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The Coupling of Photocatalytic Oxidation Processes with Activated Carbon Technologies and the Comparison of the Treatment Methods for Organic Removal from Surface Water

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***Abstract*—**The surface water used in this study was collected from the Chao Praya River at the lower part at the Nonthaburi bridge. It was collected and used throughout the experiment. TOC (also known as DOC) in the range between 2.5 to 5.6 mg/l were investigated in this experiment. The use of conventional treatment methods such as FeCl3 and PAC showed that TOC removal was 65% using FeCl3 and 78% using PAC (powder activated carbon). The advanced oxidation process alone showed only 35% removal of TOC. Coupling advanced oxidation with a small amount of PAC (0.05g/L) increased efficiency by upto 55%. The combined BAC with advanced oxidation process and small amount of PAC demonstrated the highest efficiency of up to 95% of TOC removal and lower sludge production compared with other methods.

***Keywords*—**Advanced oxidation process, TOC, PAC

I. Introduction

ORGANIC pollutants are major environmental contaminant in surface water supply. Various water treatment processes can either directly or indirectly, to varying degrees, remove aquatic organic matter from raw water, depending on their operational conditions and the specific characteristics of the organic matters such as molecular weight distribution (MWD), carboxylic acidity, and humic substances content [1]. Conventional water treatment processes such as filtration, coagulation/flocculation and activated carbon processes are effective at removal of organic matter from water but are only able to minimize dissolved organic carbon (TOC). However, it can raise costs in areas such as sludge reduction and pH control. PAC has been effective for the removal of the herbicides; however, it is expensive and presents handling and disposal problems. In this study, TiO_2 photocatalytic degradation and PAC/TiO_2 photocatalytic hybrid system, and biofilter/photocatalytic oxidation were used. Flocculation with PAC and GAC adsorption as conventional treatment processes were demonstrated. The efficiency of organic compound removal by these techniques has been evaluated in terms of total organic carbon (TOC) reduction. However, from this study, the removal of TOC with a biofilter coupled with PAC/TiO_2 demonstrated superb removal of TOC of nearly 100%.

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This process revealed the highest removal efficiency not only of organic compound in terms of total organic carbon but also in terms of the formation of by–products that can increase mutagenic activity of the water. Another study revealed the unsuccessful removal of TOC (0 %) by using the advanced oxidation process (H_2O_2/UV, O_3/UV) and around 70% hybrid process with GAC adsorption to remove organic compounds from lake water [2]. However, this study showed the highest efficiency was 90% removal by GAC adsorption.

In Thailand, the Chao Phraya River is considered the lifeblood of Thailand. The 379 kilometer-long river supports 13 million people and is used in a variety of ways, including drinking water, irrigation, and as the primary water source for the Thachin River. As a confluent of the Ping, Wang, Yom, and Nan Rivers; the Chao Phraya River water quality is greatly affected by upstream land use activities. For example, in 1995, 2001, and 2002, upstream flooding resulted in high sedimentation rates and significant changes in water turbidity. In normal to low water levels, domestic, agricultural, and industrial discharges are greater than the river's capacity for self-purification. During 1993 to 2002, domestic, agricultural, and industrial discharges contributed 70 percent, 25 percent, and 5 percent to the waste load, respectively. In the Samut Prakarn Province Industrial Area, industry contributed over 70 percent to the total waste load.

In summary, the majority of waste discharged to the Chao Phraya River is organic waste and fecal coliform bacteria from domestic sources. Water quality is degrading with a increasingly smaller potential for restoration. Dissolved Oxygen (DO) is below the national standard in the lower part of the Chao Phraya river. This has been previously demonstrated by a larger survey by the Ministry of Natural Resource and Environment, Thailand [3].

II. Material And Methods

A. Materials

This study was carried out with Chao Phraya river water. Chao Praya River water in the lower part at the Nonthaburi bridge was collected for use throughout the experiment. TOC (also known as DOC) in the range of between 2.5 to 5.6 were investigated in this study.

TiO_2 P25 from Degusssa Frankfurt, Germany (composed of ca 80% anatase and ca20 % rutile) was used as thephotocatalysis. The surface area of the pores (BET) of the TiO_2 P25 was of 50 ± 15 m^2/ g).

Powder activated carbon (PAC MD3545WB wood based purchased from James Cumming & Sons Pty Ltd., Australia) was used as adsorbent. Its characteristics are as follows; mean pore diameter 3.061 nm, micropore volume 0.34 cm^3/g, mean diameter 19.71 μm, ash content 6% max, moisture content 5% max, and iodine number 900 mg/g min.

The GAC used in the experiments was washed with distilled water and dried in an oven at 103.5° C for 24 hours. It was kept in desiccators before packing into the column. The GAC bed was acclimatized at a low filtration rate. The filters were backwashed at 30% bed expansion for approximately 5 minutes every 24 hours of filtration run. It was kept in desiccators before packing in the columns. The physical properties of GAC are following; Iodine number 800 mg/(gm), BET surface 1112 m^2/g, Nominal size 3× 10^4 m and average pore diameter 2.614 □A

TOC removal of river water was determined by the TOC O.I analytical (1010) analyzqqer with an autosampler. All samples were filtered through a 0.45 μm membrane filter prior to the TOC measurement. Thus the TOC values obtained are, in fact, dissolved organic carbon (DOC) values.

B. Methods

1. Coagulation/Flocculation

The treatment processes of coagulation, flocculation and settling were simulated in the laboratory using a jar test procedure. Water samples were placed in a gang stirrer with predetermined doses of ferric chloride (30 to 150 mg/L) and mixed at 110 rpm for 1 minute. Then the mixing speed was reduced to 30 rpm and left for 15 - 20 minutes. Finally, a 20 minutes settling was provided and the supernatant was analyzed for TOC removal.

2. PAC adsorption

Mechanical stirrers with speed controllers were used to experimentally study the adsorption kinetics. The batch experiment was carried out using a series of beakers containing 2 L of wastewater at 25 °C. The PAC doses were varied from 0.1 g/L, 0.5 g/L, 1 g/L, and 2 g/L. The stirring speed was maintained at 110 rpm. The samples were collected at different times to calculate the amount of adsorbed organic matter (in terms of TOC).

3. AOPs Batch experiment

A batch reactor (illustrated in Figure 1) was used to find the optimum dose of TiO2, and PAC. The UV lamps used in the batch reactor experiments were the G8T5 germicidal lamps from Sankyo Denki which can transmit UV rays at 253.7nm. A circulation of tap water was provided around the reactor to cool the reactor and to maintain the temperature. Temperatures above 80 °C will lead to a reduction in the reaction rates [4]. The batch reactor was covered with aluminium foil at all times during operation.

4. GAC biofilter

The two centimeter diameter column were packed with GAC (illustrated in Figure 2).

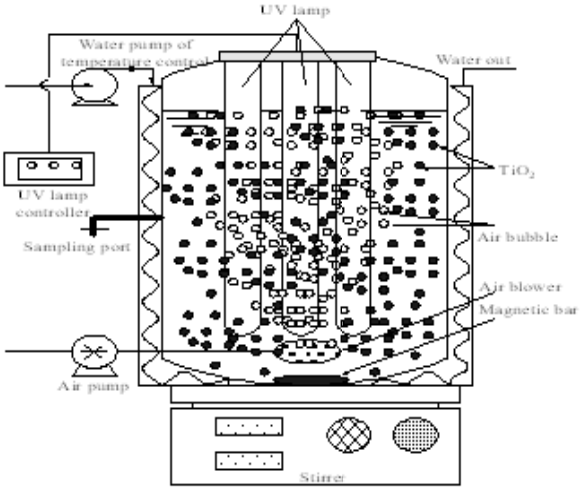

Fig. 1 Schematic of the photocatalytic batch reactor

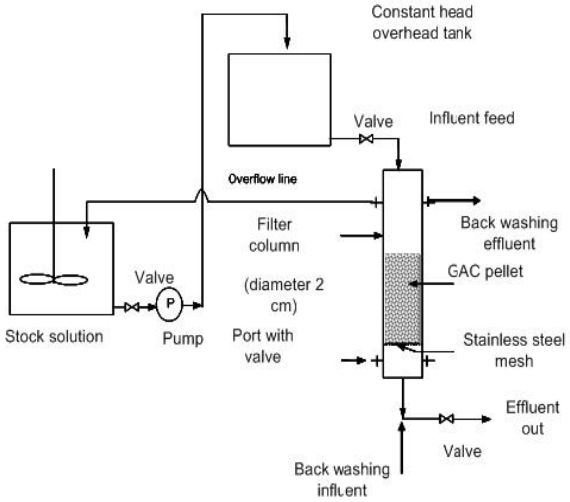

Fig. 2 Schematic of the GAC biofilter

III. Results And Discussions

The optimum dose of $FeCl_3$ as coagulant to remove TOC from the Chao Praya river water using jar tests is summarized in Fig. 3. Trends in removal efficiency with optimum dose of ferric chloride were around 60 to 70%. Increasing doses of ferric chloride resulted in slightly decreasing TOC.

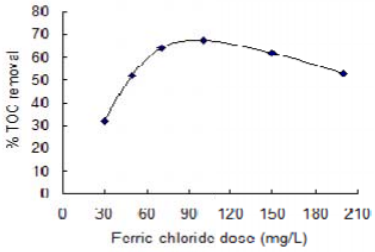

Fig. 3 TOC removal by $FeCl_3$ as coagulant

A. Results

The results from figure 4 and 5 with the use of PAC as adsorbents and catalyst support TOC removal of around 80 % by using PAC at concentrations of 2 g/L, and 1 g/L. The UV/TiO2 revealed TOC removal of around 35% and the reverse reactions occurred during 40 min of the operation. In surface water supply, their characteristics depend on the location, environment, including point source of pollutants. However, the main natural organic matter (NOM) pollutants in surface water can be classified to two categories;

• Hydrophobic NOM such as such as humic, fulvic, aromatic compounds, hydrocarbon compounds, phenolic compounds.

• Hydrophilic NOM such as hydroxyl acid, sugar, sulfonics, amino acids, polysaccharides

According to these substances, AOPs can cleavage and break the ring such as aromatic compounds of high molecular weight to low molecular weight. They also involve no sludge production due to the character of their removal mechanism, which is based on the oxidative destruction of organic carbon by conversion to a higher oxidation state [5].

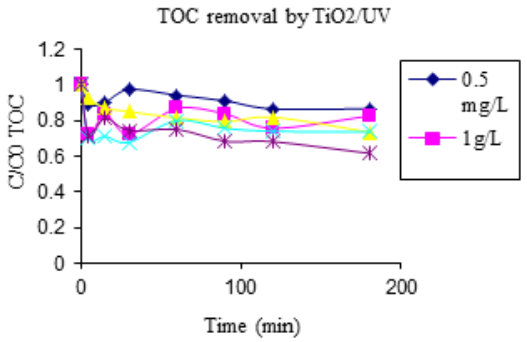

Fig. 4 TOC removal by TiO2/UV

Although the rate of TOC removal by PAC adsorption is better than that of TOC removal by AOP, the PAC process is not environmentally equivalent due to the accumulation due to the unconverted contaminants on the solid phase. However UV/TiO2 alone was also not significantly efficient in the removal of TOC and some organic pollutants may still occur in the other forms of organic compounds. In comparison with running UV/TiO2 alone, the combined chemical treatment provided distinct advantages and in particular the elimination of TOC.

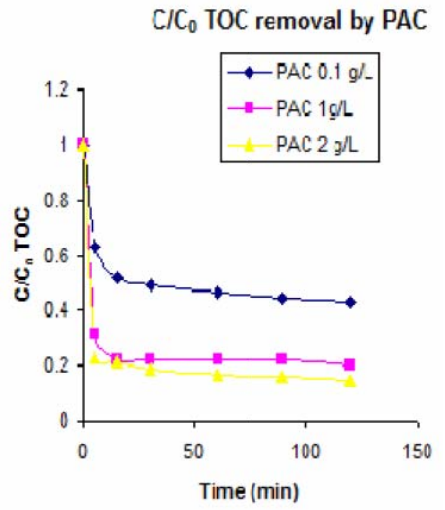

Fig. 5 TOC removal by PAC

The several treatment methods are summarize in Table I. GAC adsorption can remove up to 90%, $FeCl_3$ 65%, PAC 78% and TiO_2/UV can remove TOC 35%.

TABLE I
OPTIMUM DOSE CORRESPONDING TO REMOVAL VALUES FOR EACH PROCESS

	Optimum dose (mg/L)	Maximum TOC removal
$FeCl_3$	100	65%
TiO_2/UV	2000	35%
PAC	1500	78%
GAC adsorption (fresh) 15 cm (bed depth)	15000	90%

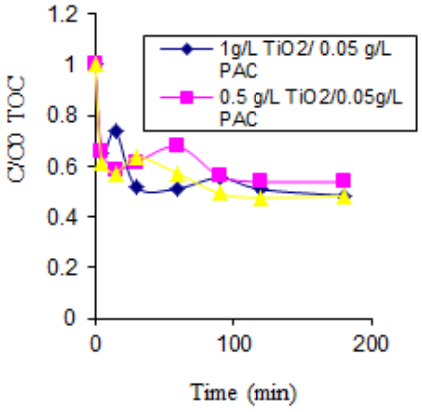

Fig. 6 TOC removal by UV/TiO2/PAC with different concentrations

B. Determination of optimum ratio TiO2/UV/PAC for degradation organic compound in surface water

Three different ratios of TiO_2/PAC were studied for degradation of dissolved organic carbon. TiO_2 and PAC were varied for different values of constant TiO_2 and PAC (Figure 6). At the PAC concentration of 0.05 g/L with different

concentration of TiO_2 the TOC removal after 70 min was around 55% with three different concentration of TiO_2 which were 0.5, 1, and 2 g/L respectively. Reverse reactions occurred during the first 50 min. of operation. The factors which affect the reactions are the inorganic and organic compounds which occur during oxidation processes. The characteristics of surface water also retard the reaction [6], [7], [8].

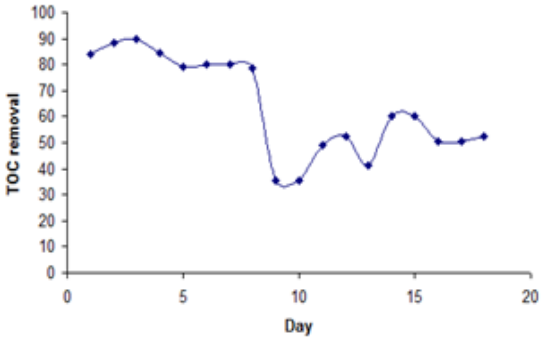

Fig. 7 Percentage of TOC removal efficiency on the GAC biofilter

The TOC removal efficiency of the biofilter is presented in Figure 7. This result shows that the GAC biofilter can be operated for a long time without regeneration of the media. After 22 days of continuous run, the biofilter maintained the organic removal efficiency of 40-50 %. It should be noted that this result was obtained with a biofilter of 15 cm GAC column depth. The TOC removal could be increased by increasing the GAC column depth. The daily backwash adopted to avoid the physical clogging of the biofilter did not affect the performance of the organic removal efficiency of the filter. Some of the biomass may naturally be lost during backwashing of the filter but the loss of biomass can create more sites for adsorption of organics and thus the impairment is balanced.

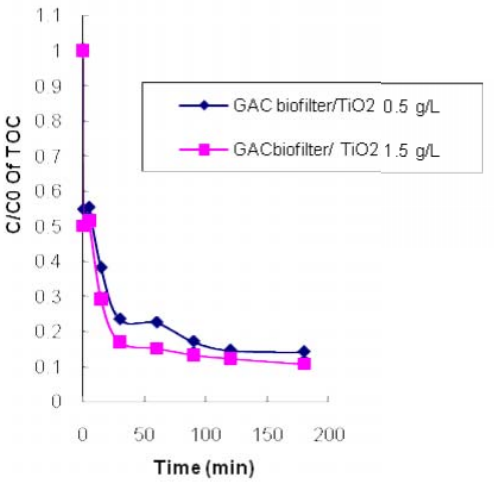

Fig. 8 C/C_0 of TOC removal by using effluent of GAC biofilter (after 20 days of operation) followed by UV/TiO_2

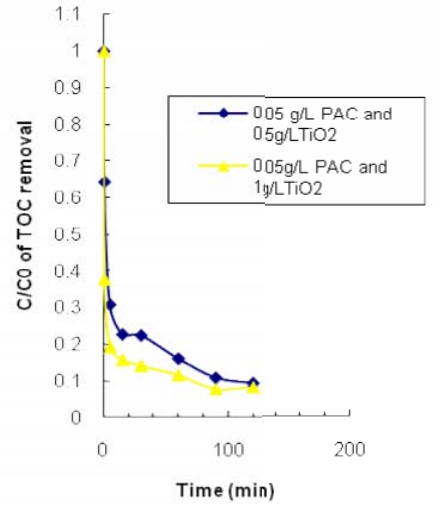

Fig. 9 C/C_0 of TOC removal by using effluent of GAC biofilter (after 20 days of operation) with TiO_2 and PAC

Comparisons of the combined system of biofilter followed by UV/TiO_2 and UV/TiO_2PAC revealed the high performance of this system. The combined biofilter/UV/TiO_2 revealed that the reverse reaction during 5 min of operation and a TOC removal of up to 87% after 60 min operation time. This is because of some aromatic and organic compound such as herbicide, pesticide, and NOM transform to other organic compound, as observed in former studies (NOM, and herbicide removal (MM))[9].

The combined GAC biofilter with UV/TiO_2/PAC revealed that more than 90% of TOC was removed in a short operation time of 5 min using $1g/LTiO_2$ and 0.05 PAC (Figure 9). Table II showed the comparison of TOC removal by GAC biofilter and combined system.

TABLE II
COMPARISON OF TOC REMOVAL BY GAC BIOFILTER AND COMBINED SYSTEMS

Process	TOC removal(%)	Optimum time operation (AOPs)
GAC biofilter	50 to 55	120 min
UV/TiO_2followGAC ads	80	60 min
GACbiofilter follow UV/TiO_2	85	10 min
GACbiofilter follow UV/TiO_2/PAC	95	

IV. CONCLUSION

The use of biofiltration followed by a photocatalysis hybrid system could remove organic matter from surface water by more than 85%. Furthermore, combining a small amount of PAC increased removal of organic matter by upto 95%. This treatment showed less sludge production and higher removal efficiency compared with other treatment processes.

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