



Continuous flow photocatalytic treatment integrated with separation of titanium dioxide on the removal of phenol in tap water

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ABSTRACT

We studied the continuous flow photocatalytic treatment integrated with separation/reuse of titanium dioxide on the removal of phenol (20 mg l⁻¹) in electrolytes containing tap water. A circulative flow tubular photoreactor and a separation tank were used, where inflow of phenol continuously flowed into a mixing tank (for titanium dioxide suspension) and treated water overflowed from the separation tank. Black light and sunlight were used by turns as the light source on the photocatalytic treatment. Photocatalytic removal of phenol was maximum at the circulative flow rate of 600 ml min⁻¹ and the transmittance of 0.3%. Integration of circulative photocatalytic treatment and titanium dioxide separation and continuous use of titanium dioxide could be performed effectively at low inflow of 10 ml min⁻¹. The titanium dioxide slurry sedimented spontaneously by standing was continuously used for at least 72 h without decreasing the efficiency of the photocatalytic treatment. The used titanium dioxide can be replaced with a fresh one by draw and fill method without interrupting the treatment.

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1. Introduction

The TiO₂ is the most often used photocatalyst due to its considerable photocatalytic activity, high stability and low cost [1,2]. The supported TiO₂ photocatalytic treatment is easily operated, however, it requires a complicated preparation of the TiO₂ immobilization and has TiO₂ detachment problems during long-term applications [3]. The TiO₂ slurry or suspension method excels over the immobilized or supported TiO₂ method with respect to the efficiency of the photocatalytic degradation [4], however, it requires separation after the photocatalytic treatment. On the other hand, the real wastewater ordinarily contains more abundant electrolytes than the original water, which lowers the degradation efficiency due to the coagulation of TiO₂ [5,6]. It was reported that the electrolytes in river and tap waters produce a slightly decreased efficiency, while they enabled easy separation of the fine TiO₂ particles using a solids-retaining centrifuge, which was combined with a batch photoreactor [6]. However, it was necessary to remove the accumulated TiO₂ from the rotor (21) by interrupting the operation for every 1315 l-treatment of the model wastewater and relatively high electrical energy cost. The recovered TiO₂ in pure water by neutralization-microfiltration [5], microfil-

tration [7,8] and coagulation-sedimentation [9] were reused at the repeated treatments [5,8,9]. However, periodical back-washing of membrane filter [5,7,8] and addition of coagulant [9] were required and also sufficient caution has not been paid to the integration of photocatalytic treatment and separation and continuous use of TiO₂. A fast, cheap and easy separation of TiO₂ is preferred for reuse of TiO₂ in the continuous photocatalytic treatment. On the other hand, the photocatalytic degradation of phenol, a commonly found pollutant in industrial waste effluent, using TiO₂ has been studied [10–15].

Therefore, we studied the continuous flow photocatalytic treatment on the tubular photoreactor integrated with TiO₂ separation. Phenol was used as a model pollutant in tap water. The effect of flow rate to the photocatalytic treatment and the TiO₂ separation and reuse were investigated. The separation and continuous use of the TiO₂ particles for photocatalytic treatments promotes the application of the TiO₂ slurry or suspension than those of the TiO₂ immobilization.

2. Experimental

2.1. Materials

All chemicals were of reagent-grade quality and were used as received. The phenol solutions were prepared with tap water from Toyama city. The electrolytes (mg l⁻¹) in the tap water were as follows: [Na⁺] = 1.9, K⁺ = 0.5, Ca²⁺ = 7.8, Mg²⁺ = 1.0, Cl⁻ = 3.3, SO₄²⁻ = 9.0,

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$\text{HCO}_3^- = 18.9$. Deionized water was used when examining the effect of the electrolytes on the photocatalytic degradation of phenol and coagulation. The TiO_2 particles of Degussa P-25 (Nippon Aerosil Co., 15–40 nm particle size) were used as a photocatalyst.

2.2. Apparatus

Fig. 1 shows a scheme of the photocatalytic treatment- TiO_2 separation system. The photocatalytic treatment was carried out in the tubular photoreactor. Pyrex tubes (24 pieces, 1 piece: 75 cm length and 0.6 cm i.d., total volume: 510 ml), of which each end was attached to tygon tubes, were installed onto a horizontal stainless steel plate (200 cm \times 100 cm) at the same distance (8 cm) and furthermore the head and tail parts of the combined pyrex tubes were combined with a tygon tube covered black hose. Irradiation was performed with black light lamps (20 \times 20 W, λ_{max} : 352 nm) or sunlight to the tubular photoreactor only. Black light irradiation was performed inside a surrounding wall of which the inside is covered with reflecting stainless steel sheets. A top panel covered stainless steel sheets, under which the black lights were attached and hanged, was inserted inside the surrounding wall and held 20 cm above the tube with plugs set inside the wall. Sunlight irradiation was performed by removing the surrounding wall and the lamps attaching top panel. The mixing tank (31 cm height and 21 cm i.d.) was equipped with a mechanical stirring and covered with black flannel. The flow of the TiO_2 slurry or suspension was adjusted by a rolled pump. The photocatalytically treated effluents were flowed into a separation tank (31 cm height and 21 cm i.d., inside column: 10 cm i.d., total volume: 10 l) and overflowed out.

2.3. Procedures

At first, a batch circulation photocatalysis was performed to determine the optimums of TiO_2 , initial phenol and flow rate. The TiO_2 suspended phenol solution of 800 ml (in 1 l beaker glass) was circulated into the photoreactor (valves 1 and 2 open) at the defined flow rate for 45 min with the irradiation of black lights.

A circulative flow photocatalysis in the tubular photoreactor integrated with TiO_2 separation in a continuous mode was exam-

ined. The TiO_2 particles (10 g) were added to the phenol solution in the mixing tank (10 l) and mechanically stirred (850 rpm). The TiO_2 suspended phenol solution was circulated at the defined flow rate with valves 1 and 2 open. When the phenol concentration (valve 2) was less than 0.1 mg l^{-1} , the inflow started and a part of photocatalytically treated effluent flowed into the separation tank (valve 3 open) at the same flow rate as the inflow. The TiO_2 particles were separated from the water by a spontaneous sedimentation method. The treated transparent water in the separation tank was overflowed and the sedimented TiO_2 (or slurry) was recycled (valve 4 open) intermittently for 10 min every 1 h. In all the experiments, the pH of the phenol solutions was not adjusted during the course of the treatment.

A single pass flow photocatalytic treatment was also examined. The TiO_2 particles (10 g) were added to the phenol solution in the mixing tank (10 l) and mechanically stirred (850 rpm). The inflow was started when the TiO_2 suspended phenol solution was flowed with valves 1 and 3 open. The photocatalytically treated effluent flowed into the separation tank at the same flow rate as the inflow. The treated transparent water in the separation tank was overflowed and the sedimented TiO_2 (or slurry) was recycled (valve 4 open) intermittently for 10 min every 1 h.

2.4. Analysis

About 2 ml of the effluents that flowed out from the photoreactor were withdrawn at timed intervals and immediately filtered using a syringe equipped with a disposal filter having a pore size of $0.2 \mu\text{m}$. The concentration of phenol was measured by an HPLC system equipped with a PU-980 pump, a 970 UV-Vis detector (Jasco), and a Mightysil RP-18 column (Kanto Chemicals). The measurement was made using the mobile phase of $\text{CH}_3\text{CN}:\text{NaH}_2\text{PO}_4$ (20 mM) = 50:50 at the wavelength of 215 nm. The transparency of the treated water was measured at 400 nm by a UV-1600 Shimadzu spectrophotometer. The light intensities of the black light and sunlight were measured by an illuminometer (ORC UV-MO2) at the wavelength of 320–390 nm and estimated to be 1.7 mW cm^{-2} and $2.9\text{--}3.3 \text{ mW cm}^{-2}$, respectively.

3. Results and discussion

3.1. Photocatalytic treatment

An optimum concentration of TiO_2 was examined at the initial concentration of phenol of 20 mg l^{-1} (Fig. 2). The optimum was found to be 0.50 g l^{-1} , wherein first order rate constants k_{obs} (slope of $\ln(C_t C_0^{-1})$ versus t) slightly decrease with the increasing TiO_2 concentration to 1.0 g l^{-1} . This result is consistent with previous report [10].

Fig. 3 shows the effect of the initial concentration of phenol on the degradation of phenol. Similar to the photocatalytic degradation of agrochemicals in a batch photoreactor [16], the degradation followed the Langmuir–Hinshelwood relationship (Eq. (1) or (2)),

$$r_0 = k\theta_{\text{ads}} = \frac{kKC_0}{1 + KC_0} \quad (1)$$

$$\frac{C_0}{r_0} = \frac{C_0}{k} + \frac{1}{kK} \quad (2)$$

where C_0 is the initial concentration of phenol, θ_{ads} is the initial surface coverage of the adsorption sites occupied by phenol, r_0 is the initial rate, k is the Langmuir–Hinshelwood rate constant, and K is the adsorption constant of phenol on TiO_2 . The values of k and K depend on the reaction conditions and pollutants. The equation is typically used for discussing the surface reaction on TiO_2 . Plot A shows that r_0 first sharply increases and then progressively levels

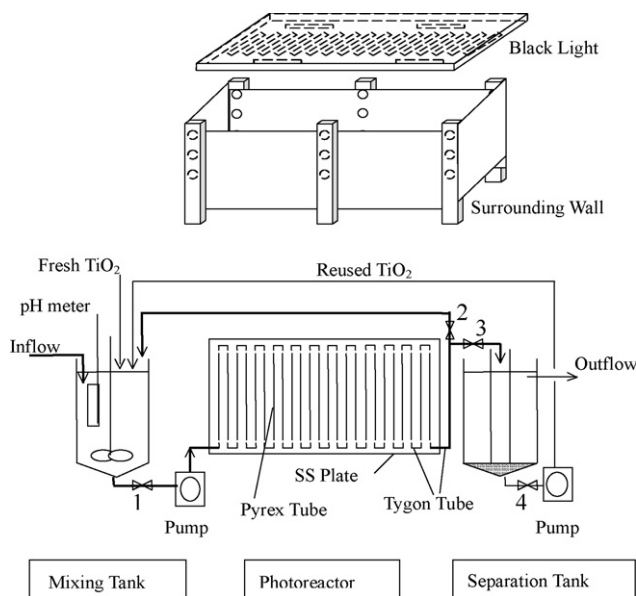


Fig. 1. Scheme of the photocatalytic treatment- TiO_2 separation system. Single flow method: inflow, valve (v) 1, v3 are the same rate; v2 is closed; v4 is intermittent flow. Circulative flow method: inflow and v3 are the same rate; v1 is 600 ml min^{-1} ; v2 is 600 ml min^{-1} minus inflow; v4 is intermittent flow.

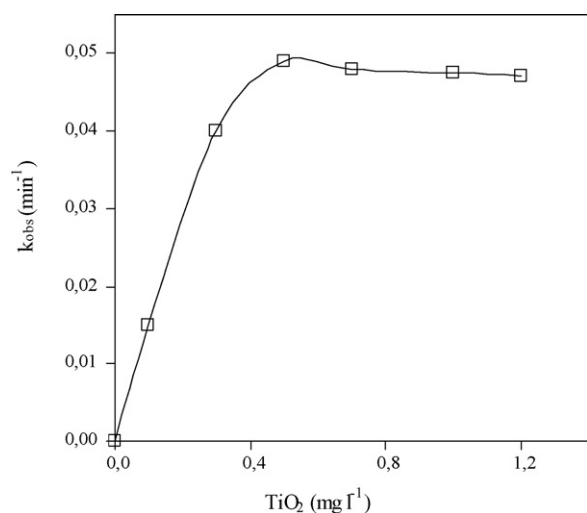


Fig. 2. Effect of concentration of TiO_2 on the photocatalytic degradation of phenol in tap water (20 mg l^{-1} , 800 ml) at circulation flow rate of 600 ml min^{-1} and 45 min irradiation of black light.

off with the increasing C_0 . The plot of C_0/r_0 versus C_0 (line B) yields a straight line. According to the regression calculation, the values of k and K were determined to be $11.8 \mu\text{M min}^{-1}$ and $0.052 \mu\text{M}^{-1}$, respectively. The concentration of phenol ($20 \text{ mg l}^{-1} = 212 \mu\text{M}$) used in the following experiments is situated in the bend of curve A and corresponds to $\theta_{\text{ads}} = 0.92$ as calculated from Eq. (1). Below 20 mg l^{-1} , r_0 rapidly increases with the increasing concentration of phenol, whereas above 20 mg l^{-1} , r_0 levels off with the increasing concentration of phenol. Therefore, the optimum initial concentration for the degradation was 20 mg l^{-1} .

Fig. 4 shows the effects of the flow rate on the degradation of phenol (20 mg l^{-1}) and the transmittance of the effluent from the photoreactor (from valve 2). Tap water and deionized water were used as the solvent of the phenol and the results were compared. When tap water was used, the removal of phenol increased with the decreasing transmittance of the TiO_2 suspension. At the flow rates lower than 50 ml min^{-1} , the transmittances of the effluents were above 90%, and most of TiO_2 particles remained in the tubular photoreactor during the treatments. These results are

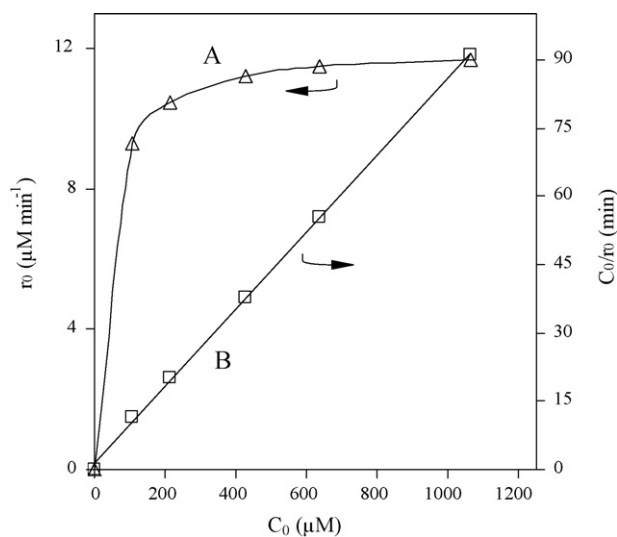


Fig. 3. Effect of initial concentration of phenol on the photocatalytic degradation of phenol in tap water (800 ml) at circulation flow rate of 600 ml min^{-1} , 45 min irradiation of black light and $0.50 \text{ g l}^{-1} \text{ TiO}_2$.

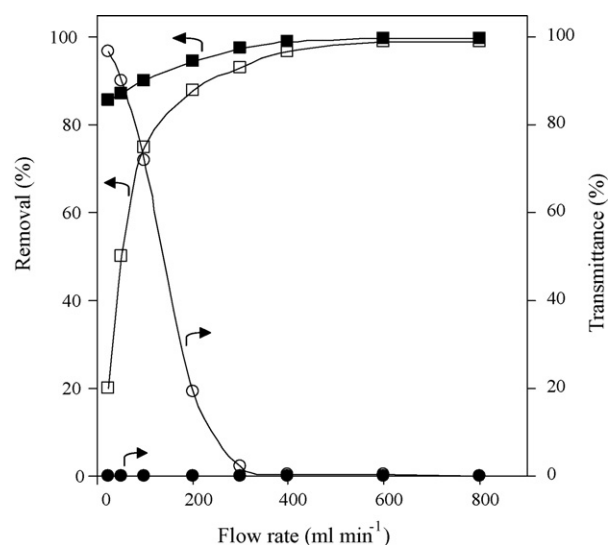


Fig. 4. Effects of flow rate on the circulative photocatalytic degradation of phenol (20 mg l^{-1} , 800 ml) at 45 min irradiation of black light and the transmittance of the effluent from the photoreactor. \circ, \square : Tap water; \bullet, \blacksquare : Deionized water.

reasonably explained by the increase in the coagulation which was caused by the electrolytes dissolved in the pH 7 of tap water. The concentration of TiO_2 ($C = \text{mg l}^{-1}$) in the effluent was estimated from the calibration obtained between the TiO_2 concentration and transmittance ($T = \%$) and was as follows, tap water: $C = 1000$ ($T = 0.01$); $C = 700$ ($T = 0.05$); $C = 400$ ($T = 0.11$); $C = 150$ ($T = 2.31$); $C = 50$ ($T = 19.3$); $C = 5$ ($T = 72.1$); $C = 2.5$ ($T = 82.4$); $C = 2$ ($T = 90.2$); $C = 1.5$ ($T = 95.4$); $C = 1$ ($T = 97.3$); $C = 0.75$ ($T = 98.1$); deionized water: $C = 500$ ($T = 0.07$); $C = 450$ ($T = 0.09$); $C = 400$ ($T = 0.11$); $C = 350$ ($T = 0.14$); $C = 300$ ($T = 0.17$). The pH of the TiO_2 suspensions was around 6.5 (isoelectric point (IEP) of TiO_2 : 6.4–6.6 [7]). At the IEP, the net interfacial effect shows a maximum attraction resulting in a maximum particle size. Furthermore, common electrolytes (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , HCO_3^-) present in the tap water can be bound to the TiO_2 particles or very close to its surface, so that they can have significant effects on the interfacial behavior of the TiO_2 particles to promote coagulation [7]. Therefore, the removals of phenol were low at the flow rates lower than 50 ml min^{-1} .

At the flow rate greater than 50 ml min^{-1} , the transmittance decreased from 90% and finally reached below 3% at the flow rate greater than 320 ml min^{-1} due to the suspended TiO_2 particles were forced into the tubular photoreactor by the hydraulic force of the water flow. These results indicate that the TiO_2 particles were perfectly suspended in the narrow pyrex tube at higher flow rate. The high flow rate in the tubular photoreactor supported the suspension of TiO_2 particles in tap water, while sedimentation of the TiO_2 occurred at the low flow rate. The removal of phenol was 99% (concentration: 0.2 mg l^{-1}) at the flow rate of 600 ml min^{-1} and the transmittance of 0.3%. The increase of removal was not significant with increasing flow rate to 800 ml min^{-1} . On the other hand, when deionized water was used, the removal of phenol was 99.7% at the highest flow rate of 600 ml min^{-1} and the transmittance was 0.1% even at the lowest flow rate of 100 ml min^{-1} . The transmittance in deionized water relatively did not change with the decreasing flow rate. However, a little decrease in the removal was observed with the decreasing flow rate. Previous studies using batch cylinder photoreactor reported a low degradation of phenol in distilled water under no stirring [11] and no transmittance change of the TiO_2 suspension in tap water under mechanically stirring [6]. The high circulative flow rate using pure water as the solvent of the water pollutants has been reported [5,12], although the effect of flow rates

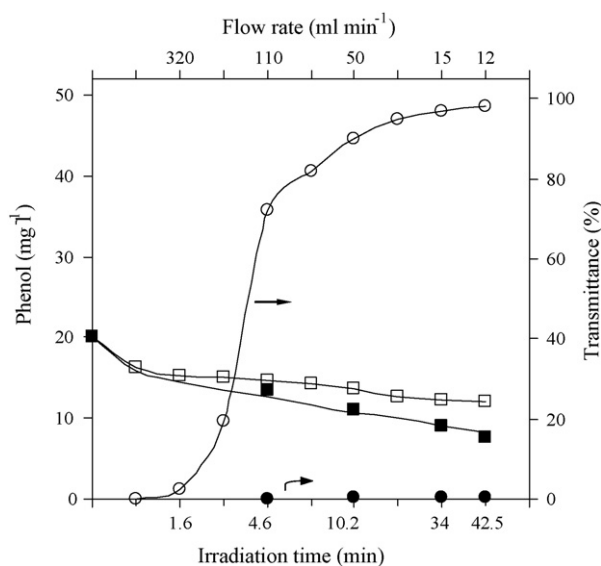


Fig. 5. Effects of flow rate on the single pass photocatalytic degradation of phenol (20 mg l^{-1}) with irradiation of black light and the transmittance of the effluent from the photoreactor. \circ , \square : Tap water; \bullet , \blacksquare : Deionized water.

was not investigated. The high flow rate supposedly also supported a mixing in the TiO_2 suspension. The optimum photocatalysis was achieved at the circulative flow rate of 600 ml min^{-1} and the higher flow rates did not increase the efficiency significantly. Under sunlight irradiation, the removal of phenol was 99.3%. The removal efficiency with sunlight irradiation was a slightly higher than that with black light irradiation due to a slightly higher intensity of sunlight than that of black light. Thus, the photocatalytic treatments can be performed with irradiations of both black light and sunlight by turns.

For comparison, a single pass flow photocatalytic treatment was also examined (valves 1 and 3 opened). Fig. 5 shows the effects of the flow rate/irradiation time on the degradation of phenol and the transmittance of the effluent flowing from the photoreactor. When deionized water was used, the decrease in the phenol concentration can be approximated by an exponential curve. When tap water was used, the remarkable difference is that the degradation of phenol gradually leveled off and $T\%$ increased with the decreasing flow rate/increasing irradiation time. At the flow rates lower than 50 ml min^{-1} , the transmittances of the effluents were above 90%, and most of TiO_2 particles remained in the tubular photoreactor during the treatment. At the flow rates greater than 50 ml min^{-1} , however, the removal efficiencies were still low due to the short irradiation time. It is necessary to decompose the phenol by the circulation mode to increase the irradiation time.

3.2. TiO_2 separation

TiO_2 separations in batch and flow modes were investigated, and the results were compared. Fig. 6 shows the spontaneous sedimentation of TiO_2 after photocatalytic treatment when tap and deionized waters were used as original water. In deionized water the transmittance was low even until 24 h standing, which mean no sedimentation process occurred. Adversely, in tap water, after 6 h standing the transmittance of the supernatant solution was 99.9%, which was clear enough to flow out. As explained above, the electrolytes in tap water promote coagulation of TiO_2 . In case of flow mode, the transmittance kept constant ($\pm 99\%$) until the flow rate of 15 ml min^{-1} . Then the transmittance decreased with increasing the flow rate, due to falling flow of treated water

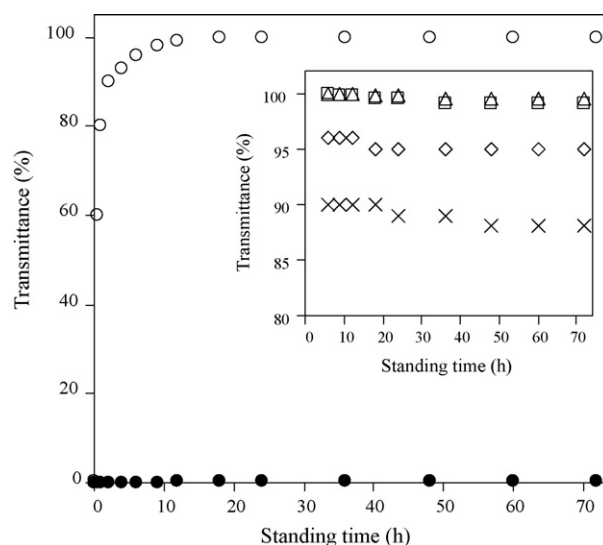


Fig. 6. Batch and flow separations of TiO_2 after photocatalytic treatment. \bullet : Deionized water, batch; \circ : Tap water, batch; Δ : 10, \square : 15, \diamond : 20, \times : 30 ml min^{-1} , tap water.

(from valve 3) led the TiO_2 particles rise up to the water surface. Separation of TiO_2 was reported, but the transmittance or the transparency of treated water was not concerned [5,7,8]. The high transmittance of treated water was achieved after separation of TiO_2 in tap water by centrifuge [6] and those in distilled water by coagulation-sedimentation [9]. However, those separations [5–9] were relatively high cost and required additional treatment and operation. While this spontaneous sedimentation was easy operated, low cost and relatively not required long time, and also can be integrated with the photocatalytic treatment in continuous operation.

3.3. Continuous flow photocatalytic treatment integrated with TiO_2 separation and reuse

Photocatalytic treatment integrated with TiO_2 separation and reuse was conducted by starting the inflow (phenol: 20 mg l^{-1}) continuously. After the circulative flow photocatalytic treatment (batch, 12 h), the inflow was started at 10, 15, 20 and 30 ml min^{-1} , respectively. The flow into the photoreactor was kept 600 ml min^{-1} . Fig. 7 shows the phenol concentration of treated water of the photocatalytic treatment integrated with TiO_2 separation/reuse. The outflow phenol concentration increases with increasing the rate of inflow. Thus, the integration method was effective at low rate of inflow (10 ml min^{-1}) and TiO_2 particles can be continuously used for 72 h (at least 6 times use). The transmittances of the treated water at valve 3 were around 0.03–0.05%, which means the concentrations of TiO_2 were around $800\text{--}700 \text{ mg l}^{-1}$. The sedimented TiO_2 (or slurry) was recycled at a low flow rate of 5 ml min^{-1} intermittently to avoid those TiO_2 particles rise up to the water surface. Furthermore, the portion of used TiO_2 particles could be replaced with the fresh one when the phenol removal decreased by draw and fill method. In the previous study, TiO_2 particles were separated with microfiltration and reused for 4 times [5]. At the inflows of 20 and 30 ml min^{-1} the sedimented TiO_2 was pale red, in considering that the remained phenol and intermediates still occupied on the surface of TiO_2 . Previous studies [13–15] reported that the incomplete degradation resulted in the intermediates (catechol, hydroquinone, and benzoquinone) and the remained phenol in the treated water.

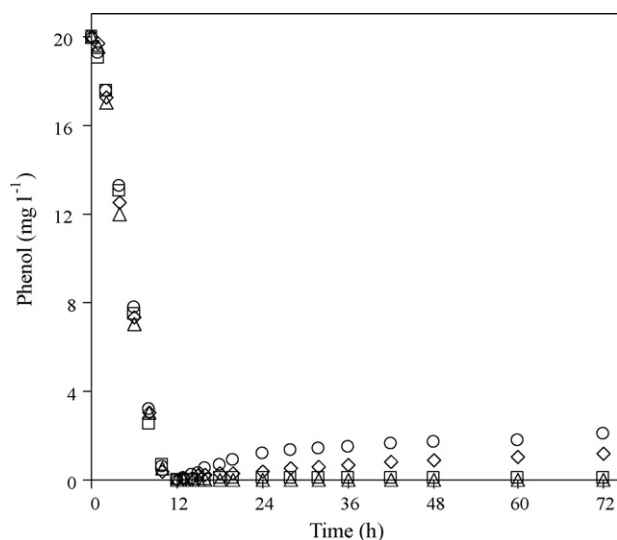


Fig. 7. Degradation of phenol by the photocatalytic treatment integrated with the TiO₂ separation/reuse. 0–12 h: batch circulation; 12–72 h: continuous inflow; Δ : 10, \square : 15, \diamond : 20, \circ : 30 ml min⁻¹.

4. Conclusions

The integration of TiO₂ slurry photocatalysis and separation/reuse of TiO₂ was effective at low continuous inflow of phenol solution in tap water. The circulative flow rate of 600 ml min⁻¹ was optimum for the photocatalytic treatment of phenol (20 mg l⁻¹) in the tubular photoreactor. The TiO₂ slurry sedimented spontaneously by standing was continuously used for at least 72 h without decreasing efficiency of the removal of phenol. This continuous use of TiO₂ particles seems to be promising for the application of the TiO₂ slurry or suspension in the photocatalytic treatment of wastewater.

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