Investigation of Photocatalytic Degradation of Phenol by UV/TiO₂ Process in Aquatic Solutions

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Abstract

Background: The main objective of this research was to study photocatalytic oxidation of phenol in aquatic solutions by using of UV, TiO_2 and the combination of them. Phenol compounds are widely used in industries and other daily life. Highly toxicity and carcinogenicity of these compounds can causal considerable adverse effects on the aquatic ecosystems and human health.

Methods: The study was an experimental research and carried out by phenol 100 mg L^{-1} solution and contact time, pH and amount of TiO₂ were considered in photocatalytic system as the basic variables affecting removal efficiencies. Phenol concentration in inlet and outlet samples was detected by spectrophotometery at 500nm.

Results: Combination of UV and TiO_2 can cause higher efficiencies of phenol removal. The removal efficiencies of UV, TiO_2 and UV/TiO_2 photocatalytic oxidation system with various operation conditions had a range of 1.8%-19.64%, 2.38%-17.8% and 34.65%-82.91%, respectively. It was found that increasing of TiO_2 concentration and contact time and pH , increasing the amount of phenol that oxidized in combined system and maximum removal coefficients obtained in pH=11 , 9 h contact time and 0.2 gr of TiO_2 .

Conclusion: Combinated UV/TiO₂ process may be applied as an effective process for the removal of phenol from aquatic solutions such as industrial wastewaters and polluted water resources.

Keywords: Phenol, UV ray, TiO₂, Photocatalysis

Introduction

In industries and daily life, phenol compounds are widely used and have become common pollutants in water bodies (1). Due to their stability and bioaccumulation, they remain in the environment for longer periods. Highly toxicity and carcinogenicity of these compounds can cause considerable adverse effects on the aquatic ecosystems and human health. Therefore use of an effective and economic method for the elimination of phenol in water solutions has been in urgent demand (2). Traditional wastewater treatment techniques for phenol removal are activated car-

bon adsorption, chemical oxidation and biological digestion (1). However each technique has some limitations and disadvantages (2). The application of photocatalysis in the treatment of phenol in wastewater is an interesting alternative and is the object of a great interest over the last years by many researchers (1, 3-5). In these researches attention has been drawn toward an alternative technique where the pollutants are degraded by irradiation suspension of metal oxide semiconductor particles such as TiO₂ or ZnO (1, 4). TiO₂ is known to be an excellent photocatalyst for complete mineralization of phenol in water and wastewater(6, 7). It is nontoxic, insoluble in water and comparatively cheap (8, 9). Many organic compounds are de-

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composed in aqueous solution in the presence of titanium dioxide powder illuminated with UV ray (6).

 TiO_2 (anatase) has an energy band gap of 3.2 eV and is capable to be activated by near UV-light with wavelengths up to 388 nm. Light energy from ultraviolet radiation in the form of photons, excites the electrons on the surface of titanium atoms suspended in the contaminated water, moving them from the valence band to the conductance band. This absorption corresponds to between 3 to 4 percent of the solar spectrum (10). The result of this energy change is the formation of holes in the surface of titanium atom, and free electrons, which are now available to form hydroxide (OH) or other radicals, which can oxidize organic chemicals, or reduce metal species (1, 2, 11). In all cases, the degradation process mainly involved the formation of hydroxyl radicals (12). Although this is a small fraction of the spectrum, many studies have been carried out to develop an efficient method for using natural solar radiation to destroy toxic organic compounds (9, 10) and to reduce toxic metals (13).

The main objective of this research was to study of photocatalytic oxidation of phenol in the presence of UV ray, TiO_2 and investigation of the role of main factors that affecting the process.

Materials and Methods

Phenol solution obtained from Merck Chemical Co., was prepared in 100 mg L⁻¹ concentrations. The concentration of phenol was measured at 500 nm by a Shimatsu spectrophotometer. TiO₂ was used mostly anatase and had a BET surface area of 50 m² g⁻¹ and an average particle diameter of 30 nm. pH adjustments in samples were done by using 0.1 N HCl acid (Merck, 37%) and 0.1N NH₄OH (Merck 25%). A low pressure UV lamp, 0.8 m in length was installed 10 cm above the samples surface and the light intensity were 0.9 J s⁻¹m⁻² measured by a Radiometer at 300 to 400 nm (Hagner EC1-UV-A). All analysis were done according to the standard methods (14).

Experimental set-up and measurements

In this research, the photochemical cell consisted of five 250 ml beaker and 5 magnetic stirrers that used for stirring the samples. The temperature of reactors was controlled at 20° C. In the first phase, the beakers were filled with 200 ml of phenol solution (100 mg L⁻¹) and in separate stages were contacted with UV, TiO₂ and combination of UV/TiO₂. Also the effects of various parameters include contact time (1, 3, 5, 7 and 9 h), pH (3, 7 and 11) and amount of TiO₂ (0.5 and 1.0 gr L⁻¹) in the removal efficiency of phenol were investigated. The polished aluminium was used as the reflective material to protect the samples in the absence of radiation.

The samples were withdrawn from the beakers with the syringe (10 ml) before and after the photochemical reaction and the residual phenol was measured. Before phenol measurement, the samples containing TiO_2 were centrifuged at 5000 rpm for 10 min, and then the upper liquid layer were sucked with a glass syringe and filtered. Then concentration of phenol in the prepared samples was measured. All experiments were conducted at lab temperature (nominally 20° C). The experimental apparatus as shown in Fig. 1 was set up in Hamadan University of Medical Sciences in 2006.

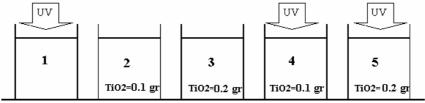


Fig. 1: Schematic of phenol removal photocatalytic pilot

Results

The results from examinations in pH= 3, 7 and 11 as the function of exposed time in the studied processes are shown in Figs. 2-4, respectively. It is found that phenol degradaion efficiency is affected by TiO₂ concentration, UV irradiation and pH of the solution. Also the effect of time variation on removal phenol at different pH values is shown in Fig. 5. The results show that degradation yield in a 9 h period with pH= 3, 7 and 11 has been 59%, 52% and 83 %, respectively.

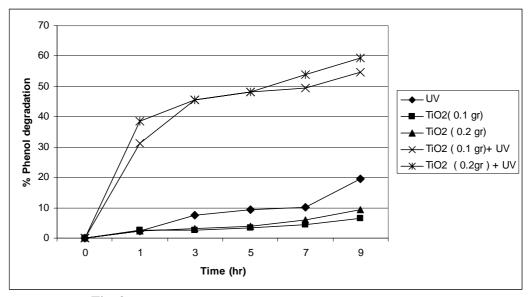


Fig. 2: Removal efficiency of phenol at various conditions (pH=3)

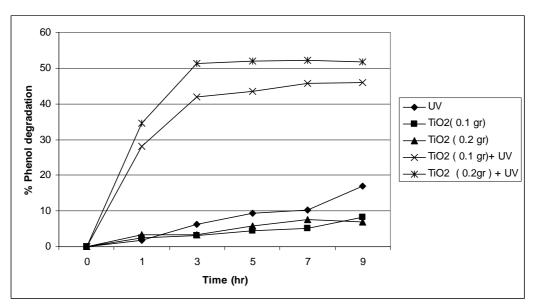


Fig. 3: Removal efficiency of phenol at various conditions (pH=7)

Rahmani AR et al: Investigation of Photocatalytic...

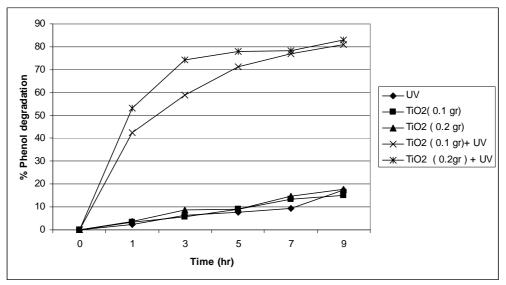


Fig. 4: Removal efficiency of phenol at various conditions (pH=11)

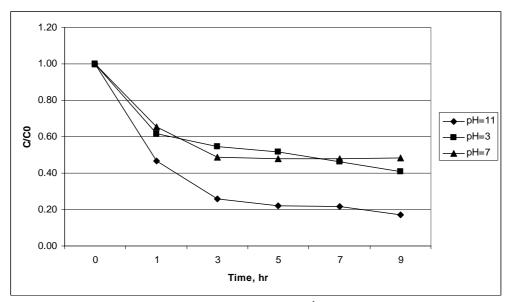


Fig. 5: Effect of time variation on phenol removal (TiO₂=1 gr L^{-1} , initial phenol concentration= 100 mg L^{-1})

Discussion

The photocatalytic degradation of various toxic organic compounds has been proposed as a viable process to detoxify aquatic solutions. Irradiating pulverulent semi-conductors like TiO_2 in suspension or fixed to various supports in aqueous solutions containing organic pollutants, creates a redox environment able to destroy these pollutants. Solar photocatalytic mineralization of organic water

pollutants has a strong potential in the industrial destruction of toxic organics in water as this has been widely demonstrated in recent years, and the applications and target compounds are numerous.

Nowadays, phenol compounds are one of the most common pollutants of water resources. Photocatalytic oxidation of phenol by using TiO_2 as a catalyst and UV ray is one of the developing methods. In this study, photocata-

lytic removal of phenol was investigated by stressing on contact time, pH and initial phenol concentrations. The results from examinations in pH= 3, 7 and 11 as the function of exposed time in the studied processes are shown that phenol degradation efficiency is affected by TiO₂ concentration, UV irradiation and pH of the solution. Also Mansouri and yang reported removal of Cr^{6+} and humic acid in aquatic solutions by application of UV/TiO₂ (15, 16).

By increasing the contact time, efficiency of phenol removal is raised. The most observed yield is related to pH=11 and the least to pH=7. Use of UV ray to degrade phenol has less efficiency. Presence of TiO₂ in these processes can promote removal efficiency, remarkably. The results show that the phenol degradation increases with increasing TiO₂ concentration but the difference neglect able, Sun and et al reported that TiO₂ concentration affected the phenol oxidation by visible light (17). Phenol was more effectively eliminated by using combined UV/TiO₂ condition than either than UV or TiO_2 separately. Lee et al. reported a similar results for the removal of organic compounds (18).

The results show that in all mentioned pH scales, UV and TiO_2 in separate stage can not degrade phenol remarkably. In use of UV and TiO_2 synchronize, pH has an important effect. Yang and Iliev reported that the increase of pH, increased the removal efficiency of humic acid and phenol in aquatic solutions (15, 19).

As a result, increasing pH leads to reducing the process time. The process efficiency in pH=11, during 3 h was 74% and by increasing contact time to 9 h, the yield is just 8.8 % developed (3). The reason is that the reaction rate is related to phenol concentration and by going on time, decrease in concentration of phenol results in decreasing the efficiency (1, 2, 4).

Thus, when phenol as a hydroxide possessing material was solute in water bodies with alkali pH, it was converted to phenoxide ion that more degradable than phenol. Conversely in acidic pH, phenol has a little degradability. Since TiO_2 that was used in this study, is a recoverable photocatalyst, UV/TiO_2 process for phenol degradation is compatible with the environmental.

In conclusion, the reaction rates of photocatalytic degradation of phenol were influenced by pH value. Photodegradation can be an alternative treatment method for those contaminants resistant to conventional methods. Photodegradation can be used for complete mineralization of phenol. Since TiO₂ that was used in this study, is a recoverable photocatalyst, UV/TiO₂ process for phenol degradation is compatible with the environmental.

Acknowledgments

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