



Metal catalysts impregnated on porous media for aqueous phenol decomposition within three-phase fluidized-bed reactor

M. Mungmart^a, U. Kijsirichareonchai^a, N. Tonanon^a, S. Prechanont^a, J. Panpranot^a, T. Yamamoto^c, A. Eiadua^c, N. Sano^d, W. Tanthapanichakoon^a, T. Charinpanitkul^{a,b,*}

^a Center of Excellence in Particle Technology, Faculty of Engineering, Chulalongkorn University, Patumwan, Bangkok 10330, Thailand

^b Energy Research Institute, Chulalongkorn University, Patumwan, Bangkok 10330, Thailand

^c National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan

^d Department of Chemical Engineering, Kyoto University, Katsura, Kyoto 671-2201, Japan

ARTICLE INFO

Article history:

Received 15 February 2010

Received in revised form 26 August 2010

Accepted 17 September 2010

Available online 25 September 2010

Keywords:

Phenol

Metal catalyst

Porous media

Three-phase fluidized bed

ABSTRACT

Performance of metal catalysts to decompose aqueous phenol was experimentally investigated. Comparison of the phenol decomposition rates within three-phase fluidized-bed reactors utilizing only O₃, TiO₂ deposited on silica beads, metal catalyst (Ni or Co) impregnated on mesoporous carbon beads, or O₃ in combination with each catalyst was thoroughly examined. It was found that the use of Co catalyst with the presence of O₃ led to the best removal condition which aqueous phenol was completely decomposed within 10 min ($k = 0.1944 \text{ min}^{-1}$). In contrast, the use of TiO₂ without O₃ resulted in the worst decomposition of phenol ($k = 0.0066 \text{ min}^{-1}$). Some intermediate products, such as hydroquinone and catechol, were also detected but their final concentrations were negligibly low.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Situation of environmental threats due to chemical contamination in public reservoirs has become increasingly serious and directly related to industrial development in various countries for many decades. Among various contaminants, phenol and its derivatives are found in many industrial wastewaters, such as wood preservative, pesticide, textile, paper and dye industries [1,2]. There are requirements of efficient treatment systems, which could meet the regulated standards and economic constraints. In general, there are various processes to treat industrial wastewater containing those organic compounds. However, it is well recognized that phenolic compounds are difficult to be removed by conventional methods, which would be biological decomposition or adsorption by granular activated carbon [3]. Hence catalytic oxidation systems have been proposed by various research teams as proper alternative methods which include some advantages, such as non-toxicity, insolubility and high activity [4–7].

Photocatalysts with sufficient light irradiation have been used for the decomposition of waste materials, pollutants, and harm-

ful bacteria. Meanwhile, there are other types of catalyst, such as metal catalyst which can also degrade such phenolic compounds without light irradiation [7–11]. This means that when the metal catalyst is employed lower operating and regenerating cost could be expected [5]. At the mean time, some oxidative compounds, such as ozone, have been of interest for pollutant decomposition due to their excellent performance. Thereby, investigation on comparison of photocatalyst and metal catalyst performance with synergetic enhancement of ozone has recently been of interest. However, loss of those catalysts due to their size and instability would be a serious issue to investigate for further improvement.

It should also be noted that three-phase fluidized bed reactors, which could provide intimate contact among gas, liquid, and solid phases, have gained increasing attentions in a wide range of industrial applications [8,12]. These kinds of reactors have various advantages, such as simplicity in construction and operation, low operating costs and flexibility in liquid and solid phase residence times. Furthermore merits of having intimate contact between the phases, high degree of mixing among phases, high values of effective interfacial area and overall mass transfer coefficient and flexibility of introducing continuously catalyst with less erosion would also be reasons for employing three-phase fluidized beds in many industrial applications, such as, coal conversion process, catalytic hydrogenation, and desulfurization of residual oil [13,14]. The current applications for wastewater treatment and biochem-

* Corresponding author at: Center of Excellence in Particle Technology and Energy Research Institute, Chulalongkorn University, Payathai Rd., Patumwan, Bangkok 10330, Thailand. Tel.: +66 2 2186480; fax: +66 2 2186480.

E-mail address: ctawat@chula.ac.th (T. Charinpanitkul).

Table 1
Characteristics of catalysts and support.

Material	Diameter (mm)	Carbonization temperature (°C)	BET surface area (m ² /g)	Mesopore volume (mL/g)	Crystalline size (nm) ^a
MC	0.6	600	784	1.55	–
Co/MC	0.6	600	736	1.23	2.4
Ni/MC	0.6	600	761	1.49	3
TiO ₂ /SiO ₂	0.85–1.7	–	325	0.84	–

Remark: MC: mesoporous carbon bead; Co/MC: cobalt impregnated on mesoporous carbon bead; Ni/MC: nickel impregnated on mesoporous carbon bead; TiO₂/SiO₂: titanium dioxide on silica bead.

^a Calculated from Scherer's equation.

ical processes are also commonly encountered by many research teams [2–4,7,10].

In this work the performance of metal catalysts (nickel or cobalt) impregnated on mesoporous carbon beads which were prepared by the sol–gel method was systematically investigated and compared with a commercial TiO₂ photocatalyst doped on silica beads within a three-phase fluidized-bed reactor. The combining effect of ozone oxidation with the presence of catalyst was then examined and discussed.

2. Experimental

2.1. Catalyst preparation

Two types of catalysts were used in this research. The first was commercial TiO₂ impregnated on silica beads (Fuji Silysia Chemical, Japan) and the second was metal catalyst (nickel (Ni) or cobalt (Co)) impregnated on mesoporous carbon (MC) beads. The impregnation of each catalyst was conducted with a certain amount of silica beads for reproducibility [15]. In brief, the catalyst preparation was started from impregnation of the catalyst precursor solution with a concentration of 1 mol/L onto the support material in a vacuum evaporator at 333 K until the

solution phase could no longer be observed. After impregnation, the impregnated samples were dried overnight at 353 K and subsequently calcined at 873 K under nitrogen atmosphere (N₂ gas flow rate of 0.8 L/min) for 5 h. Basic characteristics of all catalysts employed in this work are compared in Table 1. The mesoporous carbon beads were prepared with the nearly monodisperse size of 600 μm with specific surface area of 784 m²/g. Impregnation of metal catalyst onto the mesoporous carbon beads did not affect its particle size because of its comparatively low dosage.

2.2. Experimental apparatus

The equipment used in this work consists of a three-phase fluidized-bed reactor (TPFBR) which includes a hold up tank, an ozone generator (SO-O3UN-OX, Tokyu Car) and two 15-Watt 254-nm UV-C lamps (only for examining performance of TiO₂). The reactor had an effective volume of 235 mL, 31.6 mm inside diameter and 300 mm height (Fig. 1). The central portion of the reactor was made of quartz tube to allow the UV irradiation from the UV-C lamp to penetrate into simulated wastewater in which organic phenol was introduced with designated concentration in a range of 10–100 ppm was fed through a pump with a regulated flow rate.

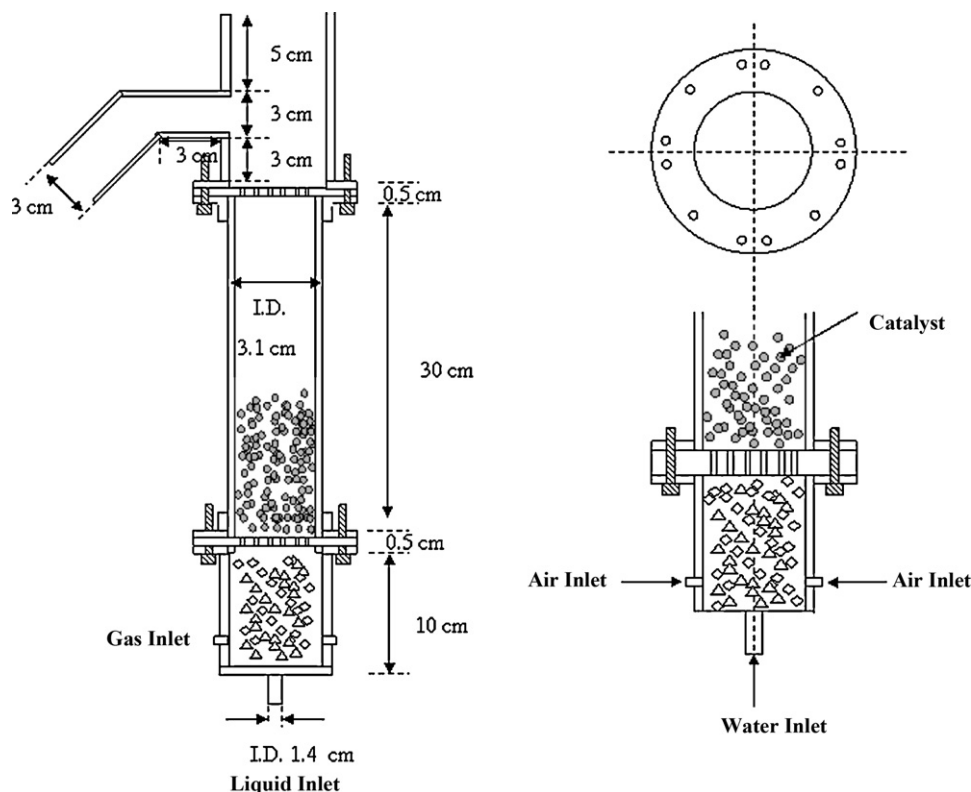


Fig. 1. Schematic diagram of three-phase fluidized bed reactor.

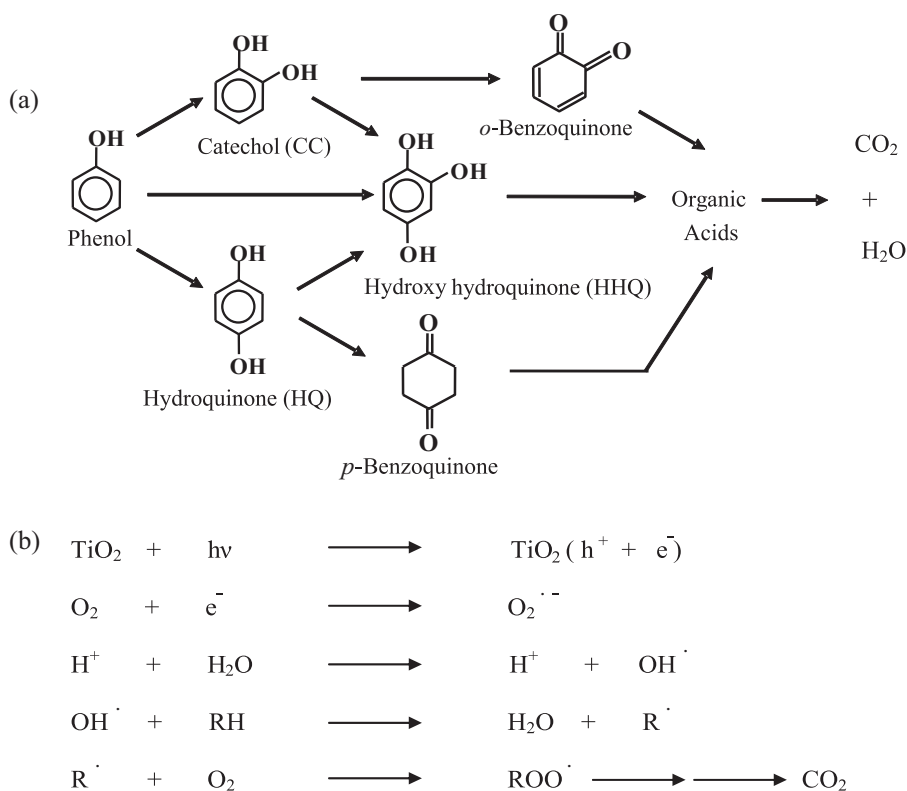


Fig. 2. (a) Pathways of formation of phenol intermediate products and (b) mechanism of degradation of organic species by TiO_2 catalyst

All experiments were carried out under ambient conditions with co-current upward flows of gas and liquid. The phenol-containing liquid and/or ozone-containing gas were introduced through the gas distributor at the bottom of the reactor and then flowed out from the top of the reactor. The entire volume of liquid was recirculated via the hold-up tank. The ozone generator was used to ozonize 1 L/min of influent air (or pure oxygen) for supplying ozone into the reactor. The liquid flow rate was also kept constant at 1 L/min. The designated initial concentration of phenol and the designated catalyst loading was intentionally prepared for repeatable investigation. The concentrations of phenol and their intermediate products were analyzed by a high performance liquid chromatography (HPLC, LC-20A, Shimadzu), while the total organic carbon (TOC) and the inorganic carbon (IC) were measured by a TOC analyzer (TOC-VCPH, Shimadzu). For examining the concentration of metal catalyst which would possibly be washed out from the surface of supporting material, consecutive samples of treated liquid were characterized by an inductively coupled plasma atomic emission spectrometry (ICP-AES, iCAP 6300, Thermo Electron Corp.).

3. Results and discussions

3.1. Pathways of the phenol intermediate products

Once phenol is decomposed no matter by catalytic oxidation, catechol (CC), hydroquinone (HQ) and hydroxyl hydroquinone (HHQ) would be generated as by-products in the initial stage of the degradation [4–6]. These aromatic intermediates would undergo further ring cleavage reaction to yield carboxylic acids and aldehydes, which would subsequently convert to CO_2 and H_2O due to decarboxylation [2]. The existence of those chemical species could be confirmed by our HPLC analyses. Based on our experimental results, possible pathways of the intermediate products were proposed in Fig. 2(a). It should be noted that o-benzoquinone

and p-benzoquinone would also be generated due to dehydrogenation reaction of catechol and hydroquinone, respectively [5]. Those organic intermediates would also be detected as organic carbonaceous compounds which were confirmed by TOC analysis.

3.2. Phenol decomposition by TiO_2 photocatalyst

When TiO_2 is irradiated by UV irradiation with energy greater than its band gap energy ($h\nu > E_g = 3.2 \text{ eV}$; $\lambda < 390 \text{ nm}$), a strong oxidizing agent, such as OH^\cdot radicals would be generated [1]. The possible steps of relevant reaction mechanism are proposed in Fig. 2(b). Some emerging radicals would attack any organic molecules adsorbed on or located close to the surface of the catalyst or the catalyst support, thus leading to their complete degradation into small inorganic carbon species.

In order to confirm the effect of loading of TiO_2 doped silica beads, the experiments were carried out in the systems with the solid loading in a range of 2.5, 5.0, 10.0 and 20.0 g for treating wastewater containing 10 ppm phenol solution with a constant liquid circulating rate. In practical situation, optimal loading of the TiO_2 doped silica beads is desirable for effective operation of the pollutant decomposition systems [5,6]. However, the optimal loading would depend on the configuration of the reactor system and on types of pollutant [15]. Fig. 3(a) shows that the effect of phenol degradation on TiO_2 loading. In this work, phenol decomposition was increased as the loading of the TiO_2 doped silica beads was doubled from 2.5 to 5 g. However, a further increase in the solid loading over 5.0 g oppositely resulted in the decreasing removal efficiency. Based on experimental results, it could be observed that the rate of phenol oxidation would be lower with the excessively high loading of TiO_2 doped silica beads due to the hindered UV penetration [6]. Thereby, the oxidation level decreased to a saturated value upon the further increase in the loading of TiO_2 doped silica beads. Similarly, an increase in fluid opacity and light scattering by

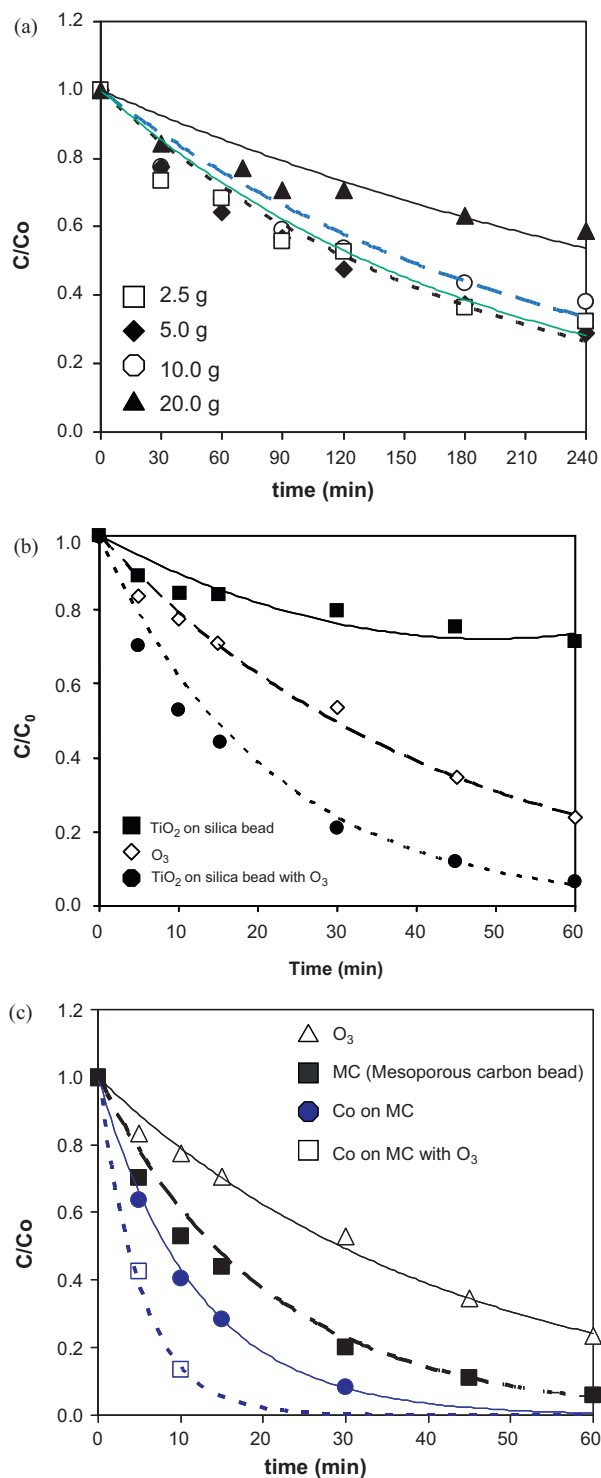


Fig. 3. Time dependence of phenol decomposition within: (a) systems using TiO₂ impregnated on silica beads with different loading, (b) systems using ozone and/or TiO₂ photocatalyst, and (c) systems using ozone and/or Co metal catalyst. Remark: for (b) and (c) phenol initial concentration = 10 ppm; ozone concentration 24.4 g/m³; catalyst dosage = 5 g.

TiO₂ doped silica particles progressively occurred at a higher solid loading, leading to the hindered passage of irradiation through the sample [14–16]. Based on our experimental results, the optimal amount of TiO₂ doped silica beads was found to be at 5.0 g so that it was considered as the a reference for comparison with other metal catalysts.

3.3. Comparison of phenol degradation by TiO₂ photocatalyst and metal catalysts

To study the effect of ozone on the degradation of phenol with the presence of different catalysts, 5 g of each catalyst was used to decompose 10 ppm aqueous phenol with liquid flow rate of 1 L/min. It should be noted that in this part the ozone gas was generated from air at a constant flow rate of 1 L/min. As could be observed in Fig. 3(b) the experiment using only TiO₂ photocatalyst resulted in the lowest degradation efficiency. It took a long time, approximately 8 h, to decompose the phenol concentration from 10 ppm to a level of less than 1 ppm. On the other hand, experiments using TiO₂ catalyst with ozone generated from air revealed higher decomposition efficiency. For comparison, the degradation efficiency of system using metal catalyst was also investigated and compared with that of system using only ozone generated from air or mesoporous carbon bead (MC). The experiments were operated under the same conditions as the case of system using the commercial TiO₂.

As shown in Fig. 3(c), contrasting to the result of TiO₂ doped on silica beads, Co catalyst impregnated on mesoporous carbon beads is more effective than ozone generated from air. Combination of Co metal catalyst and ozone oxidation could provide the best result by degrading 10 ppm phenol to a concentration less than 1 ppm within 15 min. For the case of using mesoporous carbon beads without Co catalyst, the mesoporous carbon beads still provided phenol removal efficiency higher than ozone. This result suggested that adsorption by mesoporous carbon beads would play an important role in removal of phenol in our system. Nevertheless, phenol molecules were just adsorbed onto the substantially large surface of mesoporous carbon beads but not degraded [4]. It could also be observed from the formation of intermediate products (catechol or hydroquinone) was undetectable regarding to the precision of our HPLC. After operated for a while, the regenerated process would be required for eliminating the adsorbed contaminant molecules [16].

Using the metal catalyst impregnated on mesoporous carbon beads for phenol treatment would prolong the catalyst service lifetime and then increase the decomposition efficiency. The mesoporous carbon beads would also help adsorb the contaminants on their surface and pores, resulting in a simultaneous removal process of phenol [4]. Comparison of experimental results using only mesoporous carbon beads and Co deposited on mesoporous carbon beads with the presence of O₃ would suggest that catalytic decomposition could also provide synergetic effect on phenol removal. Therefore, most of the phenol and intermediate products would be decomposed and removed faster. It should be noted that in the case of using only mesoporous carbon beads, the contaminants would be adsorbed into the pores or on the surface. With this reason, only the mesoporous carbon beads would be exhausted faster than mesoporous carbon beads impregnated with metal catalysts because of catalytic activities [10].

From the above results, adding ozone would potentially increase phenol degradation efficiency due to two possible ways which are direct oxidation and radical reaction. With the direct oxidation, ozone reacts directly with phenol molecules and cleavage the aromatic part to yield paraffinic molecules [14]. Meanwhile, with the radical reaction (1), ozone and water could provide hydroxyl radical (OH[•]) which could further react with phenol to for some organic derivatives [16]:



It should be noted that the bulk decomposition performance could be interpreted in terms of phenol conversion, X_{ph} , which is

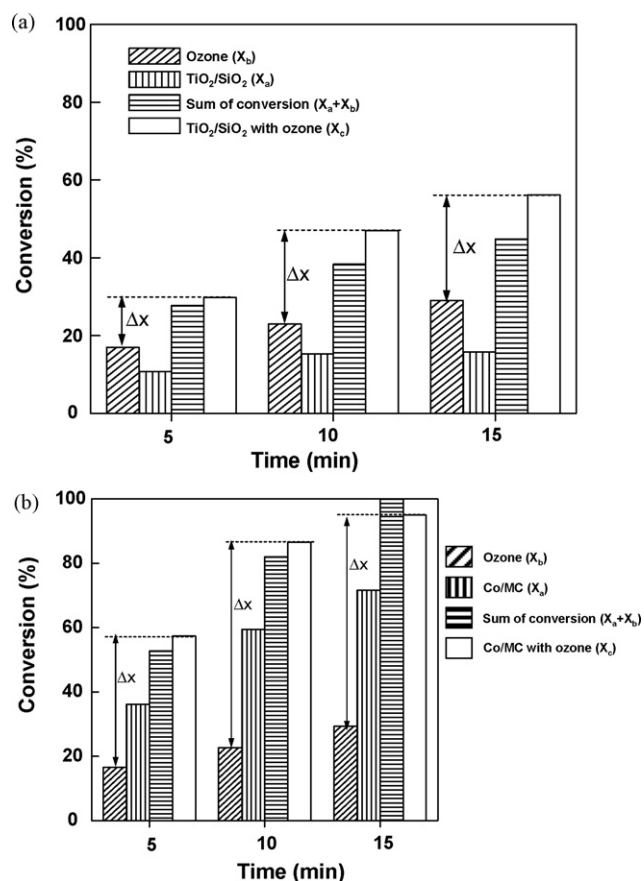


Fig. 4. Conversion of aqueous phenol in ease system: (a) using ozone and/or TiO_2 photocatalyst and (b) systems using ozone and/or Co catalyst. Remark: phenol initial concentration = 10 ppm; ozone concentration 24.4 g/m^3 ; catalyst dosage = 5 g.

defined as

$$X_{Ph} = \frac{[Ph]_0 - [Ph]_t}{[Ph]_0} \times 100 \quad (2)$$

The conversion of aqueous phenol in each case was plotted in Fig. 4(a) and (b). The conversions of phenol by using metal catalyst, ozone and metal catalyst with the presence of ozone are denoted as X_a , X_b and X_c , respectively. At the beginning period (t equal 5 to 15 min), the conversion for the case of using metal catalyst with the presence of ozone was higher than the combined conversions between the two cases of using ozone and metal catalyst ($X_c > X_a + X_b$). These results suggested that synergetic effect of metal catalyst deposited on mesoporous support material with the presence of O_3 would be more effective because adsorption by mesoporous support material would enhance the interaction between adsorbed phenol and metal catalyst [4].

These distinct experimental results would be attributed to a couple of possible reasons. One is the ability of liquid dispersion within three-phase fluidized bed. The axial and radial liquid dispersion coefficients are complex functions of gas and liquid velocities [13]. In three-phase fluidized bed, liquid axial dispersion would increase with the increasing gas velocity. By adding ozone, liquid dispersion would be more enhanced, leading to an increase in opportunity for aqueous phenol to react with ozone and to be adsorbed on the catalyst surface. The turbulent flow would result in a decreasing film resistance around the beads, which in turn enhance the phenol molecule diffusion to the solid catalyst surface.

The other attribution would be the ability of ozone to restore specific surface area of porous materials. Some previous works also reported that ozone could help regenerating the spent acti-

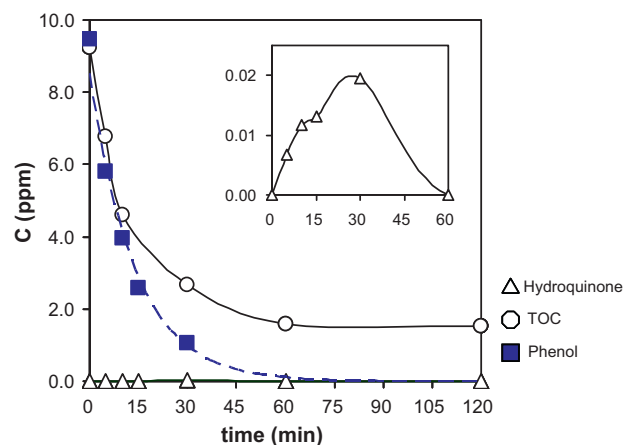


Fig. 5. Time dependence of concentration of phenol, TOC and HQ decomposed by Co catalyst impregnated on mesoporous carbon bead with the presence of ozone generated from air. Remark: ozone concentration 24.4 g/m^3 ; catalyst dosage = 5 g.

vated carbon by reacting with the adsorbed phenol then the active surface of the spent activated carbon could be restored to some extent depending on the ozonation time [4,14]. Therefore, using ozone together with these catalysts would enhance the capability of adsorption phenol molecule to the surface catalyst.

As shown in Fig. 4(a), though the conversion of phenol decomposition by using TiO_2 impregnated on silica beads with UV light irradiation combined with ozone was less than that of Co impregnated on mesoporous carbon beads with ozone but the increasing conversion (ΔX) of this case was clearly higher than any other cases. This results was attributed that with the presence of ozone, the overall phenol degradation was due to synergistic effects of catalytic decomposition and ozonation as well as formation of hydroxyl radicals (OH^*) which could be induced by ozone decomposition in water [4,12]. According to the abovementioned reaction (1), ozone under UV light would enhance the formation of hydroxyl radical (OH^*). Additionally, under UV light irradiation, using TiO_2 impregnated on silica beads with the presence of ozone would undoubtedly increase the phenol decomposition.

Meanwhile, it could be clearly observed from Fig. 4(b) that when a catalyst of Co impregnated on mesoporous carbon beads with ozone generated from air was employed the lowest concentration of phenol remained in the investigated system. Therefore, it would reasonably be implied that decomposition of phenol by Co impregnated on mesoporous carbon beads with the presence of ozone generated from air was the best condition for aqueous phenol decomposition. However, it is worth to investigate in a further detail on intermediate TOC formation in such system.

Confirmation by TOC analysis in Fig. 5, 5 g of Co impregnated on mesoporous carbon beads with ozone generated from air took 30 min for degrading phenol to a concentration less than 1 ppm while TOC in the aqueous solution could not be completely decomposed. This result suggested that aqueous phenol would be easier to be decomposed but the intermediate products which consisted on various organic compounds were more difficultly decomposed.

3.4. Investigation of kinetic study

All the experiments in the presence of: only ozone (O_3), only TiO_2 impregnated on silica beads, only Co impregnated on mesoporous carbon beads, and ozone in combination with one of the mentioned catalysts were carried out under the same operation conditions. For the sake of comparison, change of phenol concentration with respect to decomposition time within each experiment is illustrated in Fig. 6.

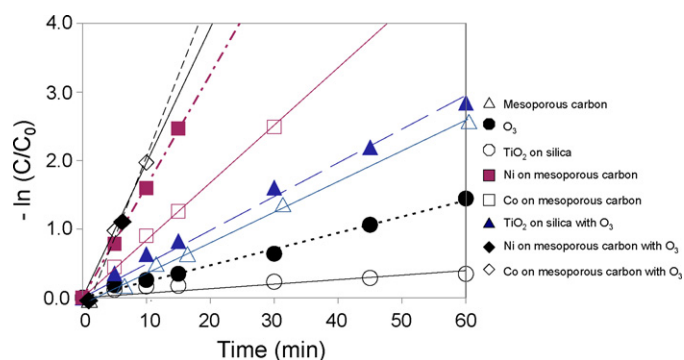


Fig. 6. Comparison of phenol decomposition rate with the presence of difference media. Remark: phenol initial concentration = 10 ppm; ozone concentration 24.4 g/m³; catalyst dosage = 5 g.

The phenol degradation by these catalysts follows the pseudo-first-order kinetics [4]. The combination between rate law of first order reaction ($-r = kC$) and the mass balance within a well mixed batch reactor ($(1/V) dN/dt = r$) yields the logarithm correlation ($-\ln(C/C_0) = kt$). The value of rate constant (k) is obtained from the slope of linear correlation of phenol concentration and decomposition time as summarized in Table 2.

According to the conversion $X_{60 \text{ min}}$ in summarized in Fig. 6 or Table 2, it is obvious that Co impregnated on mesoporous carbon beads could exhibit the highest performance in a comparison with that of adsorption by mesoporous carbon bead, oxidation by ozone and TiO₂ with silica beads, respectively. In addition, Co impregnated on mesoporous carbon beads was more efficient than TiO₂ impregnated on silica beads with the presence of ozone. Interestingly, the efficiency of adsorption by using only mesoporous carbon beads was higher than the case of using TiO₂ impregnated on silica beads and almost equal to the case of TiO₂ impregnated with silica beads with the presence of ozone. This would be attributed that many pore volume and surface area of mesoporous carbon beads would adsorb more phenol in a shorter time [4].

These experimental results reveal that the metal catalyst was more effective than the commercial TiO₂. Thereby, the next experiments were focused on the case of metal catalyst together with ozone. As expected, decomposing phenol by metal catalyst with the presence of ozone generated from pure oxygen was more efficient than the case of using ozone generated from air. It is noteworthy that in an actual wastewater treatment process it is crucial to minimize the total costs of the treatment system. Therefore, phenol decomposition using the metal catalyst with the presence of ozone generated from the air should be recommended as the most appropriate condition.

Table 2
Dependence of conversion of phenol decomposition on system configuration.

System configuration	C ₀ (ppm)	X _{60 min} (%)	k (1/min) ^a
MC	8.41	91	0.0432
O ₃ generated from air	10.21	76	0.0236
TiO ₂ /SiO ₂	9.99	29	0.0066
Co/MC	9.73	100	0.0839
Co/MC with O ₃ generated from air	10.36	100	0.1944
Ni/MC with O ₃ generated from air	9.70	100	0.1713
Ni/MC with O ₃ generated from O ₂	9.06	100	0.2158
TiO ₂ /SiO ₂ with O ₃ generated from air	9.57	94	0.0492

Remark: MC: mesoporous carbon bead; Co/MC: cobalt impregnated on mesoporous carbon bead; Ni/MC: Nickel impregnated on mesoporous carbon bead; TiO₂/SiO₂: titanium dioxide on silica bead; phenol initial concentration = 10 ppm; ozone concentration 24.4 g/m³; catalyst dosage = 5 g.

^a Pseudofirst order rate constant determined at 60 min.

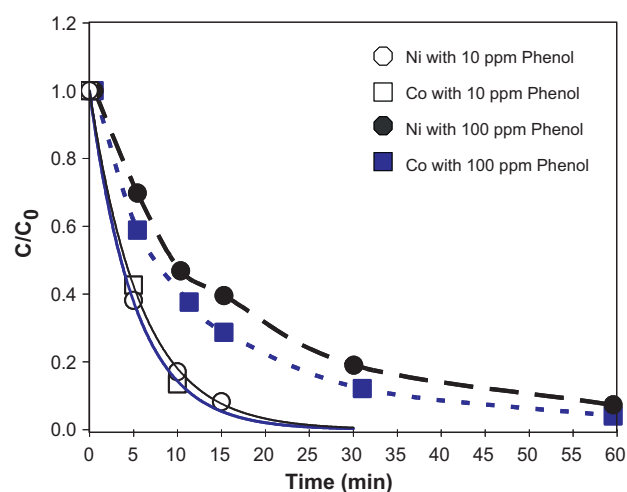


Fig. 7. Dependence of phenol decomposition on its initial concentration with different metal oxide catalyst. Remark: ozone concentration 24.4 g/m³; catalyst dosage = 5 g

3.5. Comparison of phenol decomposition efficiency of Co and Ni metal catalysts

As abovementioned, the metal catalyst combined with ozone generated from air could provide a significant improvement in aqueous phenol decomposition. Therefore it was selected to decompose the higher concentrate aqueous solution. The concentration of phenol was varied from 10 to 100 ppm. With the initial concentration of 10 ppm, it took about 15 min for 5 g of Ni or Co catalysts to complete the decomposition of aqueous phenol. After increasing the initial concentration to 100 ppm, both catalysts used longer time (60 min) to degrade 90% of the initial content of phenol. The decrease in phenol removal performance would be attributable to faster deactivation of catalyst due to the presence of other by-products. Similarly, some previous works reported that adsorption of organic compounds on the surface of catalyst would result in deterioration of the catalyst performance [4,10]. However, it should be noted that metal leaching due to the contact between liquid flow and metal species on the solid support would affect the stability of catalyst and consequently the reactor performance. Under the complicated influences of shear stress due to the liquid and gas flow as well as mass transfer due to metal concentration gradient between the solid surface and bulk liquid, some Ni and Co catalysts would be washed out and detached from the surface of carbon beads [17]. Therefore, additional investigation on loss of metal catalysts into the treated solution of phenol has also been conducted. It was found that under all investigating conditions, Ni or Co species existing in the treated phenol solutions did not exceed the traceable concentration of 1–2 ppm. This would be attributed to the relatively low superficial velocity of the treated liquid and strong attachment of metal catalyst onto the surface of carbon beads containing very high specific surface area. As a result, within the system investigated in the work, the effect of metal catalyst leaching would reasonably be neglected.

As could be observed in Fig. 7, Co catalyst could decompose aqueous phenol faster than Ni. At the lower phenol concentration of 10 ppm, both Co and Ni catalysts exhibited comparable decomposition efficiency. However, when the initial concentration of phenol was raised to 100 ppm, the decomposition efficiency of Co catalyst was significantly higher than that of Ni catalyst. As suggested by Kochetkova et al. [9], the number of active sites analyzed by gas chemisorption is 16.3×10^{-19} sites/g-catalyst for Co, and 8.1×10^{-19} sites/g-catalyst for Ni. It could be confirmed that Co catalyst has better efficiency due to the existence of more

active sites compared with those of Ni. It should be noted that adsorption of excessive pollutant due to its higher initial concentration would attribute to the decrease in the active site as also reported in some previous works [4,10]. The lower accessibility to active site of Ni and Co catalysts due to the 10 times higher phenol concentration would lead to the remarkable decrease in phenol conversion. However, Co catalyst still exhibited the better performance when compared with Ni. A comprehensive investigation on the catalytic activity of metal catalysts for oxidation of phenol reported that the following order of catalyst activity ($\text{CuO} > \text{CoO} > \text{Cr}_2\text{O}_3 > \text{NiO} > \text{MnO}_2 > \text{Fe}_3\text{O}_3 > \text{YO}_2 > \text{Cd}_2\text{O}_3 > \text{ZnO} > \text{TiO}_2 > \text{Bi}_2\text{O}_3$) was experimentally confirmed [9]. Based on such previous report, it could reasonably be concluded that the catalytic activity of Co is higher than Ni catalyst. As abovementioned, ICP-AES analysis revealed that leaching of metal catalyst from the surface of mesoporous carbon beads was negligible, suggesting that the prepared catalyst could stably be deposited on the surface of mesoporous carbon beads which would be beneficial to its repetitive usage. Therefore, it is obvious that selection of appropriate metal catalyst would be important issue for aqueous phenol decomposition regarding to its activity.

4. Conclusions

Based on our investigation, there is an optimum amount of commercial TiO_2 doped silica beads loaded into the fluidized bed reactor which could provide the optimal decomposition performance, which would be lower than that of Co catalysts. This result is attributed to the higher active sites on the surface of Co catalyst. In addition, applying the metal catalyst with ozone generated from pure oxygen could provide the best decomposition results. However, using air instead of pure oxygen could reasonably provide lower operating cost whereas the total efficiency differs insignificantly. Meanwhile, an effective regeneration method of those metal catalysts would be the next issue to be investigated further.

Acknowledgements

This work is mainly supported by the NEDO grant provided to AIST-HU-CU in the period of 2005–2006. Also partial support from the Centennial fund of Chulalongkorn University and NANTOTEC, NSTDA are gratefully acknowledged.

References

- [1] M. Sameiro, T. Gonçaves, E.M.S. Pinto, P. Nkeonye, A.M.F. Oliveira-Campos, Degradation of C.I. Reactive Orange 4 and its simulated dyebath wastewater by heterogeneous photocatalysis, *Dyes Pigments* 64 (2005) 135–139.
- [2] K. Tanaka, K. Abe, T. Hisanaga, Photocatalytic water treatment on immobilized TiO_2 combined with ozonation, *J. Photochem. Photobiol. A: Chem.* 101 (1996) 85–87.
- [3] J.H. Lee, W. Nam, M. Kang, G.Y. Han, K.J. Yoon, M.S. Kim, K. Ogino, S. Miyata, S.J. Choung, Design of two types of fluidized photo reactors and their photocatalytic performances for degradation of methyl orange, *Appl. Catal. A: Gen.* 244 (2003) 49–57.
- [4] T. Charinpanitkul, P. Limsuwan, C. Chalotorn, N. Sano, T. Yamamoto, P. Tongpram, P. Wongsarivej, A. Soottitawat, W. Tanthapanichakoon, Synergetic removal of aqueous phenol by ozone and activated carbon within three-phase fluidized bed reactor, *J. Ind. Eng. Chem.* 16 (2010) 91–95.
- [5] C.R. Huang, H.Y. Shu, The reaction kinetics, decomposition pathways and intermediate formations of phenol in ozonation, UV/O_3 , and $\text{UV}/\text{H}_2\text{O}_2$ processes, *J. Hazard. Mater.* 41 (1995) 47–64.
- [6] D. Chen, A.K. Ray, Photodegradation kinetics of 4-nitrophenol in TiO_2 suspension, *Water Res.* 32 (1998) 3211–3223.
- [7] P.M. Alvarez, F.J. Beltran, V. Gomez-Serrano, J. Jaramillo, E.M. Rodriguez, Comparison between thermal and ozone regenerations of spent activated carbon exhausted with phenol, *Water Res.* 38 (2004) 2155–2165.
- [8] A. Eiad-ua, T. Yamamoto, T. Ohmori, W. Tanthapanichakoon, T. Charinpanitkul, Porous characteristics of carbon-coated silica gel beads prepared by liquid phase deposition of organic colloidal nanoparticles, *J. Non-cryst. Solids* 355 (2009) 2508–2513.
- [9] R.P. Kochetkova, A.F. Babikov, L.I. Shiplevskaya, I.P. Shiverskaya, S.A. Eppel, F.K. Smidt, Liquid-phase oxidation of phenol, *Chem. Abstr.* 117 (1992) 156952.
- [10] R.M. Liou, S.H. Chen, M.Y. Hung, C.S. Hsu, J.Y. Lai, Fe (III) supported on resin as effective catalyst for the heterogeneous oxidation of phenol in aqueous solution, *Chemosphere* 59 (2005) 117–125.
- [11] Y. Ungkoon, C. Sittipunt, P. Namprakai, W. Jetipattaranat, K.S. Kim, T. Charinpanitkul, Analysis of microstructure and properties of autoclaved aerated concrete wall construction materials, *J. Ind. Eng. Chem.* 13 (2007) 1103–1108.
- [12] S.H. Roh, J.W. Nah, J.H. Cha, S.I. Kim, Effect of PAC addition on dyeing wastewater treatment in a hybrid process of Fenton oxidation and membrane separation, *J. Ind. Eng. Chem.* 12 (2006) 955–961.
- [13] L.S. Fan, *Gas-Liquid-Solid Fluidization Engineering*, Butterworth, New York, 1989.
- [14] D. Suryaman, K. Hasegawa, S. Kagaya, Combined biological and photocatalytic treatment for the mineralization of phenol in water, *Chemosphere* 65 (2006) 2502–2506.
- [15] R.M. Mohamed, Characterization and catalytic properties of nano-sized Pt metal catalyst on TiO_2 - SiO_2 synthesized by photo-assisted deposition and impregnation methods, *J. Mater. Proc. Technol.* 209 (2009) 577–583.
- [16] M. Dore, B. Langlais, B. Legube, Ozonation des phenols et des acides phenoxy-acetiques, *Water Res.* 12 (1978) 413–425.
- [17] A. Xu, M. Yang, R. Qiao, H. Du, C. Sun, Activity and leaching features of zinc-aluminum ferrites in catalytic wet oxidation of phenol, *J. Hazard. Mater.* 147 (2007) 449–456.