# Parameters effecting on photocatalytic degradation of the phenol from aqueous solutions in the presence of ZnO nanocatalyst under irradiation of UV-C light

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Phenol or hydroxyl-benzene is one of the toxic hydrocarbons that grouped as a priority pollutant by EPA. It is one common compound that exists in industrial wastewaters including petroleum refining and petrochemistry, pesticide, oils and painting, organic chemicals, plastics, resins etc. that leads to environment pollution especially water resources.
The aim of this study was evaluation of phenol degradation by use of nano-photocatalytic UV/ZnOprocess in a pilot. In the study, a 125 Watt UV lamp was used. Phenol measurement carried out using spectrophotometer. Results showed that there is reverse relationship between removal efficiency of phenol with increasing of pH in the case of nano-photocatalytic UV/ZnO process. Optimum conditions in nano- photocatalytic UV/ZnO process obtained in 10 mg/l phenol, contact time 30 min at pH=5.Results indicate thatnano-photocatalytic UV/ZnO processcan be used as an effective method forphenol removal from aqueous solutions**.**

**Keywords:** phenol, industrial wastewaters, UV, ZnO.

## INTRODUCTION

Nowadays, conventional water and wastewater treatment processes are inadequate and sometimes disabling in treatment of toxic and resistant materials in water, because the production of toxic and complex substances. Hence, considering the performance technologies in this field is required to ensure the provide public health and environmental protection. The chemical compounds in industrial wastewater, especially petroleum compounds, phenol and its derivatives are very inclusive [1].Phenol is the aromatic alcohol with $C_6H_5OH$ formula and main component of coal tar that its compounds are the most important aromatic compounds. Phenol has another name, including benzenol, phenolic acid, phenol alcohol, phenic acid, hydroxy benzene, carbolic acid and phenyl hydroxide [2-4]. Beside the artificial way, Phenol can entrance to water resources in natural ways, and because the physical structure can be found in most chemical compounds. Phenol, even exist in the urban wastewater and is taken into consideration due to environmental stability, solubility in water and health problems [1]. Chlorination of drinking water containing phenol can produce the chlorophenolic compounds that lead to the stench and the protest by consumers. Therefore, phenol is classified as priority hazardous pollutants introduced by EPA's list [5, 6]. Most water quality standards are recommended that the phenolic compounds concentration in drinking water resources to be µg/L, and maximum concentrations in effluent discharged to the environment less than 1 mg/L [7-9].In general, the phenol removal and control methods can be divided into two groups [10]:

1. Recycling methods of phenol compounds such as adsorption, ion exchange, solvent extraction, steam and hot gas removal.

2. Decomposition and destruction of methods for convert phenolic compounds into safe materials, including the use of oxidizing agents such as hydrogen peroxide, potassium permanganate, sulfur dioxide and ozone, biological methods, aeration and advanced oxidation.Physico-chemical processes for the purification of phenol including [11]:

1. Adsorption

2. Extraction by chemical solvents

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3. Water steam
4. Freezing & Crystallization
5. Chemical oxidation
6. Wet oxidation
7. Advanced Oxidation Processes

Many researches are still ongoing for reach the more appropriate methods. For this aim, advanced oxidation processes (AOP) and oxidation photocatalytic are used more than other methods. UV/ZnO photocatalytic is one of the common methods that used to degradation of water contaminants. In photocatalytic degradation of pollutants under the influence of ultraviolet radiation (UV) and in the presence of catalyst particles of metal oxides such as TiO2 and ZnO [12].Nanoparticles are essential element nanoscience that considered due to its applications in various fields. ZnO is II-VI family as a semiconductor important material due to direct energy gap and excitation binding energy at room temperature and its high bond length (3.37eV in room temperature) and has especially optical and electrical properties that can have many applications. ZnO, due to its sustainable properties of photonic and chemical corrosion similar TiO$_2$,is a semiconductor material potential in solar energy conversion. Size and morphology are two important parameters to measure and identify physical and physical chemistry properties of ZnO nanoparticles. There are two commercial methods for ZnO nanoparticles producing: The French and American methods. In both methods, the oxidation of zinc metal vapor is used both need a lot of heat, which also demands a lot of energy [13]. Considering the use of various materials nanoparticles are highly regarded for the removal of contaminants from water and sewage, therefore, in this study ZnO nanoparticles were used for photocatalytic degradation of phenol, and the effect of initial concentration, nanoparticle dosage, pH and contact time factors were studied.

## MATERIAL AND METHODS

Initially, phenol stock solutionwas prepared according to the solution provided in the standard of the examination of water and wastewater method [14]. as follows: 1.5g pure phenol solution to 1L of DI-water. Then 2mL of concentrated sulfuric acid were added to enhance stability. Subsequently 10, 40 and 90 mg/L concentration of phenol were provided. A ZnO nanoparticle manufactured by Spadana Company was used as nanocatalyst. In order to activation of ZnO, nanoparticle catalyst was placed in the oven at a temperature 500 ± 50 C° for 2 - 2.5

hours and then cooled in the desiccator and powdered.

Experiments were carried out in a cylindrical glass reactor with a 2 liters volume. UV lamp (W125) at 254 nm wavelength by following features: length 25 cm, which protected in quartz sleeve with 30 and 5 cm highest, and diameter respectively, manufacturing engineering Shekoofan Tawseh exclusive agency agreement of Arda Company France was used as irradiation source. For better irradiation of sample, the lamp was immersed in solution at center of reactor. Overall the system was wrapped with aluminum foil to prevent the leak irradiation. Reactor designs is shown in Fig. 1.Phenol photocatalytic process carried out at pH (7, 11), contact time (5, 10, 20 and 30 min), nanoparticles dosage (0.15 and 0.3 mg/L) and the initial concentration of phenol (10, 40 and 90 mg/L). then, 10, 40, 90 mg/L concentrations of phenol in a cylindrical container prepared in 2 L, then added the nanoparticles in certain dosage to obtain the optimum nanoparticles dosage. Then container placed on the magnetic stirrer in a completely dark environment for 30 minutes to reach the balance of nanoparticle emissions created in attraction and repulsion. Stirring was constantly to prevent the nanoparticle sedimentation and mix thoroughly in all parts of the solution to be created. Then UV lamp was turn on and sampling carried out according considering contact time. The samples volume was selected 10 mL to prevent the noticeable change of solution volume. Subsequently samples were centrifuged for 10 minutes at a speed of 6000 to deposit the particles.

Phenol concentration was measured based on standard method [14].The direct method photometry (that part of the book is given 5530D). Firstly, 5 mL of sample picked up and reached to 100 mL of volume with DI- water and2.5 mL ammonium hydroxide added and pH of solution was reached to 7.9 ± 0.1 with phosphate buffer. Then, 4 mL amino anti-Pyrin -added and well stirred, also, 1 mL potassium Ferro cyanide was added to solution. Similarly these steps were conducted for control sample.Adding the Ferro cyanide reagent to sample leads to create the yellow to dark red hat is depending on the concentration of phenol in the solution. Then, the absorption value was measured after 15 min at 500 nm with spectrophotometer (model UV-1650-Shimadzu. Japan). Moreover, standard curve was prepared in 5 concentrations of phenol 1, 2, 3, 4, and 5 mg/L [15]. The multiple regression analysis method were used to determine the effect of pH, contact time, ZnO dosage, initial

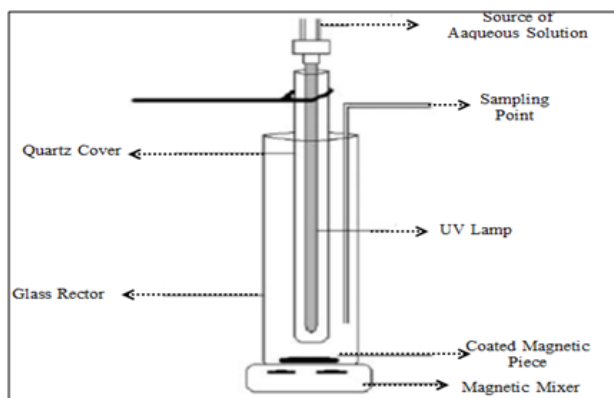concentration of phenol and UV variables on efficiency removal of phenol.



**Fig. 1.** Schematic of photocatalyc reactor.

## RESULTS AND DISCUSSION

### *Effect of pH*

The effect of pH on phenol removal was studied in nano-photocatalytic process (UV/ZnO). Results indicated that pH is an important variable in this process, and plays important role in acid-base balance in that affected on material concentration of degraded or not degraded compounds. Result indicated that with increasing of pH, the phenol removal was decreased (Fig. 2). This revealed that pH has negative effect on nano-photocatalytic process (UV/ZnO). So that the trend of phenol removal was as fallow acidic >neutral > basic condition.
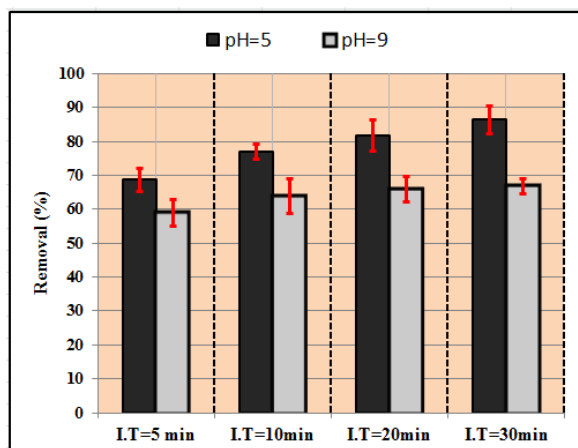


**Fig. 2**. The phenol removal in the presence of UV (W 125) in the both acidic and basic pH, $C_0$=15 mg/L.

The most phenol degradation in acidic condition can attributed to the presence of proton (H$^+$) that leads to formation of H$^0$ radicals [5, 16].Beside the above reason, the positive charge of ZnO in acidic condition can increased the phenol degradation, however, there are not evidence document about positive charge of ZnO in acidic condition [17, 18].

Therefore, the electrostatic attraction between positive charges of ZnO and phenoxic anions caused the more removal of phenol in acidic condition. The results of Kashif et al. [19] and Akbal et al [20] correspond with our study.

### *Effect of ZnO dosage*

Results showed the use of nanoparticles leads to the increasing removal efficiency of phenol due to the increasing concentration of generated radicals. Also, the number of photons absorbed will also increase [19], Resulting the availability and accessibility of active sites has also increased that leads to increasing of the adsorbed phenol molecules [19, 21].

Fig. 3 showed with constant the other conditions (phenol concentration and pH), increased the nanoparticle dosage at 0.15 to 0.3 g/L caused the decrease of kinetic reaction. Because catalyst makes reducing the UV pe netration in solution and increased dispersion of irradiation on nanoparticles surfaces, therefore, leads to reduce the amount of nanoparticles activated by photon [17, 19, 21, 22]. Similarly, Guo et al. reported this result [16]. So, 0.15 g/L dosage of ZnO was determined as the optimum value for the experiments.
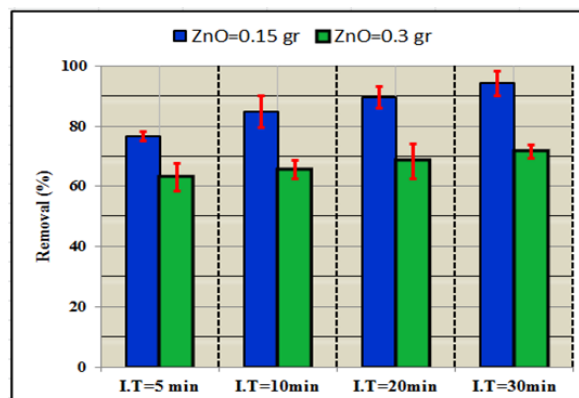


**Fig.3.** The percentage removal of phenol at various ZnO dosage in UV/ZnO process: pH=5, $C_0$= 15 mg/L.

### *Effect of initial concentration of phenol*

Results showed efficiency removal of phenol was decreased with increased of initial concentration (Fig.4), so that in constant condition (nanoparticle dosage and pH), the kinetic reaction was decreased with increasing of phenol concentration from 10 to 90 mg/L. The percentage removal of phenol at acidic pH (pH =5), the nanoparticle 0.15 g/L and 30 minutes obtained 94.24%, while, 74 and 45.88% removal obtained at 40 and 90 mg/L concentration respectively. This can due to the concentration of radicals produced in all the solutions are same, so at low concentration of phenol with the same amount of

hydroxyl radical, the degradation value will be more than high phenol concentration.

Another possible reason, production the more reactive intermediate of phenol that reacts with free present radicals. Considering the competition between phenol and intermediate products, by increasing the initial concentration of phenol and increase the accumulation and concentration of intermediate products on one hand and reducing the amount of phenol concentration in the solution, so leads to significant amount of radical formation used to intermediate products degradation. In this regard, the study of Malaki et al [5] also revealed that phenol degradation rate decreases with increasing initial concentration because it would produce more reactive intermediate products of phenol which react with free present radicals [5]. The study of Sobczyński&Duczmal [22] showed that the degradation rate decreased at the high concentration of phenol, and attributed to made polymeric compounds such as biphenol that are insoluble in water and may stick on the catalyst surface and caused reduce photocatalytic performance in high concentrations of phenol. Kashif & Ouyang proposed that the UV absorption of phenol is more than catalyst, therefore, the absorbed photon hasn't effect for degradation [19].
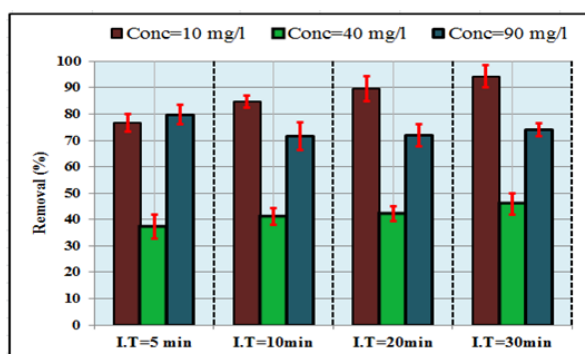


**Fig. 4.** The effect of initial concentration of phenol on its removal trend in UV/ZnO process: pH=5, ZnO=0.15 g/L.

### Effect of irradiation time

The irradiation effect was studied at 4 times (5, 10, 20 and 30 minutes). Results indicated efficiency removal of phenol was increased with increasing of irradiation time. So that the maximum removal obtained at 30 min. (Fig. 2, 3 and 4) [23].

## CONCLUSION

Results revealed that the phenol degradation rate increased in the nano-photocatalytic UV / ZnO process. Many factors affect edoxidation rate including pH, initial concentration of phenol, irradiation time and ZnO dosage. The efficiency removal of phenol increased with increasing of radiation time and efficiency decreased with increasing of pH, ZnO dosage and initial concentration.

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