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Invited feature article

Treatment of phenol in petrochemical wastewater considering turbidity factor by backlight cascade photocatalytic reactor

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ABSTRACT

The toxicity of phenol is such that even in its low concentration in industrial wastewater, it should be removed. Photocatalytic treatment is an appropriate method for treating toxic and difficult to biodegrade organic materials. However, most phenol containing wastewaters such as petrochemical wastewater, contain turbidity that limits photocatalytic treatment usage. To remove phenol from petrochemical wastewater, a novel cascade photocatalytic backlight reactor is developed. In the developed reactor, the effect of four factors including initial phenol concentration, TiO_2 concentration, turbidity, and pH on phenol removal efficiency is investigated using full factorial design. The best removal efficiency was 88% obtained after three hours when pH is 9, initial phenol concentration equals 50 mg/L, and TiO_2 concentration equals 80 g/m^2. The relationship of these parameters on phenol removal efficiency is statistically evaluated using analysis of variance. The significance of reaction parameters is shown as follows: time > initial phenol concentration > TiO_2 concentration > pH. The ANOVA analysis also reveals that turbidity has no effect on phenol removal efficiency.

1. Introduction

Phenol is the primary raw material used for manufacturing many products including herbicides, drugs, paints, cosmetics, and lubricants [1]. From the production volume viewpoint, it is categorized as one of the fifty highly produced materials in the U.S. [2]. Phenol and it derivatives is found in the wastewater of many industries such as refineries, coke making process, and petrochemical factories [1]. Phenol containing substances are toxic, carcinogenic, mutagenic and lead to teratogenic defects [3]. Due to its harmful effects on health, phenol is on the USEPA[1] priority pollutants list [4]. The maximum permissible phenol concentration in treated effluent allowed by the USEPA is up to 0.1 mg/L [5].

To confront and prevent increasing water consumption and deficiency of water resources, treated effluent recycling is considered as a strategic approach to sustained management of water resources around the world [6]. Various methods studied for phenol treatment include biological treatment [7], electrochemistry [8], absorption [9], and Cavitation [10]. During the past few decades, the advanced oxidation process (AOP) has been considered for phenol treatment by many researchers and wastewater treatment plant developers. AOPs (e.g., Cavitation, Photocatalytic oxidation, Fenton chemistry) have been successfully employed for elimination or degradation of difficult to biodegrade pollutants or for converting these pollutants to compounds with shorter chains treatable in ordinary biological methods [11]. The heterogeneous photocatalytic oxidation (HPO) process, using catalysts such as TiO2 and ZnO as well as and UV light has demonstrated promising results for the degradation of persistent organic pollutants and produces more biologically degradable and less toxic substances [12]. The advantages of the photocatalytic degradation method [13] include: 1) complete mineralization, 2) lack of waste disposal problem, 3) low cost, and 4) applicability in natural temperature and pressure conditions.

The amount of UV radiation reaching the photocatalyst surface is one of the main factors in the appropriate performance of a photocatalytic reactor. The importance of this issue is more pronounced when considering turbidity of phenol containing wastewaters such as paper and cardboard industries making 4500 NTU [14], refineries producing 30–100 NTU [15], coke making 80 NTU [16], and petrochemical industries yielding 208 FTU [17].

Common photocatalytic reactors are categorized into two groups based on photocatalyst situation: reactors in which the photocatalyst is suspended and reactors in which the photocatalyst

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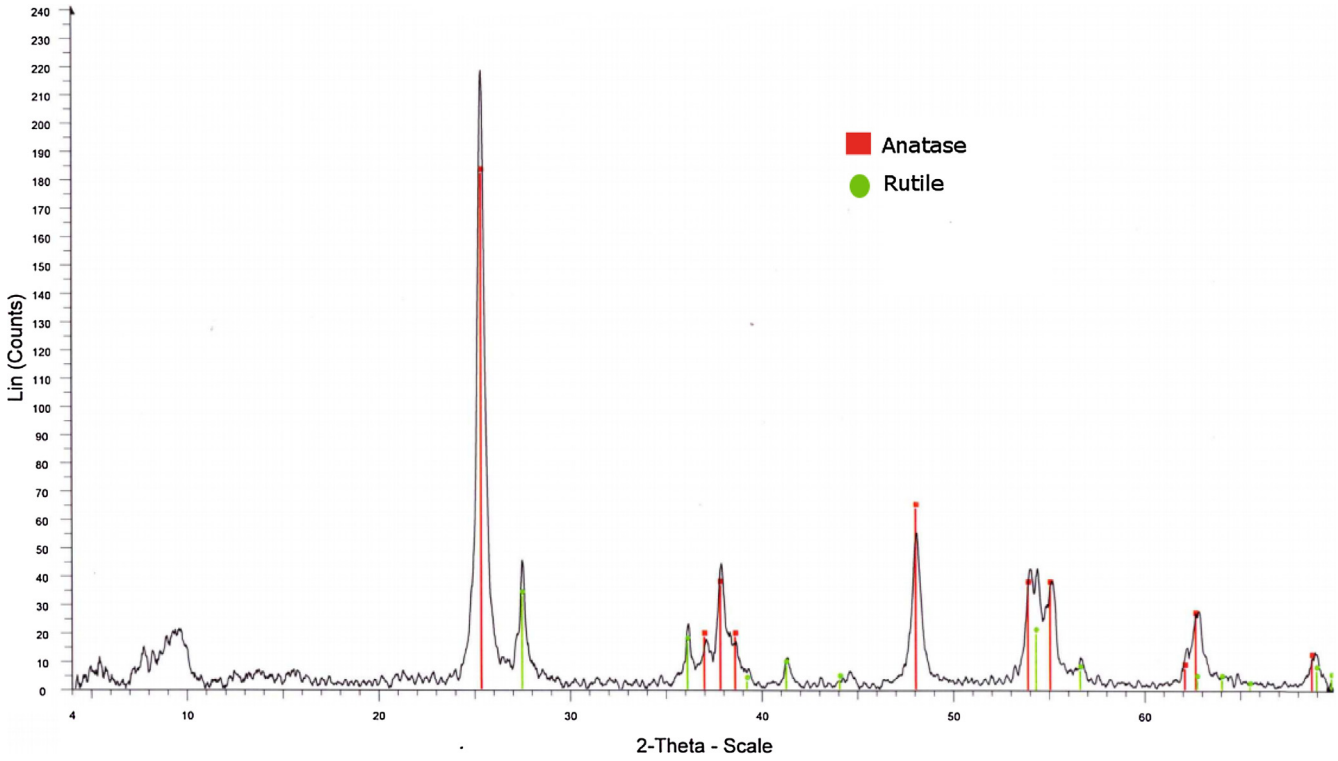

Fig. 1. XRD pattern of TiO_2 nanoparticles.

is immobilized on a surface [18]. The reactor with the suspended photocatalyst has been investigated for treating phenol containing wastewaters [19,20] and turbid wastewaters [21]; however, the configuration with suspended photocatalyst needs an additional separation unit downstream because the necessity of recovering photocatalyst powder and this increases treatment process expense [22]. On the other hand, treatment with immobilized photocatalyst reactors let wastewater flow continuously and is more economical than the suspended one. However, light absorption by wastewater is considered a serious problem in this type of reactor. Treatment of phenol containing wastewaters with the fixed bed photocatalytic reactor has been studied [23,24], but there has been no research thus far on turbid phenol containing wastewater treatment with fixed bed photocatalytic reactors.

This research's objective was to develop the innovative backlight cascade photocatalytic reactor for removing phenol from petrochemical wastewater considering the turbidity factor. The reactor parameters such as TiO_2 concentration, initial phenol concentration, pH, and turbidity were studied.

2. Materials & methods

2.1. Materials

Tecnan Spain provided titanium dioxide nanoparticles with average particle size of 10–15 nm and mostly anatase are used in this study. Fig. 1 shows XRD[2] pattern of the used TiO_2. Based on Fig. 1 the phase of the used TiO2 is 85% anatase and 15% rutile. Phenol (purity over 99%), NaOH, and HCl (for pH adjustment) of analytical reagent grade were purchased from Merk Co. Synthetic wastewater was made by adding phenol in different concentrations to the deionized water. The 160 w Narva Black Light UVA provided UV irradiation, and kaolinite was used to cause turbidity [25].

2.2. Experiments

2.2.1. TiO_2 immobilization method

For treatment of turbid wastewater using photocatalytic process a new reactor configuration proposed. In this configuration photocatalyst coated on transparent surface and exposed to UV radiation from below while wastewater was flowing above the coated surface. To provide appropriate UV-A passage, Plexiglass was selected for the TiO_2 coating [26]. To fix the TiO_2 on plates, Delnavaz et al.'s [23] method was used. In this method, epoxy concrete sealer immobilizes TiO_2 nanoparticles on the surface. For preparation of TiO2-deposited Plexiglass the following procedure is followed. First 100 mL of epoxy concrete sealer was mixed with 1 L of deionized water and the mixture was strongly stirred for 10 min. Sufficient amount of prepared emulsion was poured on the plate surface and spread with a putty scraper. The plate was let to dry in room temperature for 120 min. As a result a thin layer of semi-dry epoxy concrete sealer was created on the Plexiglass surface, which acts as the site for TiO_2 stabilization. Regarding to desired photocatalyst concentration on the Plexiglass, the required amount of TiO_2 was added to 150 mL deionized water and sonicated for 5 min in ultrasonic bath, then it was poured on the Plexiglass surface and dried for 24 h. The dried plate was washed with pure water to eliminate the excess of the catalyst. To reach the photocatalyst, the UV light should cross the Plexiglass plate and the epoxy concrete sealer. Tests with UV meter show the transparent epoxy concrete sealer only decreases the UV-A ray intensity up to 16% which makes it suitable for the reactor with backlight. Fig. 2 shows the SEM[3] image of coated TiO_2 nano-

[2] X-Ray Diffraction.

[3] Scanning electron microscope.