

Photocatalytic degradation of paracetamol and procaine

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Abstract : The current study is designed to treat the solutions of paracetamol and procaine by using UV light with using of ZnO as catalyst. This study explained the importance of the UV light and catalyst as a basic factors in the photocatalytic degradation for both paracetamol and procaine. An attempt has been done to study the effect of process parameters through amount of catalyst, concentration of drugs, pH of drug solution and temperature on photocatalytic degradation of drugs solution.

The experiments were carried out by varying pH equal to 2-12, amount of catalyst from 0.01 to 1g, initial concentration of drugs from 5 to 40 µg/ml and temperature range from 15 to 55°C. The optimum catalyst dose was found to be equal to 0.025 g and 0.1 g are considered the optimum weights of paracetamol and procaine respectively. In the case of ZnO maximum rate of photoreaction of drugs solution was observed in the increase of pH of reaction solution for both drugs have a positive effect represented by increasing the degradation rate until the pH 8 and 4 are the best acidic function of the paracetamol and procaine respectively.

Photocatalytic degradation was found to increase with increasing temperature. Arrhenius plot shows that the activation energy is equal to 8.95 KJ. mol⁻¹ for paracetamol and 15.67 KJ. mol⁻¹ for procaine. The thermodynamic parameters of the photodegradation of drugs, like energy of activation, enthalpy of activation, entropy of activation and free energy of activation revealed the efficiency of the process.

Keywords : Decolorization; paracetamol and procaine; Photocatalysis.

Introduction

In recent decades, very severe regulations have forced researchers to develop and evolve novel technologies to accomplish higher mineralization rate with lower amount of detectable contaminants. Different physical, chemical, and biological treatment processes have been employed to treat various municipal and industrial wastewaters such as chemical¹⁻², biological, food³, pharmaceutical⁴⁻⁵, pulp and paper⁶, dye processing and textile⁷⁻¹⁰, and landfill leachate¹¹ effluents.

Pharmaceutical manufacturers use water for process operations, as well as for other non-process purposes. The water may be formed as part of a chemical reaction. Process water includes any water that, during manufacturing or processing, comes into direct contact with or results from the use of any raw material or production of an intermediate, finished product, byproduct, or waste. Process wastewater includes water that was used or formed during the reaction, water used to clean process equipment and floors, and pump seal water. Non-process wastewater includes noncontact cooling water (e.g., used in heat exchangers), noncontact ancillary water (e.g., boiler blow down, bottle washing), sanitary wastewater, and wastewater from other sources (e.g., storm water runoff).

Advanced oxidation processes involve the production of highly reactive radicals such as hydroxyl radicals which have the ability to oxidize almost all complex organic molecules into smaller molecules. Complete mineralization of the compounds into CO_2 , water and inorganic structures such SO_4^{2-} , NO_3^- and N_2 is possible. These treatment processes are considered as very promising methods for the remediation of contaminated ground, surface, and wastewaters containing non-biodegradable organic pollutants. Hydroxyl radicals are extraordinarily reactive and non-selective and for this reason it reacts with all surrounding chemicals, organic pollutants and inhibitors as well.

That attacks most of the organic molecules. AOPs involve the two stages of oxidation, the formation of strong oxidants (e.g., hydroxyl radicals) and reaction of these oxidants with organic contaminants in water. The application of homogeneous photodegradation (single-phase system) to treat contaminated waters, concerns the use of UV/ozone and UV/ H_2O_2 . The use of UV light for photodegradation of pollutants can be classified into two principal areas.

- Direct photo degradation, which proceeds following direct excitation of the pollutant by UV light
- Photo-oxidation, where light drives oxidation processes principally initiated by hydroxyl radicals.

The latter process involves the use of an oxidant to generate radicals, which attack the organic pollutants to initiate oxidation. Three major oxidants used are: hydrogen peroxide, ozone and photo-Fenton system ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$)¹²

Heterogeneous photocatalysis can be carried out in various media: gas phase, pure organic phase or aqueous solutions. The overall process is controlled by several steps: mass transfer of reactants to catalyst surface, adsorption of the reactants, light absorption creating electrons (e^-) and holes (h^+), transport of photo generated charges to the adsorption sites, reaction of the adsorbed species, desorption of products and removal of the products from the catalyst surface¹³

Photocatalysis: The process is heterogeneous because there are two active phases, solid and liquid. The word photocatalysis is composed of two part, the prefix photo, defined as "light", and Catalysis is the process where a substance participates in modifying the rate of a chemical transformation of the reactants without being altered in the end. This substance is known as the catalyst which increases the rate of a reaction by reducing the activation energy. The mechanism lies in the production of OH free radical by induction of electron transformation using UV illumination. Although its mechanism is similar to that of $\text{H}_2\text{O}_2/\text{UV}$, O_3/UV , etc, TiO_2 is preferred over other due to its stability under various conditions, its high potential to produce radicals and its easy availability and low price¹²

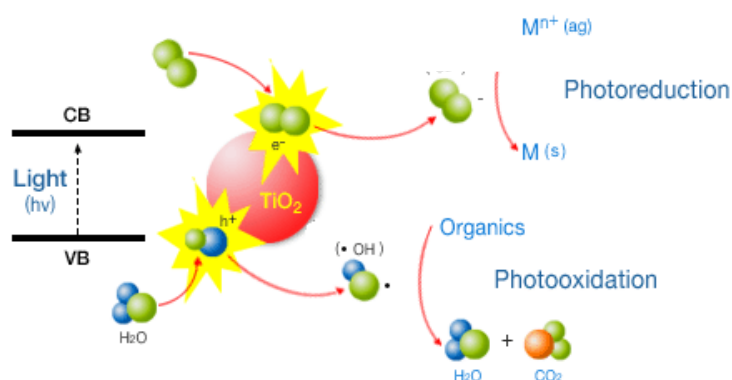


Figure (1) : Mechanism of radical formation reactions during photocatalytic process as a results of photocatalyst excitation with light⁽¹⁴⁾

Semiconductor can be defined as materials that have an electrical conductivity which position between conductor and insulator. The classification of semiconductor depends on their electrical conductivities that increase with temperature increases. About three materials are designed which depend on their electrical

conductivities. Principally, conductors involve a low resistance of electrical flowing; others associate with a moderate resistance to electrical flow as semiconductors and insulators that characterize by a significant resistance to electrical pass¹⁵.

There are two kinds of semiconductors which are classified into intrinsic and extrinsic. The existence of negative electrons in a conduction band and a positive hole in valence band are equal function a role in intrinsic semiconductor which is considers a pure semiconductor having no impurities. While an induction of impurities into semiconductor has associated with a change in the numbers and types of free charge carriers that clearly explain in extrinsic semiconductor. Which are classified into two categories including, n-type and p-type semiconductors⁽¹⁶⁾ (as shown in figure 2). Electrons represent a carries of charge in n-type semiconductor while holes are charge carriers in p-type semiconductor.¹⁷

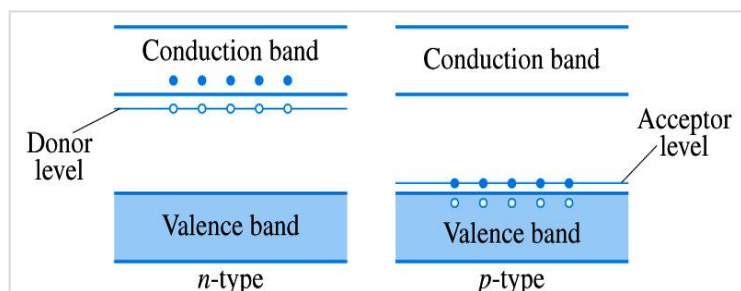


Figure (2): Energy level diagram for n-type and p-type semiconductor.

Recently, the definition of semiconductor is much more related to the energy gap through the free carrier concentration at room temperature. As shown in Table 1, metals and semimetals have a rather largest carrier density; semiconductors exhibit a moderate carrier density while insulators have a negligible carrier density at room temperature. However, the real semiconductors always contain some impurities, which can act as dopants leading to larger values of the carrier density¹⁸.

Table(1): The classification of solids according to their energy gap, carrier density and typical conductivity at room temperature⁽¹⁹⁾.

Type of solid	E_g (eV)	n (cm ⁻³)	Conductivity, σ (cm ⁻¹)	Example
Metal	No energy gap	10^{22}	$10^5 - 10^{10}$	Au, Cu, Pb
Semimetal	$E_g \leq 0$	$10^{17} - 10^{21}$	$10^2 - 10^5$	Graphite, HgTe
Semiconductor	$0 < E_g < 4$	$< 10^{17}$	$10^{-9} - 10^2$	Si, Ge, GaAs
Insulator	$E_g \geq 4$	$< < 1$	$< 10^{-9}$	Quartz, CaF ₂

The wavelength of incident light has an important role in movement the electrons between valence and conduction bands, as an example ultraviolet considers the suitable energy that is necessary to occur the photocatalyst in ZnO, that based on $E = h \nu = \frac{hc}{\lambda}$. Where E is equal to 3.2 eV, and in case of ZnO ($3.2 \text{ eV} = 3.2 \times 1.6 \times 10^{-19} \text{ J}$), and by substitution of each c and h constants by $3.0 \times 10^8 \text{ m/s}$, $6.626 \times 10^{-34} \text{ Js}$ respectively. It would be clear to know that 380 nm is a suitable wavelength to obtain the photocatalyst in ZnO²⁰.

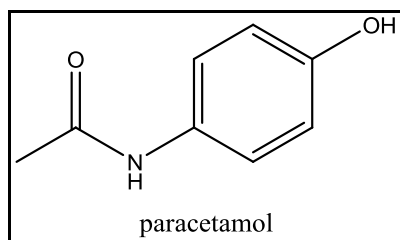
Zinc oxide is a common semiconductor that has a chemical structure ZnO. This semiconductor considers a favored type in photocatalytic reaction to handling of wastewater more than other catalysts. Low prices and consuming a solar spectrum entirely makes it the predominant semiconductor in photooxidation⁽²¹⁾. Regarding the chemical behavior of ZnO that is characterize by considering it an amphoteric oxide. This behaves is accompanied by a variation in its solubility. A slight solubility that equal to 0.19 mg/100 ml at room

temperature mainly found in water. While it involves a complete dissolving towards acids as explained below:^{22, 23}

Pharmaceutical manufacturers generate process wastewater containing a variety of conventional parameters (e.g., BOD, TSS, and pH) and other chemical constituents.

The study of pharmaceuticals in many researches indicated that a different types of medicinal compounds as main factor of contamination of wastewater⁽²⁴⁾. Some of these studies focusing on the effect of drugs on surface water²⁵⁻²⁷, while other studies deal with drugs effect on ground water^(28, 29, 30) and in oceanic system as well^{31,32}. From all the above studies it seems that drugs consume and uses of it consider to be the main cause of contamination rather manufacture process of drugs³³.

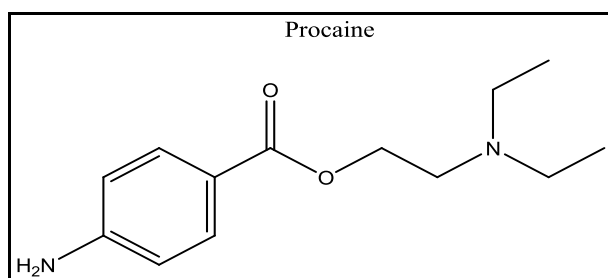
Paracetamol is the most frequent drug use to pain relief and reduce fever^{34, 35}, and the major of analgesic that used to treat the advance cases of cancer and manage of surgical pain³⁶. Paracetamol has been identified firstly in 1886 as analgesic by Harmon Northrop Morse^{37, 38}. Synthesis process are involved the reduction of p-nitrophenol with tin in glacial acetic acid. A high use of aniline derivative includes Acetanilide capable to cause methemoglobinemia the reason that leads to look for another derivative with a less toxic effect.



Figure(3):chemical structure of Paracetamol

Procaine or also called Novocain is a member of amino ester groups which used as a local anesthetic drugs that act mainly to reduce pain associated with penicillin intramuscular injection and also, it widely used in dentistry. It's anesthetic effect usually carried out by blocking a sodium channels³⁹.

Procaine is amphiphilic molecule of is comprises from 4-aminobenzoic acid that gives hydrophobic features and diethylaminoethane that cause hydrophilic properties. These molecules link together by ester bound. Iglesias-Martinez et al (2006)⁴⁰ deeply explained the importance of both molecules concentration to survive substitution reaction.



Figure(4) :chemical structure of Procaine

Now a day, due to the presence of extremely refractory organic matter in the wastewater stream, the use of conventional wastewater treatment methods are increasingly become challenged. So, now there is a clear need to test and set up the emerging alternative technologies that can deal with highly concentrated and toxic non biodegradable organic matter. So in this way advanced oxidation process (AOP's) has emerged in the last decade especially for the treatment of industrial wastewater.

The scope of this project is to see photocatalysis as a viable treatment option in case of pharmaceutical industry wastewater. Zinc oxide was used as photocatalyst. Experiments were performed in slurry mode in UV light at optimized condition.

2. Experimental

The Photocatalytic process is carried out using photocatalytic reactor that is synthesis locally. This represents an aluminum box contains wooden walls inside that help to keep light and prevent light dispersion. Also, photocatalytic reactor supplies with lamp of mercury medium pressure. It is used 250 W without use the class cover of lamp in order to focus light towards solution vertically

Zinc oxide with 99% purity were supplied by Fluka-Garantie, Solutions were prepared using double distilled water. In all experiments, the required amount of the catalyst was suspended in 200 ml of aqueous solutions of drugs, using a magnetic stirrer. At predetermined times; 5 ml of reaction mixture was collected and centrifuged (3000 rpm, 15 minutes) 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. After the second centrifugation the absorbance at (244nm for paracetamol and 290 nm for procaine.) of the supernatants was determined using ultraviolet-visible spectrophotometer, type Shimadzu UV 1650 PC /Japan.

In order to determine the effect of catalyst loading, the experiments were performed by varying catalyst concentration from (0.01 to 1)g , for drugs 10 μ g/ml solutions at natural pH . Similar experiments were carried out by varying the pH of the solution (pH 2–12) and concentration of drugs (5, 10, 20, 30, and 40) μ g/ml. the reaction temperatures amounted to 15, 25, 35, 45, and 55°C.

3. Results and discussion

3.1 Degradation of Paracetamol and procaine solutions Under Different Experimental Conditions

In the current study dark reaction is carried out by using the solutions of both paracetamol and procaine with amount of ZnO catalyst in the absence of UV light and it is clear that addition of ZnO catalyst in dark reaction with different times of adsorption had no significant changes on paracetamol and procaine degradation. Figures(5,6) show the comparison study for the degradation of paracetamol and procaine respectively , in figures (5,6) noted the values of $\ln A_0/A$ with time (0-30) min have a little increase for both dark and photolysis reactions , from this it is believed that presence monolayer of paracetamol and procaine on catalyst surface, This means that a limited free sites are available that lead to a limited degradation process⁽⁴¹⁾.

When we are studied the effect of both light and catalyst (photo catalysis reaction) on paracetamol solution, show the largest different when comparison with the dark or photolysis reactions for this current research. It is demonstrated that complete paracetamol solution degradation can be achieved in case of using both UV light and ZnO catalyst, Because this supplies source of free radical such as hydroxyl radical and super oxide radical.

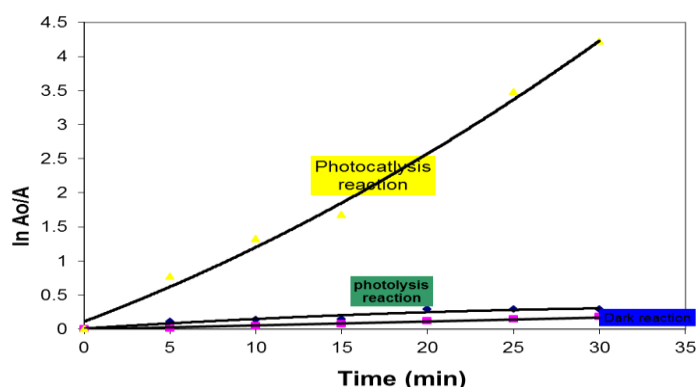


Fig 5. Shows relationship between $\ln A_0/A$ and irradiation time of Paracetamol.

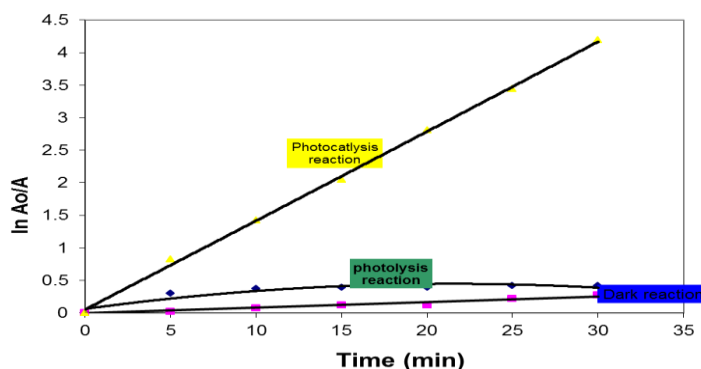


Fig 6. Shows relationship between $\ln A_0/A$ and irradiation time of procaine.

The finding result explained that a photocatalytic degradation might be facilitated by using semiconductor ZnO which is act to increase the surface area of paracetamol solution to exposed UV light, which might be resulted in reaching to photocatalytic degradation efficiency (P.D.E) equal to 100% at 30 min for paracetamol. This means that both UV light and catalyst are important factors in paracetamol degradation. Moreover, the result exhibited preferred photocatalysis than dark reaction and, photolysis

3.2 Degradation of Paracetamol and procaine by ZnO as Photocatalysts

The experiments were carried out to study the degradation of paracetamol and procaine solutions employing as catalysts under UV light. Various parameters which affect the degradation efficiency such as catalyst weight (0.01–1g), pH (2–12), initial concentration of drugs (5–40) $\mu\text{g/ml}$, and temperature (15, 25, 35, 45, and 55) $^{\circ}\text{C}$ of degradation were assessed under UV light.

3.2.1 Effect of Catalyst weight

Figures 7,8 show the effect of ZnO catalyst amount on the degradation of paracetamol and procaine solutions at natural pH. The result indicated that typical weight of ZnO 0.025 gm of paracetamol and 0.1 gm for the procaine. The presence of active site on catalyst surface play important role to explain the current result, therefore we can be illustrated on the basis that the increase of the amount of catalyst lead to increase the amount of active sites on catalyst surface, as result the number of paracetamol and procaine molecules adsorbed on the surface of catalyst increase, that lead to increase the area of illumination, also the increase in the amount of catalyst lead to increase in the number of absorbed photons²⁴⁻⁴⁵.

However, stability the rate of photocatalytic degradation when amount of catalyst reached to 0.05 gm or more for paracetamol and 0.15 gm or more for procaine, this result can be explained due to reaching plateau region. The plateau is reached when the increase in the amount of catalyst can no longer increase the overall efficiency of utilizing incident radiation⁽⁴⁶⁾. If a plateau reaches the rate of photocatalysis degradation decrease with increase the amount of the catalyst due to reduction of radiation entering the reaction vessel. It has been indicated that a higher concentration of catalyst molecules lead to light scattering that result in reducing of utilized light^{42,47, 48}.

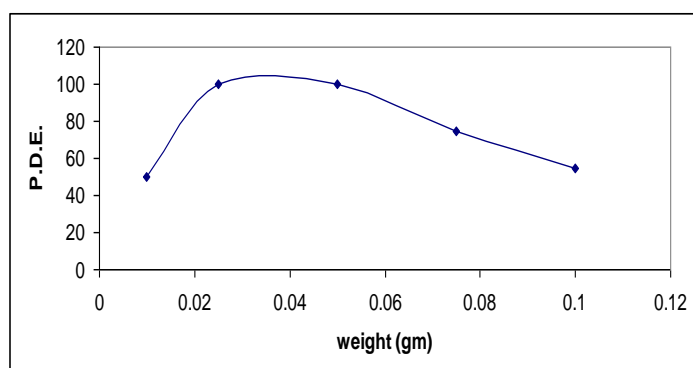


Fig 7. Shows the relationship between ZnO weights and photocatalytic degradation efficiency(P.D.E) of paracetamol.

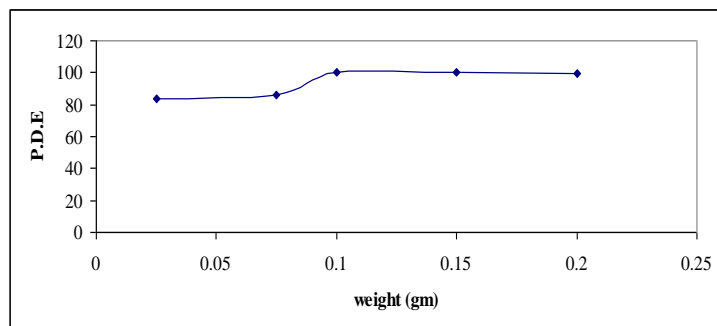


Fig 8. Shows the relationship between ZnO weights and photocatalytic degradation efficiency(P.D.E) of procaine.

3.2.2 Effect of Initial Concentration paracetamol and procaine solutions.

In the current study we are also studied the effect of initial concentration for paracetamol and procaine solutions under experimental condition which are 0.025 gm of ZnO for paracetamol and 0.1 gm for procaine, 298K and the pH equal 8 & 7 of paracetamol and procaine respectively. Concentration is studied in the range (5 – 40 μ g/ml) for both paracetamol and procaine solutions. The results revealed that degradation percentage increased inversely with initial concentration as showed in figure 9.

It is clear that an initial paracetamol and procaine concentration impact negatively on degradation rate. If initial concentration increase, the path length of the photon entering the solution decrease. As a result the number of photons reaching to catalyst surface decrease and hence rate of formation hydroxyl radicals and super oxide radical might be decreased which that subsequently decrease the rate of degradation due to decreasing the number of catalyst molecules that might be excited^{49,50}.

In addition, when a catalyst surface keeps constant, the initial concentration of paracetamol and procaine solutions will increase with a corresponding decreasing in photocatalytic degradation rate, This because only a few active sites in catalyst that can cause little adsorption of paracetamol and procaine molecules on it. That can make the molecules persist in drug solution until attached molecules are degraded. At higher concentration, numbers of paracetamol and procaine molecules high too and that will be lead to a competition between drugs molecules to link on active site, this will lead to reduction of degradation rate⁵¹.

Moreover, when the initial paracetamol and procaine concentration increase that lead to increase the numbers of adsorbed paracetamol and procaine molecules on catalyst surface. It is thought that presence of a large amount of adsorbed molecules have negative effect on drugs reaction to generate holes or hydroxyl radicals, due to a lack of direct contact between them⁵².

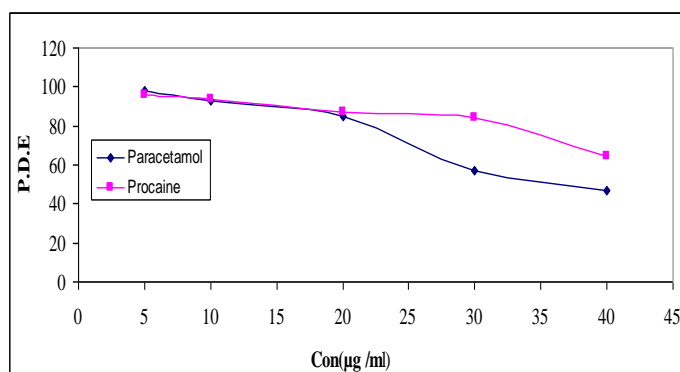


Fig 9. Shows photocatalytic degradation efficiency(P.D.E) at different concentration of paracetamol and procaine solutions.

3.2.3 Effect of pH

pH for Aqueous solution is an important factor in the evaluation of photocatalytic degradation rate because the pH change affects the adsorption quantity of organic pollutants and the ways of adsorption on the surface of photocatalyst coordination^{46,53}. As result, the photocatalytic degradation efficiency will greatly be effected by pH changes.

For this we study the effect of pH on photocatalytic degradation rate and the result indicted that optimal pH is 8.0 for paracetamol and 4.0 for procaine in the presence of certain conditions. The study of pH effect studied in the range (4, 6, 8, 10, and 12) for both paracetamol and procaine as explained in (Fig. 10). The study of pH effect changes on percentage of degradation reaction rate studied under determined experimental conditions which are included: Initial concentration 10 µg/ml for both paracetamol and procaine solutions, ZnO catalyst amount (0.025 & 0.1)gm for paracetamol and procaine respectively and at temperature 298K.

The results indicated that the rate of photocatalytic degradation increases with the increase of pH solution. But when the photocatalytic degradation rate reach to maximum value, the rate of Photocatalytic degradation decrease with increase the pH of solution.

This behavior could be explained by hypothesis of zero point charge (ZPC). The zero point charge is equal to 9.00 for ZnO⁵⁴. As well-known, when the pH solution increase the surface of catalyst will be negatively charged by adsorbed hydroxyl ions. The presence of large quantities of adsorbed OH⁻ ions on the surface of catalyst can promote OH[•] radicals formation so the rate of photocatalytic degradation increase with the increase in pH of the solution^(55,56). It has been found that in basic pH values, ZnO particles have negative surface charge and repulse drugs anion-molecules⁴⁹.

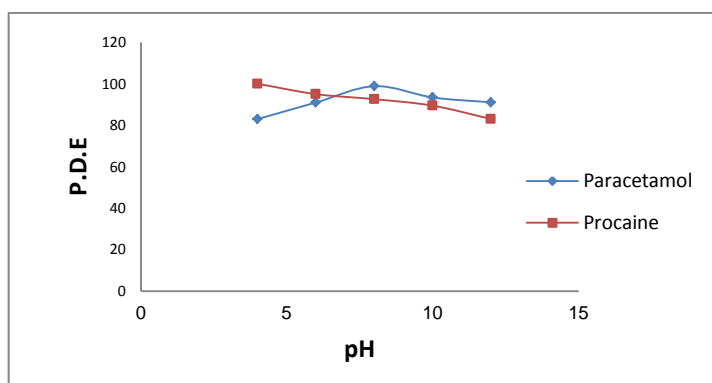


Fig 10. Shows the photocatalytic degradation efficiency(P.D.E.) at different pH of paracetamol and procaine solutions in the presence of ZnO as catalyst.

3.3.4 Effect of temperature:

The study of temperature effect on photocatalytic degradation rate in the present research indicated that optimal temperatures is 55C° for paracetamol and procaine with initial concentration 10µg/ml for both paracetamol and procaine, ZnO amount 0.025 gm for paracetamol and 0.1 gm for procaine, and pH solution 8 and 4 for paracetamol and procaine respectively.

The results revealed that the degradation efficiency had not significant effect with increase of temperature, optimal rate of degradation happened in high temperature degrees, as plotted in (Figures11,12).

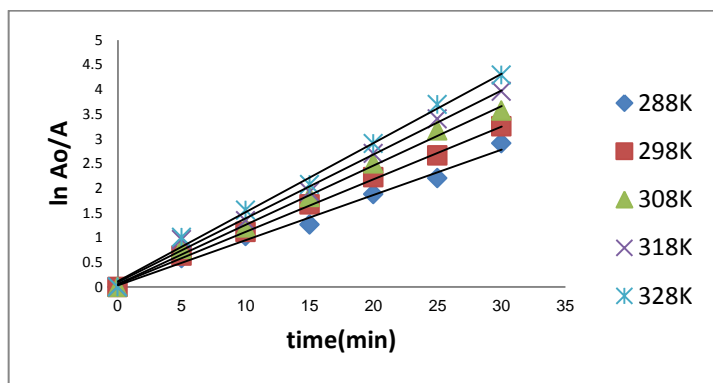


Fig 11. Shows the changes in $\ln A_0/A$ of paracetamol solution with irradiation time at different temperature in presence of ZnO as catalyst.

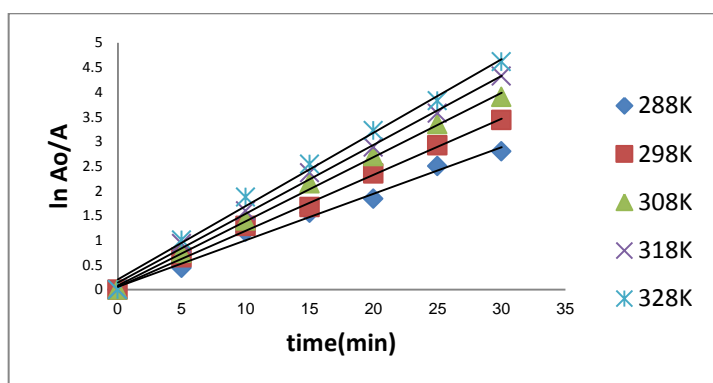


Fig 12. Shows the changes in $\ln A_0/A$ of procaine solution with irradiation time at different temperature in presence of ZnO as catalyst.

The activation energy E_a was calculated from the Arrhenius plot of $\ln k$ vs. $1/T$ the slope of linear plot is equal to $(-E_a/R)$ as show in (Figure13)

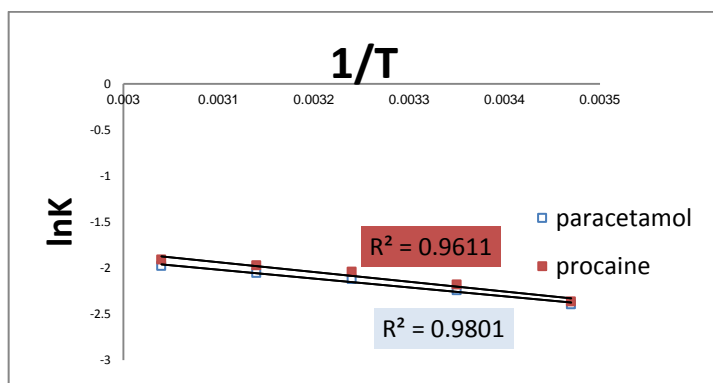


Fig 13. The relation between $\ln K$ and $1/T$ of paracetamol and procaine solutions with ZnO as catalyst.

In addition, the thermodynamic parameters of paracetamol and procaine degradation are studied. The results exhibited that reaction is non-spontaneous endothermic. These finding proved by a positive ΔH^\ddagger which refers to the change in enthalpy and a positive ΔG^\ddagger which explain the change in free energy of reaction.

Obviously that positive ΔG^\ddagger can be explained by reaching the activation state that well solvated structure formed between the drug molecules and the reaction intermediates of hydroxyl radicals. Also, regards the positive ΔS^\ddagger in present results as illustrated in tables 2 and 3 which means that complex formed is un stable

towards the reactants. At the beginning noticed that the complex formed is unstable and degradation of the reactants into products is not very slow, but takes place rapidly under present experimental conditions^{57,58}.

Table 2. Values of thermodynamic parameters for the photocatalytic degradation of paracetamol solution with ZnO as catalyst.

T(k)	K (min ⁻¹)	Ea (KJ. mol ⁻¹)	ΔH (KJ. mol ⁻¹)	ΔS (KJ. mol ⁻¹)	ΔG (KJ. mol ⁻¹)
288	0.091	7.96	5.57	0.0036	5.72
298	0.106		5.49		5.55
308	0.120		5.40		5.42
318	0.128		5.32		5.42
328	0.138		5.24		5.06

Table 3. Values of thermodynamic parameters for the photocatalytic degradation of procaine solution with ZnO as catalyst.

T(k)	K (min ⁻¹)	Ea (KJ mol ⁻¹)	ΔH (KJ mol ⁻¹)	ΔS (KJ mol ⁻¹)	ΔG (KJ mol ⁻¹)
288	0.092	15.67	13.283	0.0263	5.711
298	0.116		13.200		5.336
308	0.138		13.117		5.070
318	0.162		13.034		4.812
328	0.121		12.951		4.202

3.3.5 Kinetic Study

Figure 14 show the kinetics of degradation for paracetamol and with initial concentration 10μg/ml for both paracetamol and procaine, ZnO amount (0.01- 0.1)gm , and pH solution 8 and 4 for paracetamol and procaine respectively.

The results show that the photocatalytic degradation of drugs solution in aqueous ZnO can be described by the first-order kinetic according to the Langmuir–Hinshelwood model⁵⁹⁻⁶³, $\ln (A_0/A) = kt$, where A_0 is the initial absorption and C is the absorption at any time, t . The semi-logarithmic plots of the concentration data gave a straight line.

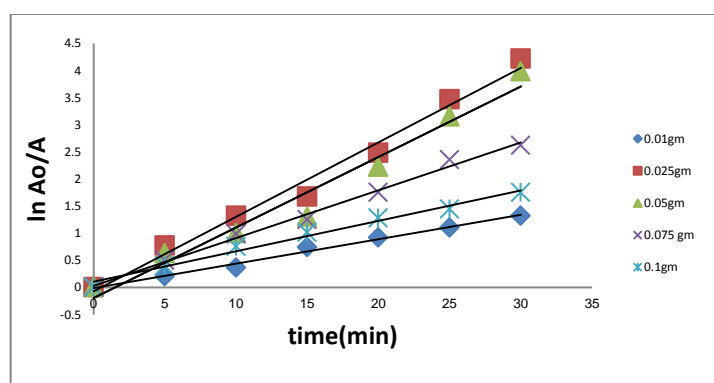


Fig.12 Kinetics analysis for paracetamol (initial concentration 10μg/ml), .

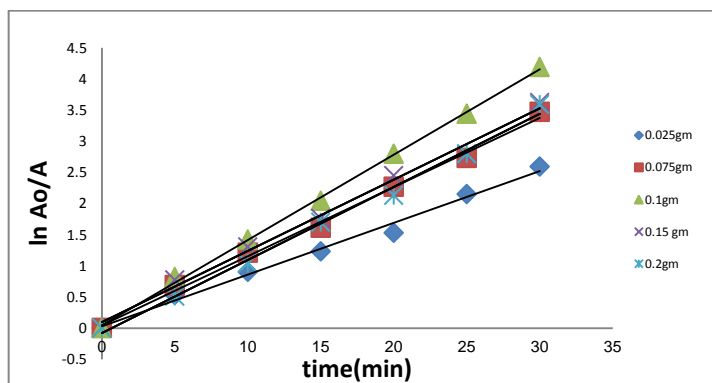


Fig.13 Kinetics analysis for procaine (initial concentration 10 µg/ml) .

4. Conclusion

The study is designed to treat the waste water of drugs by using UV light and ZnO as catalyst. This study explained the importance of the UV light and catalyst as a basic factors in the photo catalytic degradation for both paracetamol and procaine.

The study includes the measure of the rate of photooxidation by measuring the absorbance of samples from aqueous solution for both drugs which is treated by UV. light in limited time periods (every five minutes). These absorbance are compared as with the initial drug's absorbance.

Some parameters which are effected on the rate of photooxidation are studied in present research such as the amount of catalyst, initial concentration for the drug's solution, the temperature and pH for the drug's solution.

The results appeared that the photo catalytic oxidation reaction for the paracetamol and procaine from pseudo-first order according to the Langmuir-Hinshelwood relationship, and the study found that the photooxidation rate fits positively with the increase of the catalyst weight until the weights of ZnO equal to 0.025 gm and 0.1 gm are considered the optimum weights of paracetamol and procaine respectively where the best photodegradation is happened, so after these values, the photodegradation rate is decrease or stable with the increase of the catalyst weight.

In addition, the initial concentration increase for both drugs leads to reduce degradation rate with foundation of the mentioned weights of ZnO. Also this study is found the increase of pH of reaction solution for both drugs have a positive effect represented by increasing the degradation rate until the pH 8 and 4 are the best acidic function of the paracetamol and procaine respectively.

Regarding the change of the temperature has a little effect on the rate of photo catalytic degradation and it was noticed that the reaction rate increases with the increase of temperature.

Activation energy was calculated according to the Arrhenius plot of $\ln K$ vs. $1/T$, the slop of linear plot is equal to $(-E_a/R)$. Activation energy was found equal to 8.95 KJ. mol⁻¹ for paracetamol and 15.67 KJ. mol⁻¹ for procaine.

The thermodynamic functions were calculated in current study for each drug and the results for paracetamol were as follows:

$$\Delta G = 5.33 \pm 0.2 \text{ KJ.mol}^{-1}$$

$$\Delta H = 6.39 \pm 0.1 \text{ KJ.mol}^{-1}$$

$$\Delta S = 0.0036 \text{ KJ.mol}^{-1}$$

And the results of procaine were as follows:

$$\Delta G = 5.02 \pm 0.6 \text{ KJ.mol}^{-1}$$

$$\Delta H = 13.31 \pm 0.1 \text{ KJ.mol}^{-1}$$

$$\Delta S = 0.0263 \text{ KJ.mol}^{-1}$$

The results of suggested mechanism of degradation are explained that is the final products for degradation are CO₂, H₂O and mineral acids.

6. References

- Gogate P.R. and Pandit A.B., (2004) "A review of imperative technologies for wastewater treatment II: Hybrid methods". *Advances in Environmental Research*, 8 (3-4): 553-597.
- Gogate P.R. and Pandit A.B., (2004) "A review of imperative technologies for wastewater treatment I: Oxidation technologies at ambient conditions". *Advances in Environmental Research*, 8 (3-4): 501-551.
- Paraskeva P. and Diamadopoulos E., (2006) "*Technologies for olive mill wastewater (OMW) treatment: A review*". *J. Chem. Technol. Biot.*, 81 (9):1475-1485.
- Esplugas S., Bila D.M., Krause L.G.T. and Dezotti M., (2007) "*Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents*". *J. Hazard. Mater.*, 149 (3): 631-642.
- Johnson M.B. and Mehrvar M., (2008) "Aqueous metronidazole degradation by UV/H₂O₂ process in single and multi-lamp tubular photoreactors: Kinetics and reactor design". *Ind. Eng. Chem. Res.*, 47 (17): 6525-6537.
- Moo-Young H.K., (2007) "Pulp and paper effluent management". *Water Environ. Res.*, 79 (10): 1733-1741,
- Crini G., (2006) "Non-conventional low-cost adsorbents for dye removal: A review". *Bioresour. Technol.*, 97(9): 1061-1085.
- Vandevivere P.C., Bianchi R. and Verstraete W., (1998) "*Treatment and reuse of wastewater from the textile wet-processing industry: Review of emerging technologies*". *J. Chem. Technol. Biot.*, 72 (4): 289-302,
- Aye T., Anderson W.A., and Mehrvar M., (2003) "*Photocatalytic treatment of cibacron brilliant yellow 3G-P (reactive yellow 2 textile dye)*". *J. Environ. Sci. Heal. A*, 38 (9): 1903-1914
- Aye T., Mehrvar M., and Anderson W.A., (2004) "*Effects of photocatalysis on the biodegradability of Cibacron Brilliant Yellow 3G-P (Reactive Yellow 2)*". *J. Environ. Sci. Heal. A*, 39 (1): 113-126.
- Renou S., Givaudan J.G., Poulain S., Dirassouyan F., and Moulin P., (2008) "*Landfill leachate treatment: Review and opportunity*". *J. Hazard. Mater.*, 150 (3): 468-493,
- Verma A., "Advanced oxidation technologies for wastewater treatment," M.tech seminar, 2004.
- Herrmann J.M., "Heterogeneous photocatalytic : an emerging technology for water treatment ," *Catal. Today*, 53, 115-129, 1999.
- Attia A., Kadhim S. and Hussein F., (2008) "*Photocatalytic Degradation of Textile Dyeing Wastewater Using Titanium Dioxide and Zinc Oxide*," *E-J. Chem.*, 5, 219-223,
- Yacobi. B.G, (2003) "*Semiconductor Materials: An Introduction to Basic Principles*," Springer Science & Business Media, 1-3.
- Shaheen A., Zia W. and Anwar M. S, (2010) "Band Structure and Electrical Conductivity in Semiconductors," *Lums School of Science and Engineering* ,
- Herrmann M., (1999) "Heterogeneous photocatalysis: fundamental and applications to the removal of various types of aqueous pollutants ," *Catal. Today*, 53, 115–129.
- Adachi K. and Ohta K., (1994) "*Photocatalytic reduction of carbon dioxide to hydrocarbon using copper-loaded titanium dioxide*," *J. Solar energy*, 53(2): 187-190.
- Turner R.P. (1961) "Semiconductor Devices." New York. Holt, Rinehart and Winston INC.
- Litty I., Bindu K., Deepthy A. and Radhakrishnan P., (2007) "Excitation wavelength dependent Fluorescence behavior of Nano colloids of ZnO," *J. Phys. D: Appl. Phys.* 40 ,5670–5674.
- Pannee A., Chadda B. and Wichien S., (2012) "Photocatalytic Activity under Solar Irradiation of Silver and Copper Doped Zinc oxide : Photodeposition Versus Liquid Impregnation Methods," *J. of Applied Science* 12(17):1809-1816.
- Greenwood N. and Earnshaw N., (1997) "Alan. Chemistry of the Elements," Butterworth–Heinemann. ISBN 0080379419, (2nd ed.).
- Spero J. M., Devito B. and Theodore L., (2000) "Regulatory chemical handbook," CRC Press. ISBN 0-8247-0390-1.
- Derksen J.G.M., Rijs G.B.J. and Jongbloed R.H. (2004), "Diffuse pollution of surface water by pharmaceutical products," *Water Sci. Technol.*, 49, 213–221.

25. Golet E.M., Alder A.C. and Giger W., (2002) "Environmental exposure and risk assessment of fluoroquinolone antibacterial agents in wastewater and river water of the Glatt Valley Watershed," Switzerland, Environ. Sci. Technol, 36, 3645–3651.
26. Hilton M. J. and Thomas K. V., (2003) " *Determination of selected human pharmaceutical compounds in effluent and surface water samples by high-performance liquid chromatography-electrospray tandem mass spectrometry*," J. Chromatogr A, 1015, 129–141.
27. Tixier C., Singer H.P., Oellers S., and Muller S.R., " Occurance and fate of Carbamazepine, Clofibric acid, Diclofenac, Ibuprofen, Ketoprofen and Naproxen in surface waters," Environ. Sci. Technol., 37, 1061–1068, 2003.
28. Reddersen K., Heberer T. and Dunnbier U., " Identification and significance of phenazone drugs and their metabolites in ground- and drinking water," Chemosphere 49, 539–544, 2002.
29. Sacher F., Lange F.T., Brauch H.J. and Blankenhorn I., (2001) "*Pharmaceuticals in groundwaters. Analytical methods and results of a monitoring program in Baden-Wurttemberg, Germany*," J. Chromatogr. A 938, 199–210.
30. Seiler R.L., Zaugg S.D., Thomas J.M. and Howcroft D.L., (1999) " Caffeine and pharmaceuticals as indicators of waste water contamination in wells, GroundWater," 37, 405.
31. Buser H.R., Muller M.D. and Theobald N., (1998) " Occurrence of the pharmaceutical drug clofibric acid and the herbicide mecoprop in various Swiss lakes and in the North Sea," Environ. Sci. Technol. 32, 188–192.
32. Stumpf M., Ternes T.A., Wilken R.D., Rodrigues S.V. and Baumann W., (1999) "Polar drug residues in sewage and natural waters in the state of Rio de Janeiro," Brazil, Sci. Total Environ. 225, 135–141.
33. Fisher P.M.J. and Borland R.(2003)" *Gauging the pharmaceutical burden on Sydney's environment: A preventative response*," J. Cleaner. Product. 11, 315–320.
34. Aghababian R. V., (2010) "Essentials of Emergency Medicine," Jones & Bartlett Publishers. ISBN 978-1-4496-1846-9, 814.
35. Ahmad J., (2010) "Hepatology and Transplant Hepatology: A Case Based Approach," Springer ISBN 978-1-4419-7085-5, 194.
36. Scottish Intercollegiate Guidelines Network (SIGN), (2008), Control of pain in adults with cancer. Scotland: National Health Service (NHS). ISBN 9781905813384.
37. Milton S., Mia L., Philip R. L., (2012) "Bad Medicine: The Prescription Drug Industry in the Third World," Stanford University Press. ISBN 0804716692, 88-90.
38. Von Mering J., (1983) " Beitragezur Kenntniss der Antipyretica," TherMonatsch 7, 577–587.
39. Gentry C. and Lukas R., "*Local anesthetics noncompetitively inhibit function of four distinct nicotinic acetylcholine receptor subtypes*," J. PharmacolExpTher, 299(3):1038-48, 2001.
40. Iglesias-Martinez E., Brandariz I. and Penedo F., " Ester Hydrolysis and Nitrosative Deamination of Novocaine in Aqueous Solutions," 2006.
41. Monika S., "Advance oxidation Processes For The Degradation Of Pesticides," Msc Thesis, Department Of Biotechnology & Environmental Sciences. Thapar University Patiala, Malaysia, 2008.
42. Kim T. and Lee M., (2010) " *Effect of pH and Temperature for Photocatalytic Degradation of Organic Compound on Carbon-coated TiO₂*," J. of Advanced Engineering and Technology, 3(2): 193-198.
43. Goncalves M. S. T ., Oliveira-Campos A. M. F., Pinto E.M.M.S., (1999), PlasenciaQueiroz P. M. S., and M.J.R.P , "photochemical treatment of solutions of azo dyes con-taining TiO₂". Chemosphere, 39, 781-786.
44. Wang C.C, Lee C.K, Lyu M.D and Juang L.C, (2008), " Photocatalytic degradation of C.I. Basic Violet 10 using TiO₂ catalysts supported by Y zeolite: an investigation of the effects of operational parameters," Dyes and Pigments, 76, 817–824 .
45. Falah H. H. and Ahmed F. Halbus, (2012), "*Rapid Decolorization of Cobalamin*," Inter. J. of Photoenergy, 1 ,75-84.
46. Falah H. H., Photochemical Treatments of Textile Industries Wastewater, Advance in Treating Textile Effluent, book edited by Peter J. Hanser , 2011.
47. Gaya U., Abdullah A. , Zainal Z. and Hussein M., (2010), " Photocatalytic Degradation of 2,4-dichlorophenol in Irradiated Aqueous ZnO Suspension," International Journal of Chemistry, 2(1): 180-193.
48. Kavitha S. and Palanisamy P., (2011), " *Photocatalytic and Sonophotocatalytic Degradation of Reactive Red 120 Using Dye Sensitized TiO₂ under Visible Light*," International Journal of Civil and Environmental Engineering, 3(1): 1-6.

49. Daneshvar N., Salari D. and Khataee A.R., (2004), "*Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO₂*," J. Photochem. Photobiol. A: Chem, 162, 317-322.
50. Konstantinou I.K. and Albanis.T.A., (2004), " TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: a review," Appl. Catal. B 49 ,1–14.
51. Munesh S. and Meena R.C., (2012), "*Photocatalytic Decolorization of Acid Red 186 Using Alternative Developed Photocatalyst Mbir Dowex*," 11Research Journal of Chemical Sciences ,ISSN 2231-606X , 2(9): 56-62.
52. Chakrabarti S. and Dutta B.K., (2004), " Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst," J. Hazard. Mater. B 112, 269–278.
53. Obies M., "PhotocatalyticDecolorization of Bismarck Brown R," MSc Thesis, Chemistry Department, College of Science, Babylon University, Iraq. 2011.
54. Lizama C. and Freer J., (2002), " *Optimized photodegradation of Reactive Blue 19 on TiO₂ and ZnO suspensions*," J. Baeza, H.D. Mansilla, Catal. Today, 76, 235-246.
55. Akyol A., Yatmaz H.C. and Bayramoglu M., (2004)," Photocatalytic decolorization of Remazol Red RR in aqueous ZnO suspensions," Appl. Catal. B: Environ. 54 , 19-27.
56. Hustert K. and Zepp R.G., (1992), " Photocatalytic degradation of selected azo dyes ," Chemosphere, 24, 335-343,.
57. Al-Ekabi H. and Mayo P., (1985), " *Surface photochemistry: Cadmium sulfide photoinduced cis-trans isomerization of olefin*," J. Phys. Chem. 89, 5815,.
58. Susheela B. G., (2012), "*Photocatalytic Degradation Study of Methylene Blue Solutions and Its Application to Dye Industry Effluent*,"International Journal of Modern Engineering Research (IJMER), ISSN: 2249-6645, 2(3):1204-1208.
59. Alkaim AF, Kandiel TA, Dillert R, Bahnemann DW. (2016); Photocatalytic hydrogen production from biomass-derived compounds: a case study of citric acid. Environmental Technology (United Kingdom). 37(21): 2687-2693.
60. Aljeboree AM, Alkaim AF, Al-Dujaili AH. (2015);Adsorption isotherm, kinetic modeling and thermodynamics of crystal violet dye on coconut husk-based activated carbon. Desalination and Water Treatment. 53(13): 3656-3667.
61. Alkaim AF, Sadik Z, Mahdi DK, et al. (2015);Preparation, structure and adsorption properties of synthesized multiwall carbon nanotubes for highly effective removal of maxilon blue dye. Korean J. Chem. Eng. 32(12): 2456-2462.
62. Mashkour, M. S., Al-Kaim AF, Ahmed LM, Hussein FH. (2011);Zinc oxide assisted photocatalytic decolorization of reactive red 2 dye. Int. J. Chem. Sc. 9(3): 969-979.
