement with standard JCPDS card 78-430 and 07-0239 respectively[12,13]. This means that the prepared sample is a mixture of cubic MgO and hexagonal $Mg(OH)_2$ nanoparticles, this is plausibly due to the hydration of MgO in the washing step with distilled water to remove NaCl. Similar results were obtained by Mageshwari and Sathyamoorthy in the preparation of MgO nanoflakes by wet precipitation method[12].

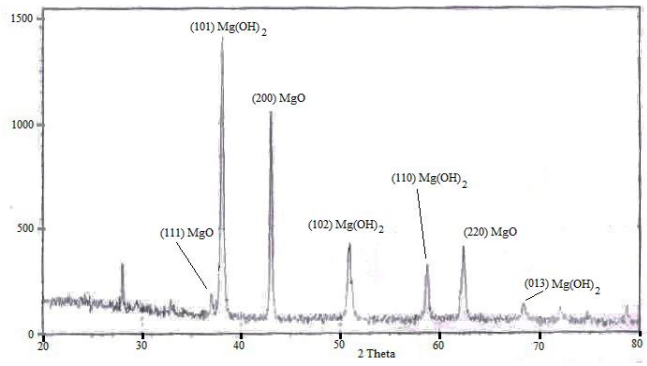

Fig. 1 X-ray diffraction pattern obtained for the MgO nanoparticles

The average crystallite size of the nanomaterial was calculated from the main diffraction peaks (table 1) using the Debye-Scherrer equation, as in (1)[12,14].

$$D = \frac{K\lambda}{\beta \cos\theta} \qquad (1)$$

where β is full width at half maximum height (FWHM) of the diffraction peak at an angle θ (in Radians), λ is wavelength in (nm) of the XRD, and Kis a dimensionless shape factor, with a value close to unity, normally taken as 0.9. The average particle size of the nanomaterial sample is presented in table 1.

TABLE I
XRD DATA FOR PARTICLE SIZE MEASUREMENT

Max. 2θ	Intensity	FWHM	Particle size (nm)	Crystal shape
37.02°	37	0.1965	42,17	Cubic MgO
38.09°	561	0.2831	29.36	Hexagonal $Mg(OH)_2$
43.02°	407	0.2351	35.93	Cubic MgO
50.90°	150	0.3637	23.93	Hexagonal $Mg(OH)_2$
58.72°	123	0.2654	33.97	Cubic MgO
62.39°	161	0.2647	34.70	Hexagonal $Mg(OH)_2$

The average particle size was found to be 33.34 nm.

SEM analysis

Fig. 2 shows the SEM photograph illustrating the surface morphology of the prepared MgO nanoparticles. The image shows agglomerated hexagonal thick plated shapes of MgO nanoparticle with smaller size cubic MgO. The particle size of nano MgO was found between 60 to 160 nm.

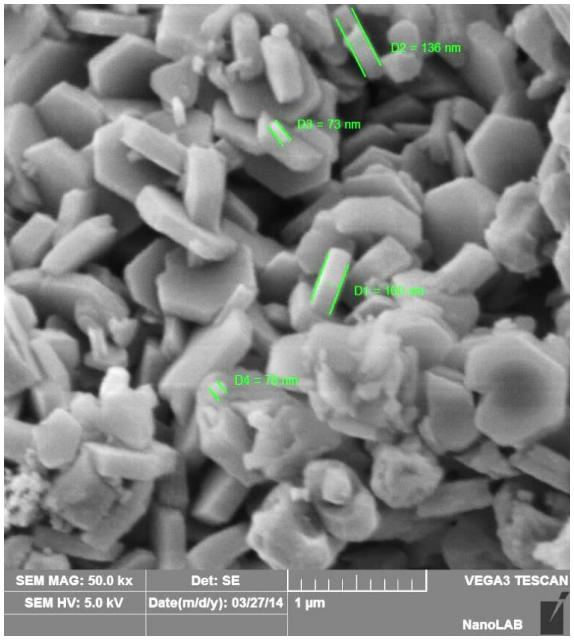

Fig. 2. SEM image of the prepared MgO nanoparticle

B. Catalytic Photodegradation studies

The band gap energy of MgO is 7.8 eV [15] normally, but for MgO nanoparticles this value is deceased to 4.2 eV [16] which make it possible to use in photocatalysis. To bring the research applicable to environment, it is necessary to find out the rate equation that fits the experimental data. Returning to literature, the catalytic photodegradation process is best described by Langmuir–Hinshelwood since adsorption is an important initial step in the heterogeneous photocatalytic degradation [17] which is expressed by equation no. 2:

$$\frac{-dC}{dt} = \frac{kKC}{(1+KC)} \qquad (2)$$

where k is the reaction rate constant (mg L^{-1} min^{-1}); *K* is the adsorption coefficient of the reactant (L mg^{-1}); and *C* is the reactant concentration (mg L^{-1}).

At very low concentrations, *C* is very small, and the Langmuir–Hinshelwood would be simplified to an apparent (observed) pseudo-first-order kinetics, as in (3):

$$\frac{-dC}{dt} = k_{obs}C \qquad (3)$$

where $k_{obs} = kK$

The linear form of this equation is given by (4):

$$\ln\left(\frac{C_o}{C_i}\right) = k_{obs}\,.\,t \qquad (4)$$

The obtained results of the effects of operational conditions were linearly fitted to the pseudo-first order kinetics by plotting $\ln\left(\frac{C_o}{C_i}\right)$ and irradiation time *t*.

1) Effect irradiation energy

The variation of both pseudo first-order rate constant and percentage of catalytic photodegradation is shown in fig. 3.

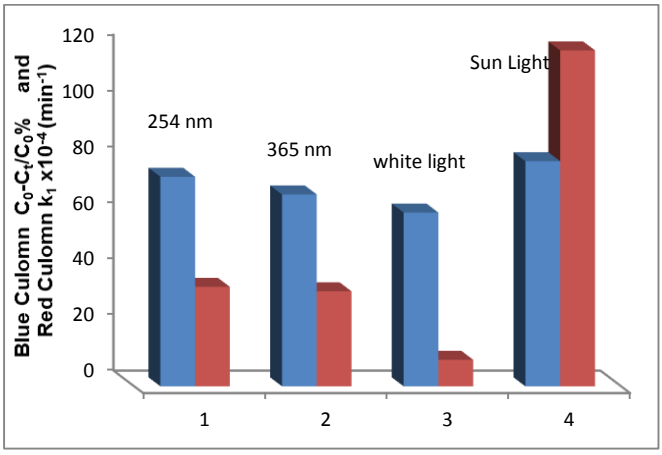

Fig. 3 Effect of irradiation energy on photodegradation rate (k_1) and efficiency.

The figure shows that both rate and efficiency of catalytic photodegradation are decreasing with the decrease in the photon energy of the irradiation, and both have highest values with sun light irradiation. This may be due to the high light intensity of sun light and wide range of photons of high energies.

The remainder studies were performed under 365nm UV irradiation source because it is close to visible light in photon energy and there was no significant difference between 245nm and 365 nm UV irradiation in the results.

2) Effect of the initial pH

Effect of the initial pH of the reaction mixture on the photodegradation efficiency as a function of time using MO (20 mg/L) is presented in Fig. 4. The highest efficiency was observed near neutral pH. In addition to this, the rate constant was also maximum near neutral pH (Fig. 5). Above pH= 7, the photocatalytic degradation of MO rapidly decreases. This can be explained in terms that MO molecules has a negative charge in a wide range of pH [18] and the point of zero charge (PZC) for MgO is a pH of 12.4 [19]. Below the PZC the surface of MgO catalyst particle is positively charged and hence methyl orange anions are readily adsorbed onto catalyst surface via coulombic interactions. But above pH= 7, the photocatalytic drgradation of MO may decrease due to the decrease of positive charge at MgO photocatalyst due to the adsorbed OH- ions at its surface.

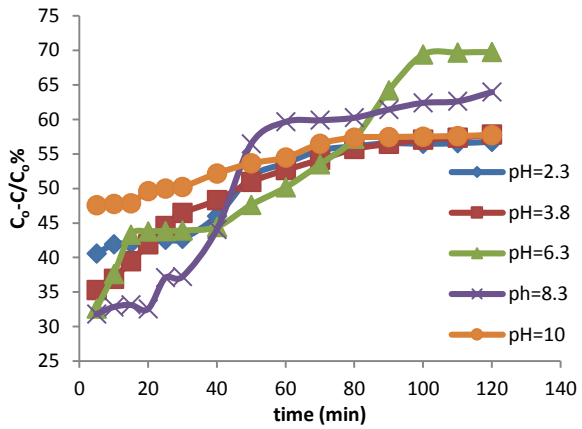

Fig. 4 Effect of pH on the photodegradation efficiency of methyl orange at different irradiation times

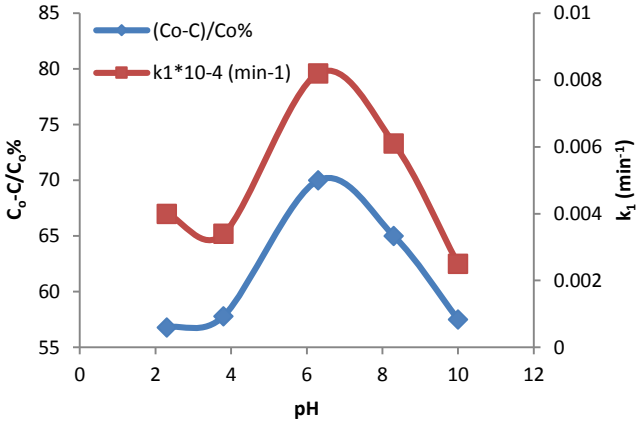

Fig. 5 Effect of pH on the rate constant and photodegradation efficiency of methyl orange

3) *Effect of Catalyst Loading*

The photocatalyst dose (MgO nanoparticles) was an important parameter of MO degradation under UV irradiation to study. The doses of MgO-NPs photocatalyst were ranging between 0.05g to 0.3g (Fig. 6).

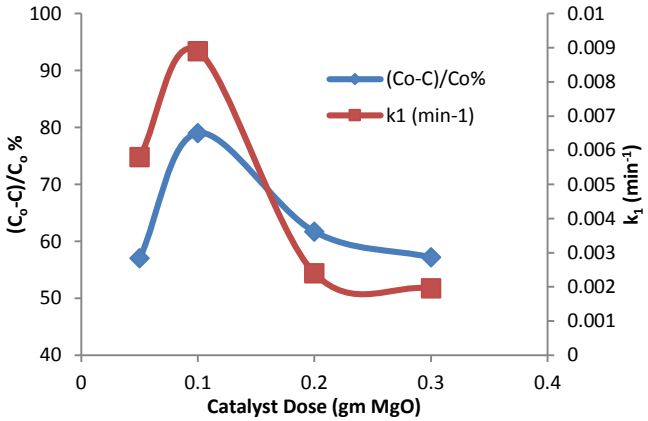

Fig. 6 Effect of catalyst concentration on photodegradation efficiency of methyl orange

A marked increase in the degradation percentage and the rate of photodegradation of MO was obtained with the increase in catalyst dose from 0.05 g to 0.1 g, after which the degradation rate and percentage of MO was decreased with increasing the MgO-nanoparticles dosage.

Generally, the number of active sites increases as the amount of the photocatalyst increased. This leads to the raise in the number of photons absorbed and dye molecules degraded. However, with photocatalyst dosages above 0.1 g, both rate constant and degradation percentage were decreased due to the blocking of light penetration by the excessive amount of photocatalyst [9,12,19]. Practically, the optimum dosage of nano-MgO was 0.1 g for 200 ml of 20 mg L^{-1} of MO solution.

4) *Effect of initial MO concentration on kinetics*

The initial MO concentration effect on decolorization efficiency and rate is important from an application point of view [20]. The effect of the initial MO concentration on the photocatalytic degradation in the presence of 0.1 g/200ml nano-MgO is shown in Fig. 7.

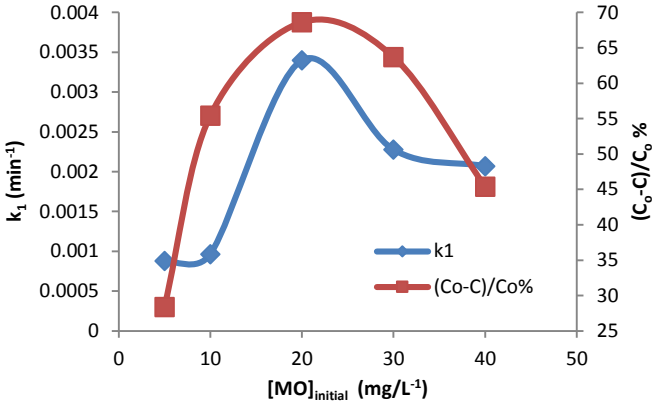

Fig. 7 Effect of MO initial concentration on rate constant and efficiency of photodegaradation of MO

In very low MO concentration range, both the rate and the degradation percentage increased with increasing initial MO concentration up to 20 mg. L^{-1}. This increase maybe due to the higher collision frequency and probability for the incoming photons with the dye molecules at the active sites on the surface of the catalyst at higher dye concentrations to a certain extent [21]. After the critical concentration, both pseudo first order rate and degradation extent decreased markedly with the increase in the initial dye concentration after 20 mg L^{-1}. There are two reasons for this decrease: firstly, when the initial concentration of methyl orange increase, the path length of the photons entering the solution decrease [10], secondly, as the initial concentration of reactants increases the molecules aggregate on the surface of the catalyst. This results in quenching of the excited molecules [22].

IV. Conclusion

MgO nanoparticles prepared by molten salt procedure was used to perform photocatalytic decolorization of MO under near UV irradiation. Results of the XRD and SEM analyses indicated that MgO nanoparticles were of a mixture of cubic and hexagonal plates. The photodegradation of MO catalyzed by MgO was significantly influenced by operational

conditions, irradiation energy, initial dye concentration, catalyst dosage, and initial solution pH. For a 200 ml of 20 $mg.L^{-1}$ MO solution at natural pH and 0.1 g photocatalyst dosage, more than 70% photodegradation was achieved after 1 h of irradiation by 365 nm UV light source and 80% under solar light. Using 365 nm UV source and the same previous conditions with TiO2 (bulk) resulted in a 41% degradation.
The obtained results show that MgO nanoparticles can be used instead of traditional photocatalyst like TiO_2 specially under solar radiation.

REFERENCES

[1] Bakhtyar K. A., Removal of textile dyes from waste water of Kiffry textile factory using natural clay of the area, 2013, *International Journal of Chemical and Environmental Engineering*, Vol. 4, No.3, 164-167.

[2] Mi-Hwa B., Christianah O. I., Se-Jin O., Dong-Su K., Removal of Malachite Green from aqueous solution using degreased coffee bean, *Journal of Hazardous Materials*, 2010, 176, 820–828

[3] Rais A., Rajeev K., Adsorption studies of hazardous malachite green onto treated ginger waste, *Journal of Environmental Management*, 2010, 91, 1032–1038.

[4] Sung W. W., Guiping W., Hui M., Qiong L., Yao Y., Longzhe C., Chengfu L., Yeoung-Sang Y., Adsorption performance and mechanism in binding of Reactive Red 4 by coke waste, *Journal of Hazardous Materials*, 2006, B138, 370–377.

[5] Ahsan H., Iqbal M. I., Abu Jafar M., Rafique U., Photocatalytic decolorization of Brilliant Golden Yellow in TiO_2 and ZnO suspensions, 2012, *Journal of Saudi Chemical Society*, 16, 423–429.

[6] Kandaswamy S. B., SriKrishna P. T., Fixed-bed column studies on biosorption of crystal violet from aqueous solution by Citrullus lanatus rind and Cyperus rotundus, *Appl Water Sci*. 2013.

[7] Barka1 N., Assabbane A., Nounah A., Dussaud J., Ait I. Y., Photocatalytic degradation of Methyl Orange with immobilized TiO_2 nanoparticles: effect pf pH and some inorganic anions, *Phys. Chem. News* 2008, 4, 85-88.

[8] Alemseged E., Yadav O. P., Bachheti R. K., Photocatalytic Degradation of Methyl Orange Dye using Cr-doped ZnS Nanoparticles under Visible Radiation, *International Journal of ChemTech Research*, 2013, Vol.5, No.4, pp 1452-1461.

[9] Alvarez M., Lo´pez T., Odriozola J. A., Centeno M. A., Domı´nguez M.I., Montes M., Quintana P., Aguilar D. H., Gonza´lez R. D., 2,4-Dichlorophenoxyacetic acid (2,4-D) photodegradation using an Mn^{+}/ZrO_2 photocatalyst: XPS, UV–vis, XRD characterization, *Applied Catalysis B: Environmental*, 2007, 73, 34–41.

[10] Xuesen B., Jianqiu C., Rong J., Degradation of 2,4-Dichlorophenoxyacetic Acid (2,4-D) by Novel Photocatalytic Material of Tourmaline-Coated TiO_2 Nanoparticles: *Kinetic Study and Model*, *Materials* 2013, *6*, 1530-1542.

[11] Arendt R. H., Rosolowski J. H., Szymaszek J. W., Lead Zirconate Tianate Ceramics form Molten Salt Solvent synthesized Powders . *Materials Researcher*, 1979.

[12] Mageshwari K., Sathyamoorthy R., Preparation and characterization of MgO nanoflakes by wet precipitation method, *Proceedings of National Conference on Developing Scenario in Applied Sciences and Communicative English*, 2012, p. 56-58.

[13] Dhal J. P., Sethi M., Mishra B. G., Hota G., MgO nanomaterials with different morphologies and their sorption capacity for removal of toxic dyes, *Materials Letters* 141 (2015) 267–271.

[14] Tamilselvi P., Yelilarasi A., Hema M., Anbarasan R., Synthesis of hierarchical structured MgO by sol-gel method, *Nano Bulletin*, 2013, Vol. 2, No.1.

[15] Taurian O. E., Springborg M., Christensen N. E., Self-consistent electronic structures of MgO and SrO, *Solid State Communications*, 1985, Vol. 55, No. 4, 351-355.

[16] Nemade K. R., Waghuley S. A., Synthesis of MgO Nanoparticles by Solvent Mixed Spray Pyrolysis Technique for Optical Investigation, *International Journal of Metals*, Volume 2014, Article ID 389416, 4 pages.

[17] Huayue Z., Ru J.,Yongqian F., Yujiang G., Jun Y., Ling X., Guangming Z., Effective photocatalytic decolorization of methyl orange utilizing TiO_2/ZnO/chitosan nanocomposite films under simulated solar irradiation, *Desalination* 2012, 286, 41–48.

[18] Changchun C., Jiangfeng L., Ping L., Benhai Y., Investigation of Photocatalytic Degradation of Methyl Orange by Using Nano-Sized ZnO Catalysts, *Advances in Chemical Engineering and Science*, 2011, 1, 9-14.

[19] Roy M. H., Stephen J. D., Introductory Chemistry for the Environmental Sciences, *Cambridge University Press*, *June*, 1996, p-139.

[20] Daneshvar D., Rasoulifard M. H., Khataee A. R., Hosseinzadeh F., Removal of C.I. Acid Orange 7 from aqueous solution by UV irradiation in the presence of ZnO nanopowder, *Journal of Hazardous materials*, 2007, 143(1-2):95-101 ·

[21] Wai S, ChiWai K, Yuen C. W., Shun-Wan C., Kim H. L., Effective Photodegradation of Methyl Orange Using Fluidized Bed Reactor Loaded with Cross-Linked Chitosan Embedded Nano-CdS Photocatalyst, *International Journal of Chemical Engineering*, 2014, p. 1-16.

[22] Seth A., Stanley M., Gift M., Ochieng A., Solar Photodegradation of Methyl Orange and Phenol Using Silica Supported ZnO Catalyst, *International Journal of Innovation, Management and Technology*, 2014, Vol. 5, No. 3.

Bakhtyar K. Aziz, is an assistant professor at chemistry department of University of Sulaimani. He has received M.Sc. degree in Physical Chemistry (Kinetics and mechanism of inorganic complexation) from University of Sulaimani (2002); and PhD degree in Physical Chemistry- (Clay chemistry and applications) from University of Sulaimani (2009), Sulaimani city, Kurdistan region, Iraq. He leads a research group (Clay and Environmental Chemistry research group).
He is the head of chemistry department since April 2015