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Decomposition of phenol in aqueous solution using synthesized anatase phase TiO_2

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ABSTRACT

Phenol is used in the industry as a starting material for chemical synthesis. This type of compounds can end up as pollutants in wastewater. In this research Photocatalytic degradation of phenol in aqueous solution was studied using synthesized TiO_2 prepared by precipitation of $TiCl_4$ solution. XRD and TEM techniques used for characterization of the prepared sample and it is shown that prepared sample contain anatase phase TiO_2 with average crystallite size of 10 nm. The effects of operating parameters such as catalyst dosage, pH of the solution and light intensity on photodegradation process were examined to achieve the optimum condition for degradation of phenol.

KEYWORDS

Phenol;
TiO_2;
UV irradiation;
Photocatalyst;
pH;
Light Intensity.

INTRODUCTION

As the standard of living is increasing, the pollution in all areas of air, water, and soil is increasing. This is due to many factors such as the growth of industrial for the production of new materials, growth of population worldwide, and hence, the consumption of more and more chemicals for different purposes. On the other hand, the demand for better and healthy environment is increasing and it is now the priority in human life. Major concern with water and wastewater pollutants is the existence of organic constituents harmful to human, animal, and in general to the life.

In modern industries such as petrochemical and chemical plants phenol compounds are widely used and have become common pollutants in water bodies. Due to their stability and bioaccumulation, they remain in the environment for longer periods[1].

Phenol is one of the wastewater compounds that is hazardous for the environment and human. Various ways have been done for treating the wastewater or polluted water. Traditional wastewater treatment techniques for phenol removal are activated carbon adsorption, chemical oxidation and bio-logical digestion[1]. However each technique has some limitations and disadvantages[2]. Photocatalytic Process is ones alternative, which expected to be able to solve this problem. It was reported in the several researches that phenol could be removed by photocatalytic process[3]. Photocatalytic process is relatively new technology in the wastewater treatment, by using semiconductor as catalyst such as TiO_2. This process has many advantages compared to the other processes due to the inert product of the process is harmless for environment[3,4].

The main objective of this research is to study the effect of operating parameters like catalyst dosage, pH

of solution and light intensity on the degradation of phenol to achieve an optimum conditions and practical way for industrial scale.

EXPERIMENTAL

Preparation of catalyst

Nanocrystalline TiO_2 which was used in this research prepared by precipitation of aqueous $TiCl_4$ solution using ammonia as precipitation agent. Prepared TiO_2 was aged for 6 h at above 90 ^{0}C and calcinated at 600 ^{0}C for 4 h.[5].

Characterization

The XRD patterns were obtained using D_8–Advanced Bruker powder diffractometer operating in reflection mode with *CuKa* radiation, and diffracted of 0.02° 2Θ. The Scherrer equation was applied to estimate crystalline size[6]. Transmission electron micrographs were obtained using Philips EM 208 microscope operating at accelerating voltage of 100 kV. The samples for electron microscope were prepared by grinding and subsequent dispersing the powder in methanol and applying a drop of very dilute suspension on carbon-coated grid. The suspensions were dried by slow evaporation at ambient temperature.

Material and methods

Phenol solution was obtained from Merck Chemical Co. was prepared in 50 mg/L Concentrations. The concentration of phenol was measured at 500 nm by a Shimatsu spectrophotometer. pH adjustments in samples were done by using 0.1 N HCl acid (Merck, 37%) and 0.1N NHOH (Merck 25%)

Photoreactor

Experiments have been performed at room temperature in a static batch photoreactor of ca. 0.5 L, consisting of Pyrex cylindrical flask open to air. A magnetic stirrer guaranteed oxygen from atmospheric air and satisfactory mixing of reacting mixture with the suspension. Irradiation set was prepared by artificial light using two UV-lamps (15 W. λ=245 nm) intensity of UV light was adjusted by varying the position of lamps. The light intensity was measured by Lux- UV- IR meter (Leybold Co.).

Procedure

0.2 L of the reacting mixture was prepared by dissolution of phenol in distilled water (50 ppm). Catalyst dispersed in the solution. The suspension was first stirred in a dark for 60 min before irradiation. This was sufficient to reach an equilibrated adsorption concentration. Therefore this time has been selected for the initial period to UV-irradiation to make sure that the initial degradation initiates at the equilibrium of adsorption. 3 ml of solution was sampled at various time intervals; it was centrifuged and then filtered through a Millipore membrane Filter (pore size 0.2m) prior to analyses.

RESULTS AND DISCUSSION

Figure 1 indicates the XRD pattern of prepared TiO_2 catalyst after calcinations, it is important to note that calcination of prepared sample increases its crystalline structure and crystallite[5]. It is understood form XRD graph that the catalyst contain only anatase phase and according to the Scherrer equation its average crystallite size is about 10 nm. This results also proved by TEM graph of TiO_2 (Figure 2) which shows crystallites size are about 10 nm.

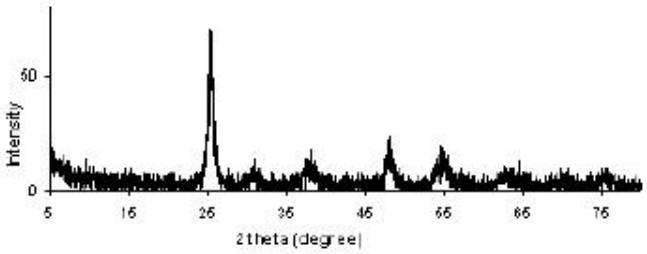

Figure 1 : XRD pattern anatase phase TiO_2 which was aged for 6 h at temperature above 90 °C and calcinated at 400 °C for 4 h.

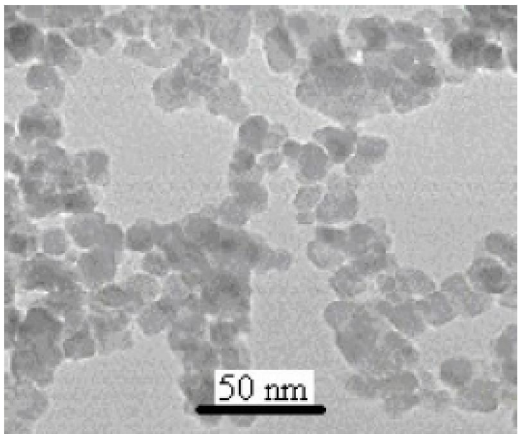

Figure 2 : TEM graph of TiO_2

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In order to determine the optimal amount of photocatalyst dosage for decomposition of phenol, some experiments were performed at the natural middle pH with different catalyst weight. Light intensity for these experiments was 30 W/m2.

It could be seen from Figure 1 that the degradation rate appeared to increase rapidly with increasing the catalyst concentration from 0.5 to 3 gr/l, probably due to the increase of active sites with the suspension of catalyst loading. The most effective decomposition of Phenol was observed with the catalyst amount equal to 3 g/l, any further increase of the catalyst concentration result in decreasing the rate of degradation. This phenomenon may be explained by the light scattering, caused by the light proof suspended catalyst[7,8]. Indeed, with increasing the catalyst loading, the light penetration through the solution, and hence, the photoactivated volume of the Suspension shrinks. In such a condition, part of the catalyst surface probably became unavailable for photon absorption and phenol adsorption, thus bringing little stimulation to the catalytic reaction[8,9].

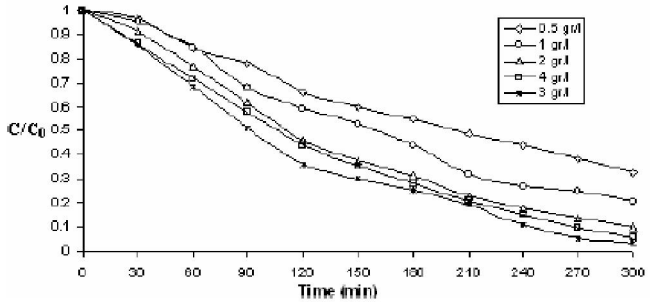

Figure 3 : Effect of catalyst dosage on degradation of phenol

Figure 2 shows the phenol removal efficiency as a function of pH, the effect of pH on photodegradation efficiency of phenol was examined in the range of 3-9 in an aqueous TiO_2 suspension with the optimum catalyst dosage. The results showed that pH of the solution had direct influence on the heterogeneous photocatalysis process. In alkaline solution photodegradation efficiency was more than that in acidic solution. In alkaline medium, high level of hydroxide Ions induced the generation of hydroxyl free radicals, which came from the photooxidation of $OH^?$ by holes forming on the TiO_2 surface. Since hydroxyl free radical is the dominant oxidizing species in the photocatalytic process, the degradation of phenol is therefore accelerated at higher solution[9,10].

Also 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[11,12].

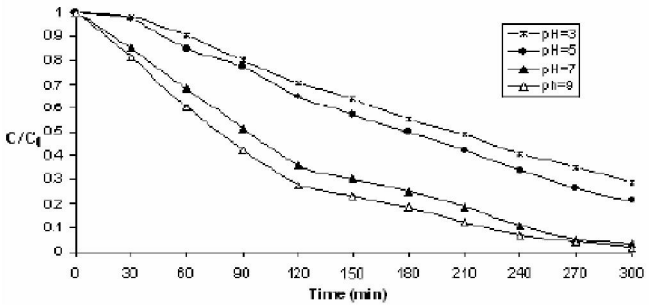

Figure 4 : Effect of pH on degradation of phenol

The influence of UV light intensity on degradation process for removal of phenol is presented in Figure 3. It is evident that degradation increases with increasing the light intensity because the UV irradiation generates the photon required for the electron transfer from the valence to the conduction band of a semiconductor photocatalyst[13,14]. The rate of degradation increases when more radiation falls on the catalyst surface and hence more hydroxyl radicals produced.

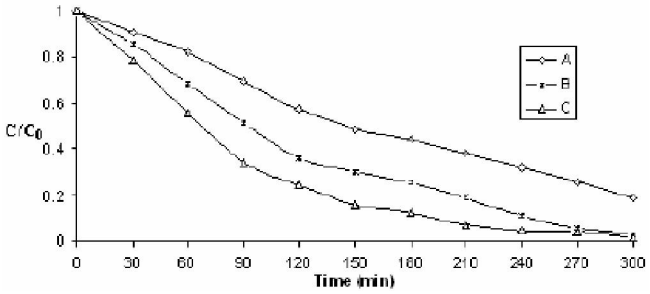

Figure 5 : Effect of light intensity on degradation of phenol A) I_0=25 W/M^2 B) I_0=30 W/M^2 C) I_0=35 W/M^2

CONCLUSION

Nanocrystalline titanium dioxide was synthesized by precipitation of aqueous $TiCl_4$ solution. Prepared TiO_2 aged for 6 h at temperature above 90 ^{0}C and calcinated at 400 ^{0}C for 4 h. XRD and TEM tests showed formation of anatase phase TiO_2 with average crystallite size of 10 nm. It was used for photocatalytic degradation of Phenol under UV light. Several experiments carried out to analyze the effect of

operation parameters like catalyst dosage, pH of solution and light intensity on degradation process. Results of experiments indicated that the optimum dosage for catalyst was 3 gr/l and any increasing in catalyst amount leads to decreasing the photocatalytic degradation due to the decreasing the light penetration. It is understood that the reaction efficiency in alkaline solution is more than acidic solution and increasing the pH of solution led to increase in the degradation progress. It was also shown that intensity of UV light has important influence in degradation process which its increasing results in increasing the degradation rate.

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REFERENCES

[1] F.Akbal, A.N.Onar; Environ.Monit.Assess., **83**, 295 **(2003)**.
[2] K.H.Wang, Y.H.Hsieh, M.Y.Chou, C.Y.Chang; Applied Catalysis B: Environmental., **21**, 1 **(1999)**.
[3] J.Theurich, M.Linder, D.W.Behnemann; American Chemical Society, Langmuir., **12**, 6368 **(1996)**.
[4] Y.Ohko, I.Ando, C.Niwa, T.Tatsuma, T.Yamamura, T.Nakashima, Y.Kubota, A.Fujishima; Environ Sci Technol., **35**, 2365 **(2001)**.
[5] H.Eslami Namin, H.Hashemipour, M.Ranjbar; International Journal of Modern Physics B., **22**, 3210 **(2008)**.
[6] S.Bakardjieva, J.Subrt, V.Stengl, M.J.Dianez, M.J.Sayagues; Applied Catalysis B: Environmental., **58**, 193 **(2005)**.
[7] J.G.Blanco, R.Sixto Malato; Handbook of 'Solar Detoxification', Natural Sciences, Energy, Including world solar programme, Unesco, 1996 **(2001)**.
[8] G.A.Eplingand, C.Lin; Chemosphere., **561**, 46 **(2002)**.
[9] C.C.Wong, W.Chu; Chemosphere., **50**, 981 **(2003)**.
[10] D.F.Ollis; Environ.Sci.Technol., **19**, 480 **(1985)**.
[11] J.K.Yang, S.M.Lee; Chemosphere., **63**, 1677 **(2006)**.
[12] V.Ilive, A.Mihayova, L.Bilyarska; Mol.Catalysis A Chemical., **184**, 121 **(2002)**.
[13] M.A.Behnajadi, N.Modirshahla, R.Hamzavi; J.Hazard.Matter.B., **226**, 133 **(2006)**.
[14] M.R.Hoffmann, S.T.Martin, W.Choi, D.W.Behnemann; Chem.Rev., **95**, 69 **(1995)**.