Phenolic Based Pharmaceutical Contaminated Wastewater Treatment Kinetics by Activated Sludge Process

Sumana Siripattanakul-Ratpukdi

***Abstract*—This study was to investigate phenolic based pharmaceutical-contaminated wastewater treatment using activated sludge. Activated sludge was grown and acclimated using commercial medium with Chemical Oxygen Demand (COD) of 300 mg/L. Phenol was used as a representative of phenolic based pharmaceuticals. Duplicate batch experiment was operated in horizontal shaker at 150 rpm for 8 hr. The experiment divided into 2 parts: 1) determination of phenol degradation potential by activated sludge at the concentrations of 0-100 mg/L and 2) investigation of phenol-contaminated wastewater treatment efficiency at the phenol concentrations and COD of 0-100 and 200-5,000 mg/L, respectively. COD, phenol and mixed liquored suspended solids (MLSS) were measured hourly. Based on the result from the first part, it was found that the activated sludge could treat phenol at the initial phenol concentrations of 10-100 mg/L for 7% to 100%. Higher phenol concentrations resulted in lower phenol removal efficiencies. From the second part, the activated sludge could treat COD of 23-94% and phenol of 0-98%. The result indicated that both initial phenol concentrations and COD affected wastewater treatment and phenol removal efficiencies. Treatment of wastewater contaminating phenol by the activated sludge followed competitive inhibition kinetic model with V_{max} and K_I of 220 mg/L/hr and 200 mg/L, respectively. Based on MLSS monitoring, activated sludge well grew during the tests.**

***Index Terms*—Activated sludge, competitive inhibition, phenol, wastewater treatment.**

I. Introduction

Phenolic compounds are one of the main components of anti-pruritic, anti-inflammatory, analgesic and blemish removal pharmaceuticals. A large amount of utilized phenolic compound caused phenol contamination in environment including municipal and industrial wastewater treatment systems [1]-[3]. The contamination from pharmaceutical uses and pharmaceutical production could be up to milligram per liter level [1], [4]. Although the wastewater treatment systems could be able to remove phenolic compounds, these toxic compounds at high concentrations significantly inhibited the wastewater treatment performance [2], [3]. In the case of inhibition, the phenolic based pharmaceuticals are likely to enter to the municipal wastewater treatment systems occasionally. The systems were not familiar to toxic xenobiotics including phenolic compounds. Also, microbial cells in the wastewater treatment systems were not acclimated resulting in failure of the wastewater treatment.

The previous works mostly focused on investigation of microbial cultures or systems to remove the phenolic compounds [2], [3], [5], [6]. To the best of our knowledge, no published work has been emphasized on inhibition of existing typical municipal activated sludge (AS) wastewater treatment influenced by phenolic based pharmaceuticals. Therefore, this work aims to investigate potential of AS cells for phenol (representing phenolic compounds) treatment and simultaneous (organic carbon and phenol) treatment. Inhibition kinetics of municipal wastewater treatment system caused by phenol was also determined.

II. Materials and Methods

A. Activated Sludge Cultivation and Synthetic Wastewater

The AS culture was grown using commercial synthetic medium for municipal wastewater treatment with chemical oxygen demand (COD) of approximate 300 mg/L. Reactor of AS was operated in sequencing batch mode with hydraulic and solid retention times of 1 and 30 days, respectively. These retention times were followed the wastewater treatment systems typically practiced. Dissolved oxygen concentration of higher than 1 mg/L was continuously maintained.

It is noted that phenol-free synthetic medium was used for AS cultivation to simulate traditional municipal AS systems. The culture was acclimated for 2 months before use in the batch experiments. Synthetic wastewater contained $C_{12}H_{22}O_{11}$, $CO(NH_2)_2$, and $Ca(H_2PO_4).H_2O$ at approximately COD:N:P of 100:5:1.

B. Batch Wastewater Treatment Experiments

The experiments were duplicate batch tests to determine the influence of phenol on wastewater treatment kinetics. The experiments divided into two parts: 1) potential of phenol removal by AS and 2) treatment of phenol-contaminated wastewater. The first part was to investigate whether typical AS could remove toxic substance (phenol). Phenol solution at concentrations of 0-100 mg/L was applied. In the second part, the synthetic wastewater (COD of 200-5,000 mg/L) supplementing phenol (0-100 mg/L) was used to simulate the contaminated wastewater. This part was performed for determining simultaneous (phenol and COD) treatment by AS.

Experimental setup used for both parts was the same. The reactors containing mixed liquor suspended solids (MLSS) of

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approximately 1,000 mg/L were operated in horizontal shaker at 150 rpm for 8 hr. It is noted that the 8-hr tests were conducted followed conventional AS wastewater treatment process (normally 3-8 hr) [7]. The wastewater samples (10 mL) were taken at one-hour interval for entire experiment to measure soluble COD, MLSS and phenol concentrations. The wastewater treatment efficiencies and kinetics were determined.

C. Analytical Procedures

COD and MLSS were measured according to standard methods [8]. After filtering the water sample using GF/C filter glass paper, the soluble COD was measured by potassium dichromate digestion method. Solid retaining on the glass paper was used for measuring MLSS. Phenol was measured by colorimetric method followed APHA et al. (1998) [8]. The samples were measured using UV-VIS spectrophotometer at wavelengths of 500 nm.

III. Results and Discussion

A. Potential of Phenol Removal by AS

The experiment was conducted at the initial phenol concentrations of 0 (control), 10 and 100 mg/L as results shown in Fig. 1. No phenol was detected in the control test. From the tests at the phenol concentrations of 10 and 100 mg/L, phenol continuously decreased for entire of the experiment. At the end of the experiment, phenol was removed for 100.00 and 7.30% from the tests at the phenol concentrations of 10 and 100 mg/L, respectively.

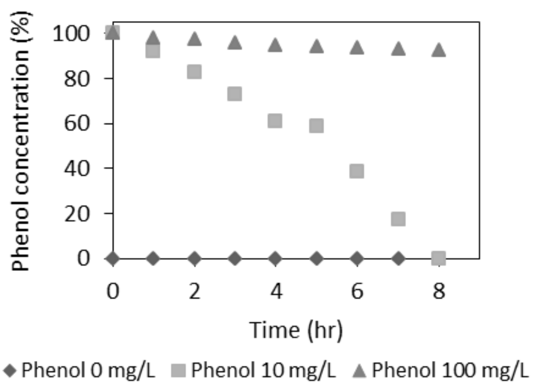

Fig. 1. Phenol removal by activated sludge.

Some previous works found that bacterial cultures could use phenol as a growth substrate even up to concentrations of 10,000 mg/L [6], [9], [10]. In this study, based on the result of the test at the phenol concentration of 10 mg/L, it is clear that AS could degrade and use phenol as a sole carbon source similar to the previous work [6], [9], [10]. Additionally, some previous works reported phenol adsorption ability of AS [11], [12]. Hence, besides biodegradation, some portion of phenol may be adsorbed on AS.

However, the removal performance significantly decreased while the phenol concentrations increased. This phenomenon was self-inhibition typically found in organic biodegradation. Moreover, the compound, phenol, is a toxic substance; therefore, this growth substrate (phenol) at high concentration (100 mg/L) could be toxic to AS resulting in lower phenol removal efficiency.

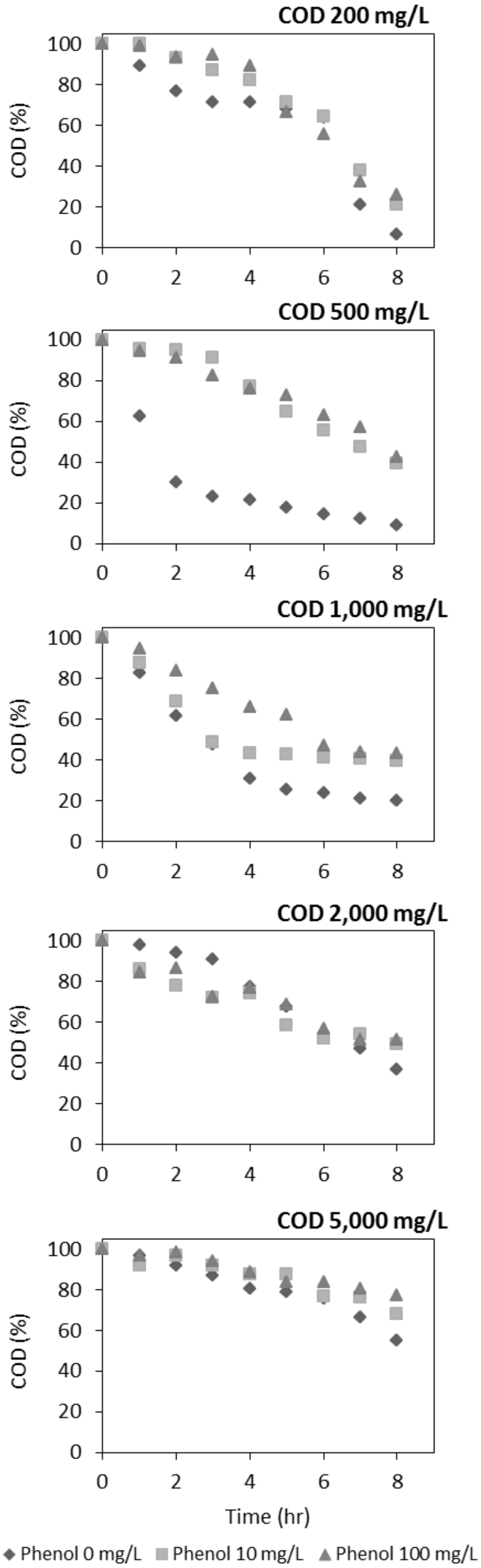

Fig. 2. COD removal by AS with different COD and phenol concentrations.

B. Treatment of Phenol-Contaminated Wastewater

1) COD removal

The experiment was conducted at the initial COD of 200, 500, 1,000, 2,000 and 5,000 mg/L and initial phenol of 0 (control), 10 and 100 mg/L as results shown in Fig. 2. From all tests, COD continuously decreased. At the end of the test, COD from the tests without phenol (0 mg/L) decreased for 45.16-93.62% while the tests with phenol removed COD of 22.58-78.95% (Table I).

TABLE I: COD REMOVAL EFFICIENCY BY AS WITH DIFFERENT COD AND PHENOL CONCENTRATIONS

COD (mg/L)	COD removal efficiency (%) at phenol concentration (mg/L)		
	0	10	100
200	93.62	78.95	74.32
500	91.07	60.71	57.62
1,000	80.00	60.76	56.67
2,000	63.40	51.00	49.02
5,000	45.16	31.75	22.58

The initial COD and phenol concentrations obviously influenced the COD removal. From the tests with the increasing of COD, there were excessive substrate for the AS culture resulting in decreasing in the COD treatment efficiencies. During the tests with phenol, COD treatment performance obviously decreased compared to one without phenol. This is because phenol inhibited COD removal. This situation also found in phenol-contaminated wastewater treatment reported in prior works [2], [3].

2) Phenol removal

The phenol removal from the tests with the initial phenol of 10 and 100 mg/L was shown in Fig. 3. From all tests, phenol continuously decreased. At the end of the test, phenol decreased for 21.94-97.50 and 0.28-14.19% from the tests with the phenol concentrations of 10 and 100 mg/L, respectively (Table II).

TABLE II: PHENOL REMOVAL EFFICIENCY BY AS WITH DIFFERENT COD AND PHENOL CONCENTRATIONS

COD (mg/L)	Phenol removal efficiency (%) at phenol concentration (mg/L)		
	0	10	100
200	0.00	97.50	14.19
500	0.00	46.18	6.13
1,000	0.00	29.51	5.07
2,000	0.00	24.40	1.42
5,000	0.00	21.94	0.28

The result revealed that the synthetic wastewater contained sucrose (used for simulating organic compounds in the wastewater) which is known as an easily-used organic carbon [13]. Sucrose is a simple carbohydrate while phenol is an aromatic hydrocarbon. Typically, microorganisms tended to uptake simple structural substrate. This resulting in lower phenol removal efficiency in the synthetic wastewater compared to that of phenol solution presented in earlier section. In the tests at high phenol concentration (100 mg/L), phenol self-inhibition took place leading to very low phenol removal.

3) MLSS monitoring

For MLSS monitoring, the initial MLSS from all tests ranged from 840 to 1,340 mg/L. It was found that MLSS increased along with the decreasing of COD for all tests (Table III). The AS culture from the tests in this section which was in the synthetic wastewater grew much more than ones in the phenol solution in the previous section since easily-uptaken carbon was supplied.

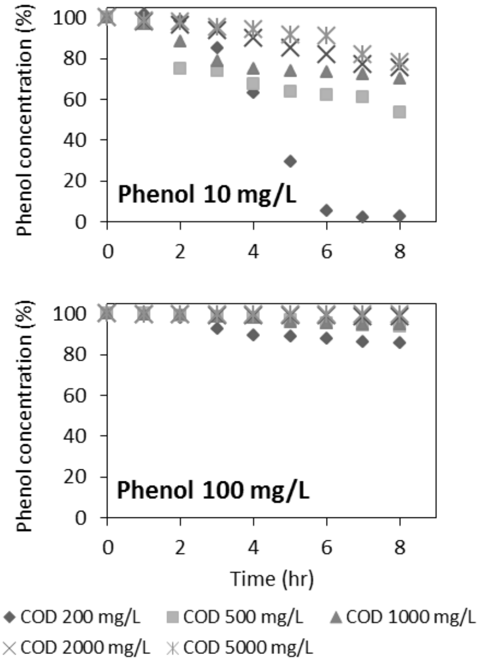

Fig. 3. Phenol removal by activated sludge with different COD and phenol concentrations.

The AS culture well grew in wastewater with and without phenol contamination. Higher COD resulted in higher microbial growth. The growth of AS culture in the tests with phenol was slightly less than ones without phenol. Based on the result, it could say that there was sufficient substrate in the synthetic wastewater resulting in the increasing of MLSS. Phenol did not play an important role on either growth promotion or growth inhibition.

TABLE III: MLSS INCREASING IN TESTS WITH DIFFERENT COD AND PHENOL CONCENTRATIONS

COD (mg/L)	MLSS increasing (time) at phenol concentration (mg/L)		
	0	10	100
200	0.30	0.15	0.25
500	1.51	1.42	0.96
1,000	1.90	1.78	1.45
2,000	2.11	2.30	1.81
5,000	2.86	2.23	2.42

4) Inhibition kinetic modeling

Based on the result presented in earlier sub-section, it was clear that phenol inhibited the wastewater treatment (COD removal) performance. Wastewater treatment kinetics based on Michaelis-Menten enzyme equation was considered. Competitive inhibition kinetic equation was fit (eq. 1);

$$V = \frac{V_{max} \cdot S}{\left(1+\frac{I}{K_I}\right) \cdot K_m + S} \quad (1)$$

where V is the COD removal rate (mg/L/hr); V_{max} is the maximum COD removal rate (mg/L/hr); S is the COD concentration (mg/L); Km is the half saturation coefficient (mg/L); I is the concentration of phenol (mg/L), K_I is the inhibition coefficient (mg/L).

The substrate and removal rate relationship presents in Fig. 4. It was found that V_{max} and K_I were 220 mg/L/hr and 200 mg/L. Phenolic compound based wastewater treatment followed competitive inhibition kinetics has been reported [10], [14]. This is due to phenol competes general organic carbon in wastewater to blind to enzyme governing wastewater treatment at the active site. This resulted in lower wastewater treatment efficiency. The result also agreed to phenol removal ability mentioned earlier. Some portion of phenol was degraded because it was used as a substrate for the AS culture.

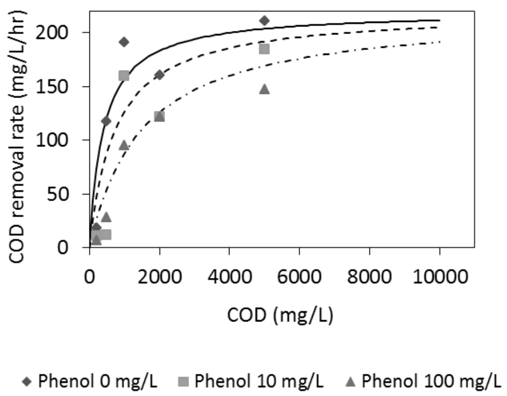

Fig. 4. Wastewater treatment based on Michaelis-Menten kinetics

It could say that phenolic compounds contaminated in wastewater affected the wastewater treatment system (Fig. 2). It is likely that in the situation with moderate phenol contamination (< 100 mg/L) may not obviously influence the systems since AS could use phenol as a substrate. However, it was notice that phenol removal was low, especially in the systems with high COD (Table II). In the real practice, phenol may accumulate in the systems and cause the problem to AS and the system performance later on.

IV. Conclusion

Phenolic based pharmaceutical has contaminated in the environment and influence the wastewater treatment system. In this study, the culture in general AS process could remove all phenol from the test at the concentration of 10 mg/L while phenol removal of only 7% from the test at the phenol concentration of 100 mg/L was observed. This is because of phenol self-inhibition phenomenon.

In phenol contaminated wastewater situation, it was found that both initial COD and phenol concentration apparently affected the wastewater treatment efficiency. COD was continuously treated while only some portion of phenol was removed. The wastewater treatment kinetics followed the competitive enzyme inhibition kinetics.

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References

[1] J. S. Ra, S. Y. Oh, B. C. Lee, and S. D. Kim, "The effect of suspended particles coated by humic acid on the toxicity of pharmaceuticals, estrogens, and phenolic compounds," *Environ. Int.,* vol. 34, no. 2, pp. 184-192, 2008.

[2] P. Praveen and K. C. Loh, "Trioctylphosphine oxide-impregnated hollow fiber membranes for removal of phenol from wastewater," *J. Membrane Sci.*, vol. 437, pp. 1-6, 2013.

[3] G. F. Yang, X. L. Guo, S. X. Chen, J. H. Liu, L. X. Guo, and R.C. Jin, "The evolution of Anammox performance and granular sludge characteristics under the stress of phenol," *Bioresource Technol*., vol. 137, pp. 332-339, 2013.

[4] S. C. Bisarya and D. M. Patil, "Determination of salicylic-acid and phenol (ppm level) in effluent from aspirin plant," *Res. Ind.,* vol. 38, pp. 170-172, 1993.

[5] T. P. Chung, H. Y. Tseng, and R. S. Juang, "Mass transfer effect and intermediate detection for phenol degradation in immobilized *Pseudomonas putida* systems," *Process. Biochem.,* vol. 38, pp. 1497-1507, 2003.

[6] L. Jiang, Q. Ruan, R. Li, and T. Li, "Biodegradation of phenol by using free and immobilized cells of *Acinetobacter* sp. BS8Y," *J. Basic Microbiol.*, vol. 53, no. 3, pp. 224-230, 2013.

[7] L. Y. Kun, *Microbial Biotechnology Principles and Applications*, 2nd ed. Singapore: World Scienctific Publishiing, 2006, ch. 16, pp. 625-666.

[8] *Standard Methods for the Examination of Water and Wastewater*, 20th ed, American Public Health Association/ American Water Works Association/ Water Environment Federation Washington DC, 1998.

[9] P. Khongkhaem, A. Intasiri, and E. Luepromchai, "Silica-immobilized *Methylobacterium* sp. NP3 and *Acinetobacter* sp. PK1 degrade high concentrations of phenol," *Lett. Appl. Microbiol*., vol. 52, no. 5, pp. 448-455, 2011.

[10] O. J. Hao, M. H. Kim, E. A. Seagren, and H. Kim, "Kinetics of phenol and chlorophenol utilization by *Acinetobacter* species," *Chemosphere*, vol. 46, no. 6, pp. 797-807, 2002.

[11] M. N. Moura, M. J. Martin, and F. J. Burguillo, "A comparative study of the adsorption of humic acid, fulvic acid and phenol onto *Bacillus subtilis* and activated sludge," *J. Hazard. Mater.*, vol. 149, no. 1, pp. 42-48, 2007.

[12] H. H. Lo and Y. T. Hung, "Phenol removal by soil adsorption with activated sludge addition," *J. Environ. Health*, vol. 56 no. 4, pp. 21-24, 1993.

[13] S. Xie, J. Liu, L. Li, and C. Qiao, "Biodegradation of malathion by *Acinetobacter johnsonii* MA19 and optimization of cometabolism substrates," *J. Environ. Sci*., vol. 21, pp. 76-82, 2009.

[14] S. S. Adav, D.-J. Lee, and N. Q. Ren, "Biodegradation of pyridine using aerobic granules in the presence of phenol," *Water Res.*, vol. 41, pp. 2903-2910, 2007.

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