

Efficiency removal of phenol, lead and cadmium by means of UV/TiO₂/H₂O₂ processes

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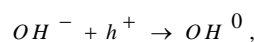
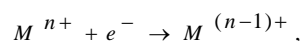
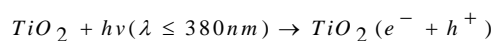
ABSTRACT: A variety of processes can be used in treatment of industrial wastewaters. The relatively newest of which is photo catalysis with titanium dioxide which may also be used plus hydrogen peroxide to improve the treatment rate. In this study, photo catalysis/ hydrogen peroxide processes had been employed for the removal of phenol, lead and cadmium by three different pHs of 3.5, 7 and 11. The treatment tests were also accomplished without UV irradiation. In both experiments, the variables were pH and concentrations of reagent chemicals, but the detention time was kept constant (180 min). Results indicated that the optimum efficiencies of phenol and Cd removal were 76 % and 97.7 % at pH=11, respectively, and for lead, it was 98.8% in all pHs. In other words, no pH dependency was regarded for lead treatment. These results were all obtained by simultaneous use of UV irradiation with 3 mL/L H₂O₂ and 0.8 g/L TiO₂. Finally, the best pH for treatment, when all the three contaminants are presented is considered to be at 11. These results should be regarded by all industrial treatment plants which have experienced the problem of these three special contaminants in their effluents.

Key words: Phenol, heavy metals, titanium dioxide, hydrogen peroxide process, photo catalysis

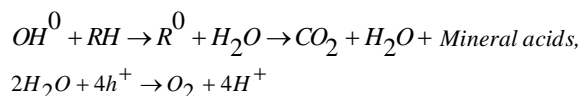
INTRODUCTION

In regard with hazardous effects of organic and mineral pollutants, today various methods are used for their removal from Industrial wastewater. One of the relatively new methods for this purpose is photocatalysis process by TiO₂ (Desrosiers, *et al.*, 2006). Titanium dioxide has a good capacity to degrade organic compounds (Akbal, *et al.*, 2003) by oxidation and also remove heavy metals by reduction of them (Prairie, *et al.*, 1998). It is relatively inexpensive, insoluble in water and nonpoisonous (Vidol, *et al.*, 1999). The process of photocatalysis is relatively simple. Light energy from ultraviolet radiation in the form of photons, below 390 nm, excites the electrons on the surface of titanium atoms suspended in the contaminated water (Poudyal, *et al.*, 2006). On the other hand, when TiO₂ is illuminated with the light of $\lambda < 390$ nm, electrons are promoted from the valence band to the conduction band of the semi-conducting oxide to give electron-hole pairs. The valence band (h^+_{VB}) potential is positive enough to generate hydroxyl radicals at the surface and the conduction band (e^-_{CB})

potential is negative enough to reduce molecular oxygen. (Daneshvar, *et al.*, 2004) The hydroxyl radical is a powerful oxidizing agent and attacks organic pollutants present at or near the surface of TiO₂. It causes photo oxidation of pollutants (Bekkouche, *et al.*, 2004). By contrast, photo catalytic reduction takes place when hole scavenger is adapted, and the photo generated electrons are allowed to undergo cathode reaction. A potential and very attractive practical application of light-driven photo catalytic reduction is the deposition of harmful toxic metal, and recovery of noble metals from industrial waste effluents. The metals are deposited onto the surface of semiconductor catalyst powders, and can subsequently be extracted from the slurry by mechanical and/or chemical means (Chen, *et al.*, 2001). Therefore, the following redox reaction cycle (photo catalytic oxidation and reduction) takes place:



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Where M represents the metal ion and RH organic compounds. In 2001, Vohra (Vohra, *et al.*, 2002) reported of his research about photo catalytic degradation of nitro toluene in aqueous TiO₂ suspension. This process was employed to treat aqueous 2,3 and 4 nitro toluene pollutants. Another study was carried out by Kostasiantinou (Konstantinou, *et al.*, 2002). In this study, the light-induced degradation of propachlor (2-chloro-Nisopropylacetanilide) under simulated solar irradiation has been investigated in aqueous solutions containing TiO₂ suspensions as photo catalysts. The study focuses on the identification of possible intermediate products and on the determination of inorganic ions formed during the process. Although many researches have been performed about use of photo catalysis processes in treatment of industrial wastewaters, this study should be regarded novel, because the efficiency of UV/TiO₂/H₂O₂ process has been determined for the first time in simultaneous removal of Phenol “as an organic pollutant “and heavy metals “Pb and Cd as two inorganic pollutants “under different conditions of treatment.

MATERIALS AND METHODS

Instruments for analysis

Atomic absorption spectrophotometer, Thermo Jarrell Ash model SH22 for heavy metals analyses. 2.

UV/VIS spectrophotometer model Shimatzu 1700 For Phenol measurement 3. Magnetic stirrer model Hanna, 4. Ultraviolet lamp (medium pressure) 300 W, French ARDA model 5. Digital Balance model Sartorius 6. pH meter model CG824 Schott.

Chemicals

The reagents and synthetic solutions used in this study were all prepared by use of analytical grade chemicals, which were supplied from MERK Co. as follows: Phenol, Lead nitrate, Cadmium nitrate, Sodium hydroxide, Hydrogen peroxide 35 % W/V, Nitric Acid, Sulfuric acid, Potassium dehydrogenate phosphate, Potassium hexa cyan ferric and 4-amino, 2,3 dimethyl, 1 phenyl, 3-pyrazolin. Other chemicals used were titanium dioxide, Degauss mark, Particles with average diameter of 30 nanometer having 50 m² area/g and potassium hydrogen phosphate which was supplied from Aldrich Co.

Batch reactor description

The treatment system consisted of rectangular glass reactor of 20 × 20 × 17 Cm dimensions, and a larger chamber as cooling bath (Fig. 1) for circulating cold water around the reactor. A 300 watts low pressure UV lamp inside a quartz jacket was submerged in the reactor to provide better irradiation of water samples. This reactor had been operated continuously, and stirred by use of a simple magnetic stirrer.

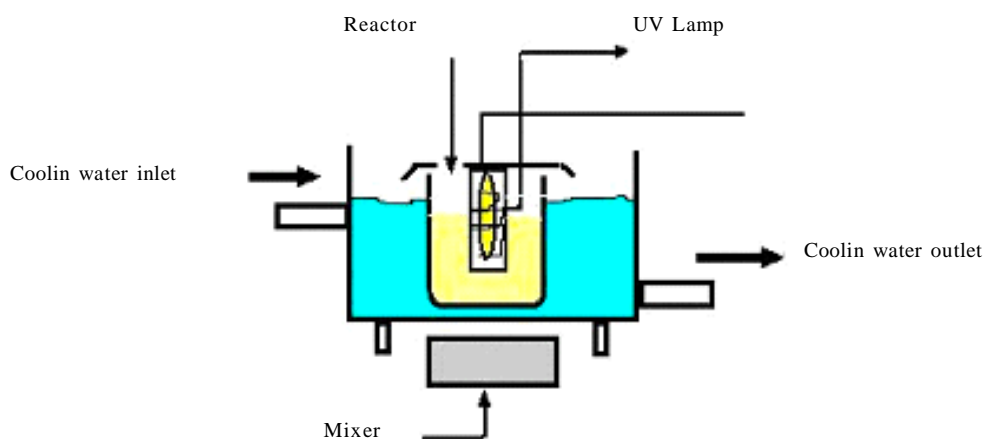


Fig. 1: Designed reactor in experimental stages

Table 1: H₂O₂ and TiO₂ concentration without UV lamp application

H ₂ O ₂ (ml/L)	3	2	1.1	0
TiO ₂ (g/L)	0.8	0.3	0.1	0

Table 2: H₂O₂ and TiO₂ concentration with UV lamp application

H ₂ O ₂ (ml/L)	2	1.1	0	0	0
TiO ₂ (g/L)	0.3	0.1	0.8	0.1	0.05

Samples

For making samples with concentration ranges similar to industrial effluents, three stock solutions of Phenol, Lead and Cd were first prepared according to directions outlined in Standard Method (Clesceri, *et al.*, 2000). Then the desired solutions were made by successive dilution of the stock solutions by de ionized water. Concentrations used for this study were 500 mg Phenol per liter and 10 mg/L for each of the metal ions.

Treatment

For bench- scale experiments, synthetic samples of Phenol, Lead and Cadmium had been used instead of industrial effluent samples. All these experiments had been accomplished in reactor with a capacity of 5 liters, and variables studied include pH, TiO₂ and H₂O₂ concentrations. The main two stages of tests were as follows:

Without use of UV lamp: In the first phase, this study tested four different concentrations of chemicals (H₂O₂ and TiO₂) at three different pHs (3.5, 7 and 11) for treatment (Table 1). The detention time of these experiments was 180 minutes. To determine the efficiency of treatment, enough samples were regularly taken before and after chemicals addition and then were analyzed for heavy metals and Phenol measurements. By use of UV lamp, the above – mentioned tests were also accomplished by use of UV irradiation. For this phase of the study, TiO₂ and H₂O₂ concentrations used were somehow different. As shown in Table 2, six concentrations of chemicals at the three same pHs of 3.5, 7 and 11 had been selected for these treatment tests.

RESULTS

Results can be classified as follows:

At the first, effect of pH changes is evaluated. Results of this part of our study can be regarded as treatment levels which are obtainable merely by changes of pH (namely without use of H₂O₂ and TiO₂). These results are presented in Table 3 under the title of stage 1 of the experiments. Secondly, effect of treatment by H₂O₂ and TiO₂ are evaluated .Without UV lamp application for this part of the study which was accomplished without UV irradiation, three concentrations of H₂O₂ (1.1, 2 and 3) had been used. In each of combinations, the

concentrations of Tio2 were 0.05, 0.3 and 0.8 g/L, respectively. The tests had been done at 3 mentioned pHs (Table 3, treatment stages of 2, 3 and 4). In the third steps of experiments, effects of combinations of chemicals and UV light are examined. Results of this part of our study clearly showed the synergistic effects of light on better removal of pollutants by H₂O₂ and TiO₂. As mentioned, these tests had been accomplished by use of six different concentrations of chemicals and in three different pHs of treatment. Results can be observed in Table 3 (treatment stages of 5, 6, 7, 8, 9 and 10). According to the results of this study (Table 3, stages 1 to 4), it should be concluded that Phenol removal is not significant without use of UV light. Besides, Phenol treatment by merely pH changes was not considered a successful process (Table 3, stage 1) and high efficiencies of Phenol removal were obtained only by combination of UV light with TiO₂ (Table 3; stages 5 to 10). The same results were also obtained in previous works (Kito, 1998) and it had been reported that photo catalytic oxidation of same organics as well as reduction of few metals is possible by coupling TiO₂ with UV light. With the increasing of pH, the solubility of metal decreases (Sawyer, *et al.*, 2003).As shown in Table 3 and Figs. 2 to 4, the treatment efficiencies of Pb and Cd removal could be both improved by pH increase. This means that pH treatment by itself had a significant effect on reduction of pollutants such that about 82 % of Lead and 69.5 % of Cd had been removed at appropriate pHs (Table 3, Stage 1). However, by applying photo catalysis process, the removal efficiencies had increased to as high as 98.8 % for lead and 97.7 % for Cadmium at the same appropriate pHs (Table 3; stage 10). This clearly indicates that photo catalysis can also be regarded as an applicable process for metals treatment. As it is shown in Table 3, the efficiency of Phenol degradation could be improved to a certain extant by addition of more H₂O₂ and TiO₂. By increasing the pH of treatment, it should be possible to increase the removal rate of phenol and metals. By applying UV light and TiO₂, Phenol could be degraded very well, and as shown in Table 3 (treatment stages of 5, 6 and 7), treatment was further improved by pH increase.

Table 3: Removal efficiency of phenol, Pb and Cd in pH= 3.5, 7 and 11 in the various stages of experiments

experimental stags	Experiment condition	Removal efficiency								
		pH=3.5			pH=7			pH=11		
		Phenol	Pb	Cd	phenol	Pb	Cd	phenol	Pb	Cd
1	H ₂ O ₂ =0 (mL/L) TiO ₂ =0 (g/l) UV*=0	0.3	24.9	0.3	0.2	63	11.8	0.29	82.1	69.5
2	H ₂ O ₂ =1.1 (mL/L) TiO ₂ =0.1 (g/l) UV=0	7.44	34.9	0.8	6.4	80.3	23.1	6	84.5	72.1
3	H ₂ O ₂ =2 (mL/L) TiO ₂ =0.3 (g/l) UV=0	5.4	36.4	0.9	4.4	55.6	23.5	4	84.5	74.2
4	H ₂ O ₂ =3 (mL/L) TiO ₂ =0.8 (g/l) UV=0	16.8	65	1.3	14	86.3	28.9	16.6	85.7	75.1
5	H ₂ O ₂ =0 (mL/L) TiO ₂ =0.05 (g/l) UV**=1	2.7	84.9	6.3	7.1	87.3	29.5	10	93.5	80.3
6	H ₂ O ₂ =0 (mL/L) TiO ₂ =0.1 (g/l) UV=1	3.71	91.3	10	4.2	92.8	38	12.7	94.7	90.1
7	H ₂ O ₂ =0 (mL/L) TiO ₂ =0.8 (g/l) UV=1	6.2	95.8	21	7.4	95.5	37.1	29.8	96.3	94.1
8	H ₂ O ₂ =1.1 (mL/L) TiO ₂ =0.1 (g/l) UV=1	14	93.3	18.5	22.1	96.6	34	38.5	96.6	95.1
9	H ₂ O ₂ =2 (mL/L) TiO ₂ =0.3 (g/l) UV=1	4.4	95	19	40	94.8	40.3	71	98.8	96.2
10	H ₂ O ₂ =3 (mL/L) TiO ₂ =0.8 (g/L) UV=1	51	96.6	26	44	96.7	46.9	76	98.8	97.7

* without UV lamp ** with UV lamp

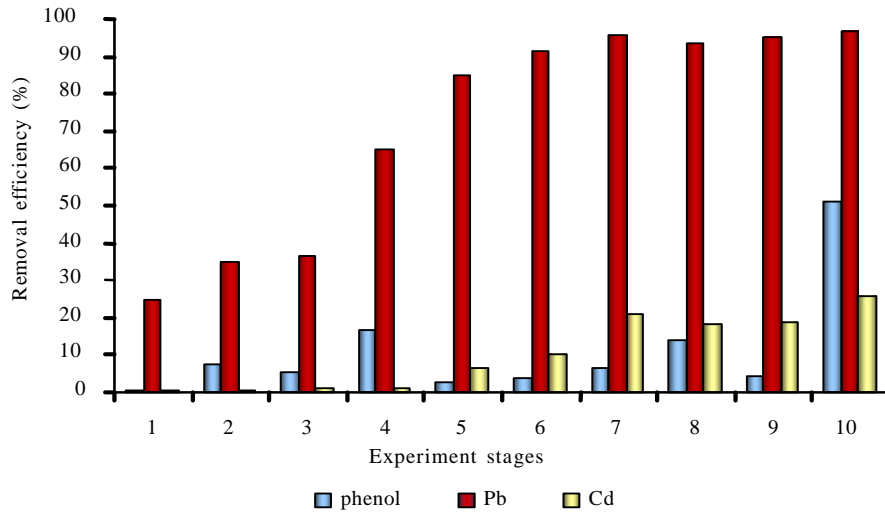
The same trend was also considered for metals treatment and both metals were removed much better when UV light was combined with TiO₂/H₂O₂ (Table 3; stages 8, 9 and 10). In this study, maximum treatment efficiency of Phenol was 76 % which was obtained at the stage 10 of the experiments (Table 3). Consumption of chemicals used for this treatment were 3 mL/L H₂O₂ and 0.8 mg/L TiO₂ and duration of UV irradiation was 180 min. The same conditions were needed for maximum removal of Cd and Pb as well. Comparisons of 10 stage experiments at three pHs of 3.5, 7 and 11 can be seen in Figs. 2, 3 and 4, respectively. According to Fig. 2, in pH=3.5 the efficiency of Pb removal during the stage 5 to 10 by H₂O₂/TiO₂/UV process was very high (maximum 96.6%) but for phenol this efficiency is relatively high (max. 51%) only at the stage of 10. The conclusion

obtained by considering Fig. 3 indicates that the efficiencies of Pb removal were also high during all stages of these experiments (max. 96.7% in the stage of 10) but for Cd and phenol, relatively high efficiencies were obtained only in the stage 10 (for phenol 44 % and for Cd 46.9 %). In Fig. 4, relatively significant removal efficiency can be considered which is about 76% in respect to phenol at the stage of 10 and about 97.7% and 98.8% for Cd and Pb, respectively, at the same stage.

Table 4: Maximum efficiency removal of phenol

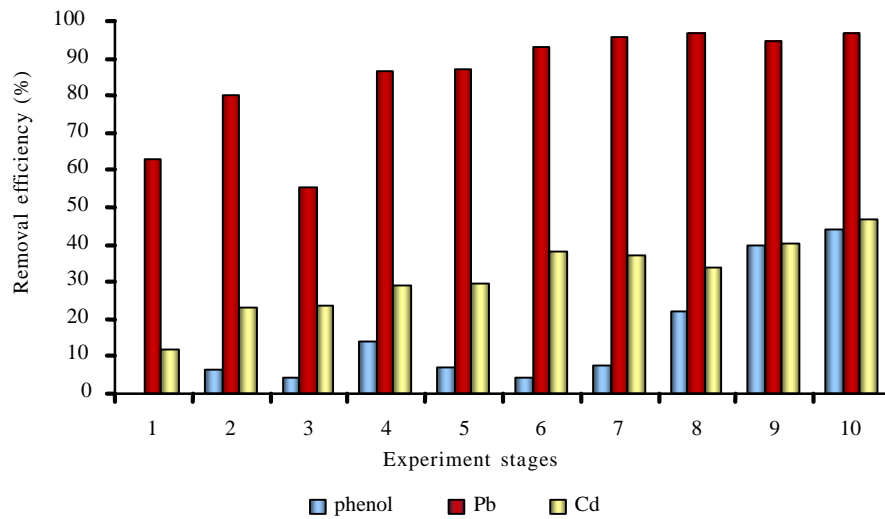
Pollutants	Cadmium	Lead	Phenol
pH			
3.5	26	99.9	51
7	39.9	99.8	44
11	94.5	99.9	76

Pb and Cd at pH=3.5, 7, 11



1: H ₂ O ₂ =0 (mL/L) TiO ₂ =0 (g/L) UV*=0	2: H ₂ O ₂ =1.1 (mL/L) TiO ₂ =0.1 (g/l) UV=0	3: H ₂ O ₂ =2 (mL/L) TiO ₂ =0.3 (g/L) UV=0	4: H ₂ O ₂ =3(mL/L) TiO ₂ =0.8(g/L) UV=0	5: H ₂ O ₂ =0 (mL/L) TiO ₂ =0.05 (g/L) UV**=1
6: H ₂ O ₂ =0 (mL/L) TiO ₂ =0.1 (g/L) UV=1	7: H ₂ O ₂ =0 (mL/L) TiO ₂ =0.8 (g/l) UV=1	8: H ₂ O ₂ =1.1 (mL/L) TiO ₂ =0.1 (g/L) UV=1	9: H ₂ O ₂ =2(mL/L) TiO ₂ =0.3(g/L) UV=1	10: H ₂ O ₂ =3 (mL/L) TiO ₂ =0.8 (g/L) UV=1

Fig. 2: Removal efficiency comparison of phenol, Pb and Cd in various stages of experiments (pH=3.5)



1: H ₂ O ₂ =0 (mL/L) TiO ₂ =0 (g/l) UV*=0	2: H ₂ O ₂ =1.1 (mL/L) TiO ₂ =0.1 (mL/L) UV=0	3: H ₂ O ₂ =2 (mL/L) TiO ₂ =0.3 (mL/L) UV=0	4: H ₂ O ₂ =3 (mL/L) TiO ₂ =0.8 (mL/L) UV=0	5: H ₂ O ₂ =0 (mL/L) TiO ₂ =0.05 (mL/L) UV**=1
6: H ₂ O ₂ =0 (mL/L) TiO ₂ =0.1 (g/L) UV=1	7: H ₂ O ₂ =0 (mL/L) TiO ₂ =0.8 (mL/L) UV=1	8: H ₂ O ₂ =1.1 (mL/L) TiO ₂ =0.1 (mL/L) UV=1	9: H ₂ O ₂ =2 (mL/L) TiO ₂ =0.3 (mL/L) UV=1	10: H ₂ O ₂ =3 (mL/L) TiO ₂ =0.8 (mL/L) UV=1

Fig. 3: Removal efficiency comparison of phenol, Pb and Cd in various stages of experiments (pH=7)

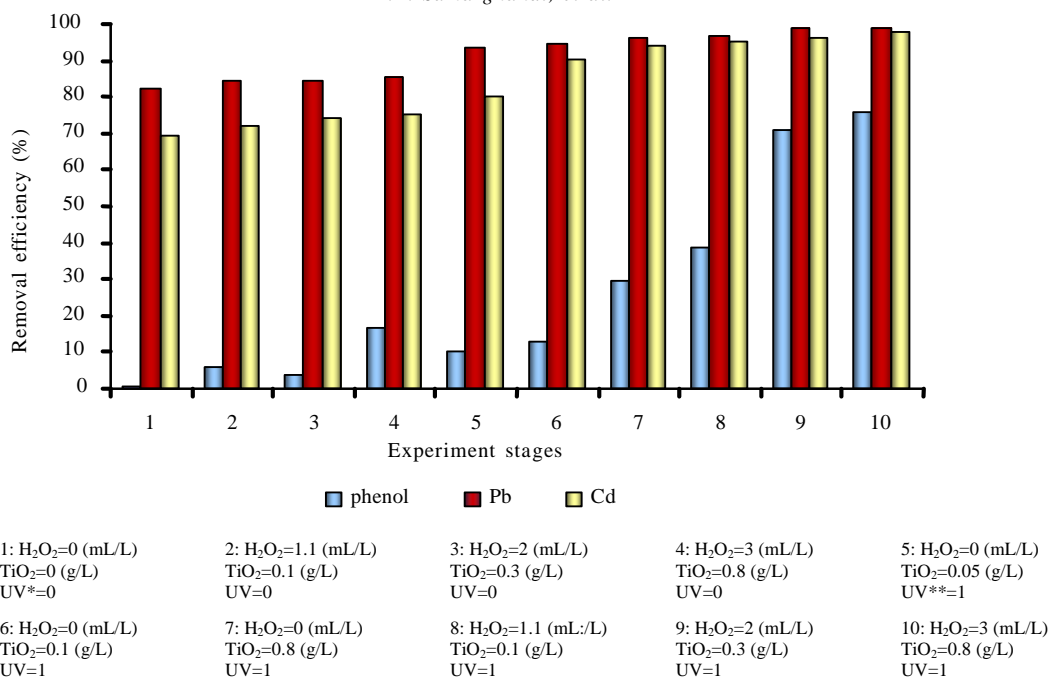


Fig. 4: Removal efficiency comparison of phenol, Pb and Cd in various stages of experiments (pH= 11)

DISCUSSION AND CONCLUSION

It could be concluded that any of the three pHs of 3.5, 7 and 11 can be used for Lead removal. Since, the main purpose of this study was to find a suitable treatment condition by which simultaneous removal of Phenol and two heavy metal could be accomplished, the pH of 11 should be preferred, because, at pH = 11 the efficiencies of treatment by UV/TiO₂/H₂O₂ had become maximized. However, relatively good condition of Phenol had been occurred at other pHs and so it is also feasible to have acceptable treatment results if less efficiencies sufficed (for example, in conditions where initial concentrations of Phenol and Cd are low). Finally, Table 4, which represents the maximum efficiencies obtainable at each pH, helps us to meet the treatment standards so that the industrial wastewater can be treated.

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