

## Performance Test of a Novel Tubular V-Collector for Phenol Removal from Aqueous Solutions over $\text{TiO}_2$ -Activated Carbon Composites

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**Abstract:** The novel tubular V-collector (TVC) with the flexible reflecting angles was constructed and evaluated for phenol removal from aqueous solutions over  $\text{TiO}_2$ -activated carbon (Ti/AC) composites. The composites consisted of  $\text{TiO}_2$  photocatalyst and activated carbon adsorbent were prepared by mixing  $\text{TiO}_2$  (Degussa P-25) sol and activated carbon powder and followed by calcination at 400 °C for one hour. The TVC reactor was designed such that the V-shape reflectors have adjustable reflecting angles and the photon source could be obtained either from sunlight or artificial lamps. Reflecting intensity measurements of the TVC showed that the optimum reflecting angles under black light lamps and the sunlight irradiation were achieved at 90° and 150°, respectively. The results also show that the phenol could effectively be removed through simultaneous adsorption and photocatalysis. Typically within the residence time of 6 minutes, 30 ppm of phenol solution continuously could be removed completely from aqueous solution for more than 12 hours. Additionally, the effects of inlet phenol concentration, flow rates of phenol solutions and composition of the Ti/AC composites on the phenol removal were also studied.

**Key words:** Tubular V-collector •  $\text{TiO}_2$  • Activated carbon • Phenol removal

### INTRODUCTION

Phenol and phenolic compounds are common pollutants in industrial waste water that may originate from coke ovens, petroleum manufacture, engineering workshops and paint stripping operations [1]. Phenols are considered toxic for some aquatic life forms in concentrations superior to 50 ppb [2]. At high concentration, phenol could make physiological disturbance on fish and obstruct microorganism and blue green algae activities at nitrification process. Phenol also gives bad impact on human, such as: heart and kidney damage, lowering blood pressure and even death. Some methods used in phenol removal are using microorganism, air stripping method, adsorption, or photocatalysis [2, 3]. The combinations of two last methods have a good prospect and being developed recently.

The most common adsorbent used in adsorption process for various types of pollutants is activated carbon (AC). However, while the adsorbent removes the pollutants from water, it doesn't destroy them so the adsorbent eventually becomes saturated and fails to

remove additional pollutants. To restore the adsorbent to its original capacity, thermal regeneration is required and it's not economical [4].

$\text{TiO}_2$  photocatalyst is widely used in many experiments because of its advantages like high activities, photo-stable, non-toxic, has a higher photocatalytic efficiency and relatively inexpensive [4, 5]. The catalyst  $\text{TiO}_2$  is also able to utilize sunlight and humid air to produce many reactive species, including the powerful and non-selective oxidant hydroxyl radicals, to destroy organic compounds [6]. However, the shortcomings of the conventional powder photocatalysts are including low photo-efficiency, difficulty of separation after reaction and low adsorption strength [5]. Furthermore, the surface of  $\text{TiO}_2$  is hydrophilic which makes most organic compounds (hydrophobic) hard to get closed, as a result the degradation process that occurred on the surface of  $\text{TiO}_2$  is inefficient [7].

Therefore, by combining both adsorption and photocatalysis, the phenol removal is expected to be more effective. The combinations of AC and  $\text{TiO}_2$  have been developed by mechanical mixing method

for phenol degradation [8] and mechano-fusion method for methylene blue degradation [4]. They reported that the combination of the adsorbent-photocatalyst is superior. However, those experiments are still in lab scale and batch system as well as in regular reactor.

Currently, wastewater treatment using photocatalytic reactors in pilot scale have been demonstrated by many researchers. Some of them are Parabolic Through Reactor (PTR), Compound Parabolic Concentrator (CPC), Thin Film Fixed Bed Reactor (TFFBR) and Double Skin Sheet Reactor (DSSR) [9-11]. However, they still have limited flexibility for application under the artificial lamps or sunlight that has various and changeable weather conditions. On the other hand, photocatalytic reactor with open system like TFFBR and DSSR show high evaporating rate under high intensity of the sunlight.

In the present study, photocatalytic tubular reactor was chosen in order to solve the evaporation effect. As of the limited flexibility of PTR and CPC's reflector, V-shape reflector/collector (TVC) with flexible reflecting angle was designed to handle the problem. Thus, the optimum condition was considered to make the photon source (sunlight or black light lamps) be collected more effective. The TVC reactor can also be operated either in the batch or continuous mode. In addition, the performance of the continuous TVC pilot scale system would be evaluated for phenol removal from aqueous solutions over  $\text{TiO}_2$ -activated carbon composites.

## Experimental

**Preparation of Ti/AC Composites:** The nano-powder of  $\text{TiO}_2$  Degussa-P25 with specific surface area of  $54 \text{ m}^2/\text{g}$  and the crystal composition of anatase and rutile of 79 and 21 wt%, respectively [12], was used as  $\text{TiO}_2$  precursor. Activated carbon, AC (KARBOSORB ANK 102, Brataco Chemica) with specific surface area of  $670 \text{ m}^2/\text{g}$  was used in all of the experiments. Water used in the experiments was Milli-Q water (demineralized water which is produced from MILLIPORE Milli-Q Plus unit).

For a typical batch, 15 g of  $\text{TiO}_2$  were mixed into 250 mL demineralized water and the mixture was sonicated for 30 minutes. After that, tetraethyl orthosilicate (TEOS) solution was added into the mixture and sonicated again for 30 minutes. TEOS solution was made from mixture of 3.72 mL TEOS, 33.35 mL ethanol, 0.06 mL  $\text{HNO}_3$  and 0.60 mL demineralized water. TEOS is the source of  $\text{SiO}_2$  which acts like adhesive between  $\text{TiO}_2$  and AC.  $\text{TiO}_2$  sol was then mixed with AC on a particular weight, followed by sonication for 30 minutes. After that, the mixture was evaporated at  $\pm 97^\circ\text{C}$  and calcinated at  $400^\circ\text{C}$  for 1 hour.

**Photo-reactor:** The experimental set-up of TVC reactor is shown in Fig. 1. Pyrex tubes were arranged horizontally as photocatalytic reaction zone and V-shape reflecting system was installed through the reactor tubes, which has flexible angles. The reflector was made from aluminium sheet. Aluminium is the best option due to its low cost

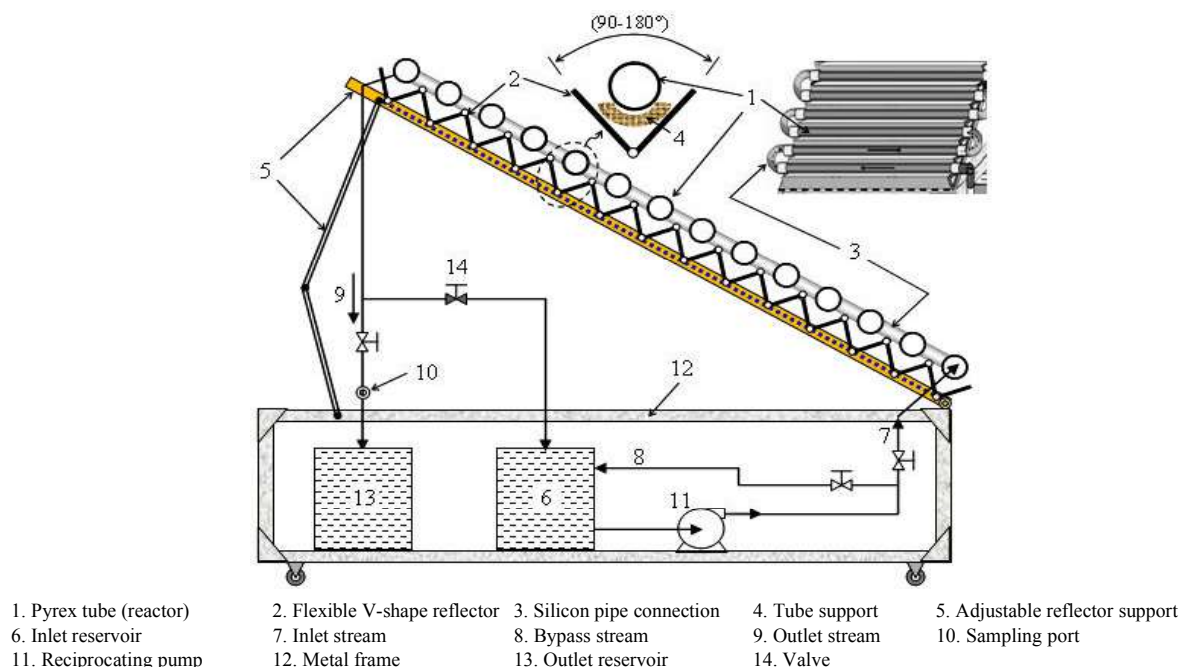


Fig. 1: Scheme of the *Tubular-V-Collector* (TVC)

and that is highly reflective throughout the ultraviolet spectrum [2]. The irradiation was carried out using 14 parallel of 18 W black light lamps ( $\lambda = 365$  nm, average illumination intensity of each lamp is  $50 \mu\text{W}/\text{cm}^2$ ) or the sunlight. The black light lamps were arranged horizontally above the tubes. A reciprocating pump was continuously draining the suspension from the inlet reservoir into the reactor system. The flow rate was controlled by valves and bypass stream.

The variation of reflecting angle was held at the beginning of all experiments. The experiment was to measure the reflecting intensity values of the reflectors using a Lutron UV light meter ( $\lambda = 290$ -390 nm).

**Performance Test of TVC Reactor and Ti/AC Composites:** Approximately 100 g of Ti/AC composites was inserted into each tube reactor. Aqueous solution of phenol with a certain initial concentration and flowrate was continuously poured into the reactor system. The concentration of phenol was periodically analyzed by the UV-VIS Spectrophotometer at 500 nm of wavelength. The effects of inlet phenol concentration, residence time and composition of the Ti/AC composites on the phenol removal were studied.

## RESULTS AND DISCUSSION

**Performance of the TVC Reactor:** The variation of reflecting angle was conducted by measuring the reflecting intensity to find out the optimum condition. Fig. 2 shows the reflecting intensity as a function of the reflecting angles in the range of  $90^\circ$ - $180^\circ$ . The results showed that the optimum reflecting angles under black light lamps and the sunlight irradiation were achieved at  $90^\circ$  and  $150^\circ$ , respectively. The black light lamps position was uprighted above the reflectors and made its light more effectively collected at the reflecting angle of  $90^\circ$  rather than at different angles. Using the smaller reflecting angle ( $90^\circ$ ), the light will be more focus if one reflector has only one black light lamp positioned above it. Otherwise, the use of sunlight as the photons source makes them less focus on one reflector. It is because the sun dimension and distance are unlimited. Consequently, under the bigger reflecting angle ( $150^\circ$ ), the sunlight, including both direct and diffuse UV-light, would be more effectively collected on the glass tubes.

Performance of the TVC reactor was also evaluated for phenol removal under the UV lamps and the sunlight irradiation. Fig. 3 shows a comparable good performance

of the TVC for phenol removal, either with sunlight or artificial UV lamps as a photon source. Unfortunately, the weather during the experiment day was cloudy, so that the phenol degradation rate with the sunlight is slightly lowers than the UV lamps.

**Performance of Ti/AC Composites:** When the UV lamps are not used, only adsorption plays a role in the phenol removal process, but when the lamps are turned on, the combination of adsorption and photocatalysis occurs. As shown in Fig. 4, it is indicated that the phenol removal by adsorption is more dominant than by photocatalytic oxidation. However, there is a significant difference between the adsorption only and the simultaneous of adsorption and photocatalysis. Hence, the phenol could effectively be removed through simultaneous adsorption and photocatalysis.

This synergistic effect was attributed to the formation of a contact interface between both solid phases ( $\text{TiO}_2$  and AC) and to the transfer of phenol adsorbed on activated carbon (AC) to titania, where the phenol was immediately photocatalytically degraded. This mechanism (illustrated in Fig. 5) could maximize the contact between reactant, catalyst and photon, so that the phenol degradation took place effectively [8, 13]. Contribution of the photocatalysis can be increased if the UV intensity is also increased [5, 14]. Furthermore, the immobilized state of  $\text{TiO}_2$  also affects the UV penetration in activating of  $\text{TiO}_2$  [15].

Fig. 6 plots the effect of titania loading on phenol removal, indicating that the phenol removal is increased by  $\text{TiO}_2$  loading, but then decreased when the  $\text{TiO}_2$  loading exceeds 7.5 wt%. Obviously, more  $\text{TiO}_2$  loading can increase phenol removal due to the increasing amount of the active sites. As a photocatalyst, the presence of  $\text{TiO}_2$  in the Ti/AC composites will increase the surface area for adsorption and photocatalytic reaction [16, 17]. So it can serve as hydroxyl radicals [5] that significantly increasing the phenol degradation.

However, Ti/AC composites with more than 7.5 wt%  $\text{TiO}_2$  loading cannot further increase the phenol removal due to its shading effects which are much higher, consequently reducing the photo exciting capacity of  $\text{TiO}_2$  [18]. Furthermore, increasing the  $\text{TiO}_2$  also decrease the amount of AC pores and it would decrease the adsorption capacity. Therefore it is estimated, under the experimental conditions of this work, that an optimum amount of  $\text{TiO}_2$  loading is approximately 7.5 wt%.

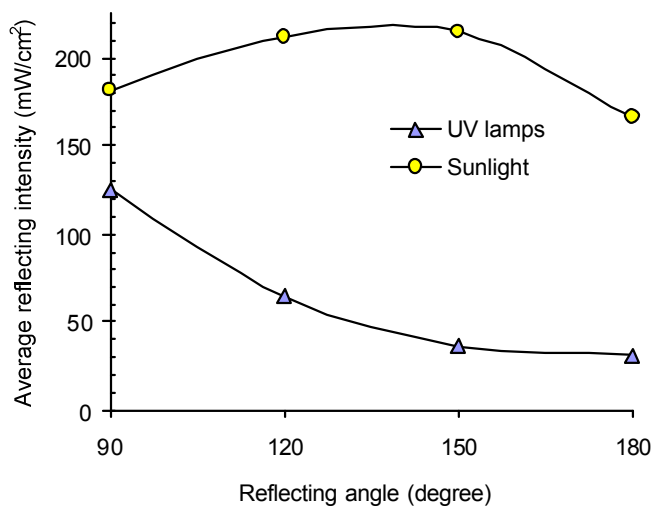


Fig. 2: The average of reflecting intensity measured above the V-shape aluminium at various reflecting angle.

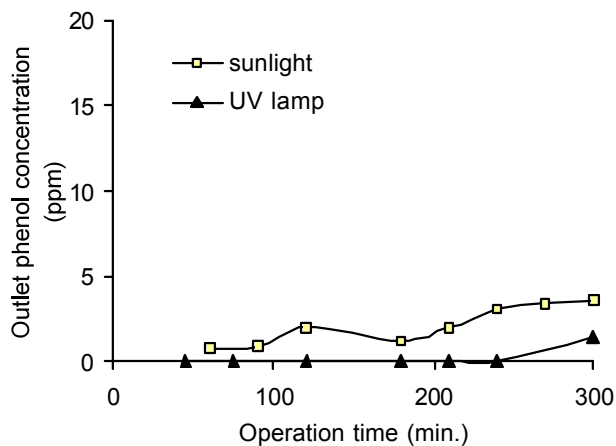


Fig. 3: Effect of photon source on the TVC performance ( $C_0 = 50$  ppm,  $v = 480$  mL/min., 12 tubes)

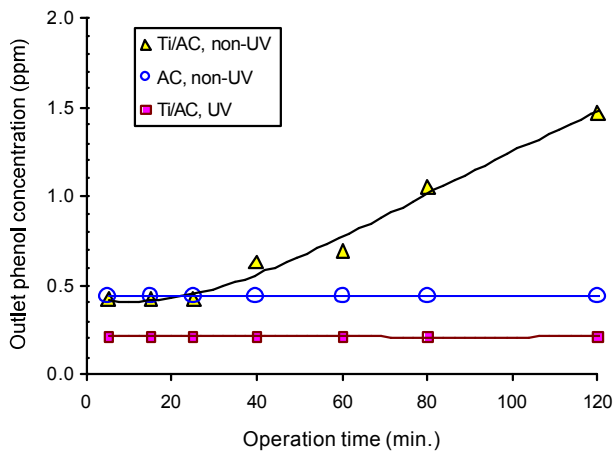


Fig. 4: Effect of UV lamps on the outlet phenol concentration ( $C_0 = 30$  ppm)

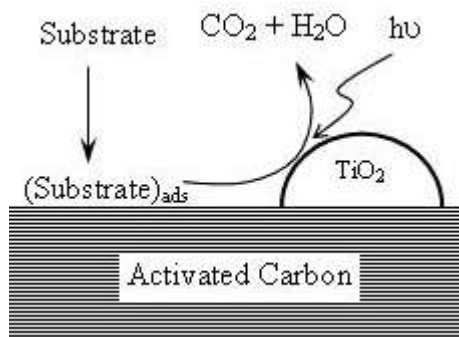


Fig. 5: Illustration of the phenol degradation mechanisms in the Ti/AC composites

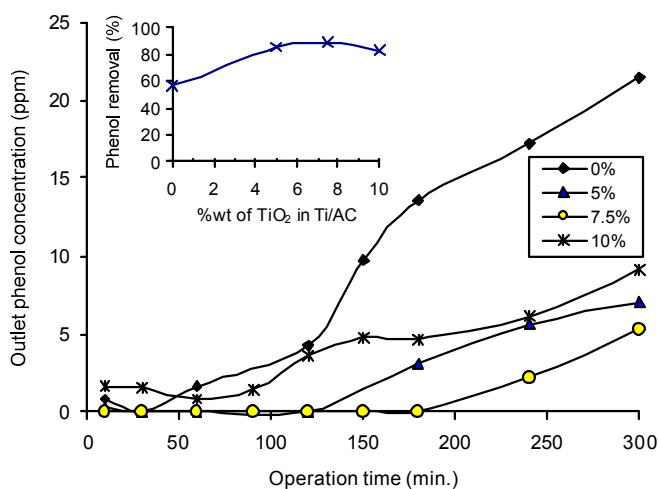


Fig. 6: Effect of TiO<sub>2</sub> loading on the phenol removal ( $C_0 = 50$  ppm,  $v = 120$  mL/min, 3 tubes)

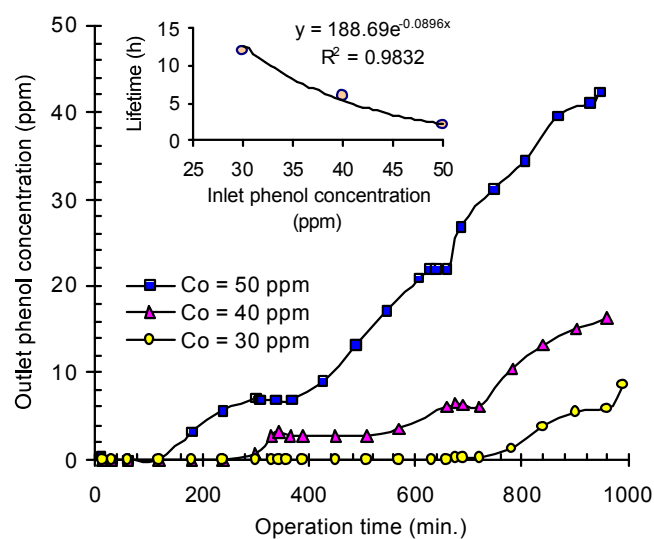


Fig. 7: Effect of inlet phenol concentration ( $C_0$ ) on the outlet phenol concentration and lifetime ( $v = 120$  mL/min., 3 tubes)

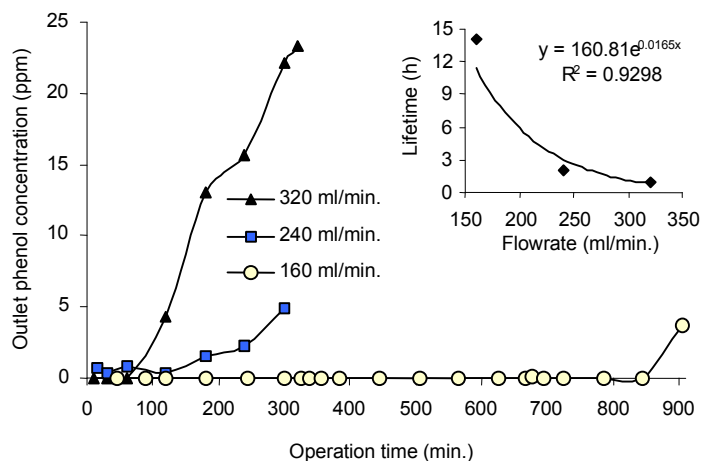


Fig. 8: Effect of phenol flow rate on the outlet phenol concentration and lifetime ( $C_0 = 50$  ppm, 6 tubes)

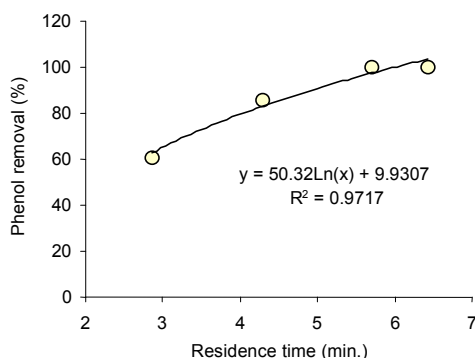


Fig. 9: Plot of residence time vs. phenol removal

**Effect of the Inlet Phenol Concentration:** Fig. 7 illustrates the results for outlet phenol concentration as a function of continuous operation time, with different inlet phenol concentrations ( $C_0$ ). Initially phenol can be completely removed from the solutions and continuously removed until its lifetime, depending on the inlet phenol concentrations. Lifetime is a condition in which the outlet phenol concentration from Ti/AC composites is still below the threshold of environmental quality standard (0.5 ppm). On the batch experiment using  $\text{TiO}_2$  P25 [15], increasing the initial phenol concentration can increase the percentages of phenol degradation until it reaches 50 ppm and decreases afterwards. This phenomenon does not occur in our continuous experiment because inlet phenol in the system is always fresh (not circulated); therefore analysis of the continuous system will be focused on the Ti/AC lifetime in removing phenol.

Inset of Fig. 7 plots the lifetime of Ti/AC composites that is depending on the inlet concentration of phenol. It is clearly demonstrated that the longer of the lifetime

is resulted from the smaller of the inlet phenol concentrations. In other word, increasing the inlet phenol concentration will exponentially shorten the lifetime of Ti/AC composites. More specifically, 50 and 30 ppm of the inlet phenol solution give the outlet phenol concentration at less than 0.5 ppm for more than 2 and 12 hours, respectively. Although the synergism effect between adsorption and photocatalysis was demonstrated (Fig. 4), however due to the concentration of activated carbon in the composites is more dominant, decreasing the lifetime with increasing the inlet phenol concentration appears to be more related to the adsorption capacity. In certain adsorption capacity, the Ti/AC be able to eliminate low-phenol concentration with a longer lifetime and vice versa a shorter lifetime for the higher concentration.

**Effect of Phenol Flow Rate:** Different flow rates of phenol solutions will influence the residence time of phenol inside the TVC reactor. Increasing the flow rates will decrease the residence time of phenol. As the influence of inlet phenol concentration, increasing the flow rates will exponentially reduce the lifetime of Ti/AC composites (Fig. 8). The composites will be more quickly saturated with increasing flow rate of phenol solutions.

The phenomenon above related to the phenol molecule structure being persistent enough to remove using Ti/AC composites (oxidation) method, especially in wet state. It seems that the phenol degradation reactions involve some mechanisms either influenced by  $\text{TiO}_2$  or AC simultaneously, such chain reactions. If this is the case, the flow rates play an important role for the phenolic removal.

Furthermore, increasing the flow rates also leads to lower percentage of phenol removal as a result of reducing the residence time. Fig. 9 reveals the influence of residence time on the phenol removal. In a particular lifetime, it is very easy to understand that with the increase in residence time of phenol solution in the Ti/AC composites, the percentage of phenol is also growing up.

## CONCLUSIONS

The present work illustrates a novel tubular V-collector (TVC) with the flexible reflecting angles and photon source. Optimum reflecting angles of the TVC depend strongly on the kind of photon source, which are achieved at 90° and 150° for black light lamps and the sunlight irradiation, respectively. The TVC shows a comparable superior performance for phenol removal through simultaneous adsorption and photocatalysis, either with sunlight or artificial UV lamps. Optimal composition of the Ti/AC composites is obtained for AC loaded with TiO<sub>2</sub> 7.5%-wt, whereas higher TiO<sub>2</sub> contents have a detrimental effect on the composites performance. Increasing the inlet phenol concentration as well as the flow rates of phenol solutions exponentially shorten the lifetime of Ti/AC composites. Typically within the residence time of 6 minutes, 30 ppm of phenol solution continuously could be removed below the threshold of environmental quality standard for more than 12 hours.

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