PHOTOCATALYSIS HYBRID SYSTEM IN REMOVING ORGANIC MATTER FROM WATER

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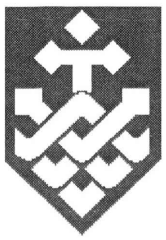

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Certificate

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Abstract

Conventional processes used to treat water and wastewater mainly removes the suspended solids, pathogens and biodegradable organic matter. The majority of persistent organic pollutants are not generally removed by these processes.

Persistent organic pollutants (POPs) constitute a class of anthopogenic substances (man-made) and can be found as trace quantity elsewhere in environment. They are toxic and bio-accumulate in humans, plants, animals, and have significant adverse impacts on human health and the environment, even at very low concentrations. They may cause cancer and disorders in the reproductive and immune systems as well as affecting the human developmental process. POPs do not readily break down in the environment with half-lives in soils in the order of years, although they may be transformed both physically and chemically over long periods of time. They exist in agricultural runoff, drainage to the sewerage system and industrial discharge.

In this study, three organic pollutants were selected for investigation humic acid as natural organic matter (NOM), metsulfuron methyl herbicide as POP, and biological treated sewage effluent (BTSE).

In the first part of the study, removal of humic substance representing NOM was investigated with various types of photocatalytic reactors. The percentage of dissolved organic carbon (DOC) removal with a batch reactor with titanium dioxide (TiO_2) as the photocatalyst ranged from 20 to 60 %. When powdered activated carbon (PAC) was added together with TiO_2 in the photo reactor, an improvement of more than twice DOC removal was noticed compared with the same amount of TiO_2 used alone. From these

results, the use of PAC - TiO_2 demonstrated superior removal of humic substance within a shorter contact time and higher removal efficiencies compared with using TiO_2 alone. Solid phase micro extraction coupled with Gas Chromatography and Flame ionisation detector (SPME/GC FID) equipped with DB-5 column was used to investigate the intermediate photo products during the photo-catalytic reaction. The manner in which intermediate photoproducts evolve and transform was demonstrated by the GC FID peak. The photo reaction can be summarised in the following way. The photo resistant by-products was adsorbed on the PAC-TiO_2 surface as shown in GC peak results. From DOC measurements, it is estimated that less than 25 % of the initial material remained. It is noted that during the PAC-TiO_2 batch process humic substance was removed immediately without forming a large amount of intermediate macro-molecules of humic substance.

In the photocatalysis continuous reactor, the humic substance removal efficiency was studied at different detention time (different flowrates). Better results were achieved at longer detention times as there was more contact time. When the PAC was added, the results also indicate that the photo-catalytic adsorption hybrid system removed a significant amount of humic substance (80% DOC removal) within a shorter contact time compared with using TiO_2 alone.

In a recirculated continuous plug flow reactors the factors for controlling removal rates in heterogeneous catalysis are mass transfer and surface reaction controls. These factors were improved when a high recirculation flow rate of 250 mL/min was used where flow is turbulent. When a small amount of PAC was added in addition to TiO_2, DOC removal improved to 80% in a shorter operation time of less than 10 minutes. The results with

various types of reactors indicate that recirculated continuous reactor gave the highest efficiency for removal of NOM (humic substance) in a shorter detention time.

In the second part of the study, the removal efficiency of metsulfuron methyl representing persistent organic pollutants (POPs) was studied. Batch reactor experiments conducted with different doses of TiO_2 and a small amount of PAC of 0.05 g/L revealed that the TOC removal efficiency can be significantly increased up to 80%. Further, the concentration profile and the rate constant showed superior photocatalysis performance in the presence of PAC. The PAC added during the photo-oxidation absorbed the intermediate compounds and thereby promoted the photocatalytic oxidation. The photooxidation with a detention time of 0.5 to 2 hours resulted in intermediate products of smaller molecular weight substances. In this study, a detailed analysis with SPME/GC (solid phase micro extraction/gas chromatography) was made to study on the photo oxidation intermediates. Following 10 min of residence time in the batch reactor the MM partitioned to smaller molecular weight compounds (or substrate) which occurred at different peak times during the GC (12.10, 14.25, 17.40, 19.63 and 20.18 minutes). After 5 hours of residence time in batch reactor, same substrate was found to be degraded. The photo oxidation was faster when activated carbon was used together with TiO_2. The substrate that occurred at the peak times of 19.96 and 18.32 minutes during the GC had nearly disappeared, while the peak at time 14.27 minutes was lower. Some anionic by - photoproducts was investigated by using ion-chromatography. Nitrate and nitrite ions were formed as by-photoproducts. The formation of NO_3^- and NO_2^- anions occurred was faster when PAC was added to the photo-oxidation. Similarly, SO_4^{2-} ions form during the photo-oxidation of MM. Where PAC is present in the reactor, the concentration of SO_4^{2-} ions peaked earlier at approximately 50 min and thereafter reduces

its (SO_4^{2-}) concentration. The reduction in concentration of SO_4^{2-} after 50 min may be due to a portion being adsorbed on the PAC-TiO_2 surface and a portion being transformed to SO_2. In this study, the increase in efficiency of MM degradation is similarly attributed to the adsorption of photo-products on the more surface available with TiO_2 coupled with the PAC and active sites available to react with the pollutants. This reduces the competitive adsorption on active sites of PAC-TiO_2 increasing efficiency of degradation of MM. However, complicated photo-oxidation and by-products occur during these processes, and it is difficult to determine the actual mechanism of photo-catalytic reaction on the PAC-TiO_2 surface and the role of active sites because sophisticated instruments are required to do this. Experiments with recirculated continuous reactor were also conducted by using TiO_2 and TiO_2-PAC. The coupling of PAC with continuous heterogeneous TiO_2 photocatalysis leads to a faster degradation of MM than the heterogeneous TiO_2 photocatalysis alone. The incorporation of a small amount of PAC of 0.05 g/L with 1.5 g/L of TiO_2 led to 78% removal even with a short residence time of 5.25 minutes.

The granular activated carbon (GAC) filter was found to be very effective as a pre-treatment for the removal of herbicide (MM). Fixed bed column experiments packed with GAC were conducted with different GAC bed heights (5, 10 and 15 cm) and different effluent velocities. The GAC photocatalytic hybrid system showed upto 90% removal with GAC bed depth of 10 and 15 cm. The 10 and 15 cm deep GAC columns showed a steady state of effluent concentration. The retention time of GAC followed by photoreaction was less than 10 minutes.

Recirculated photocatalytic batch reactor experiments conducted with the biological

treated sewage effluent showed effective DOC removal. After start up, with the recirculated flow of 60 mL/min the effluent DOC was reduced by 60% in a period of 180 min, and became relatively stable. There were no large differences between results obtained with various recirculation flow rates. About 70 to 75 % DOC removal was achieved using flow rates of 100 mL/min and 250 mL/min. However, with a recirculation flow of 250 mL/min, DOC removal decreased to 65% down from the 73% DOC removal obtained with that of 100 mL/min rate. This can be explained in terms of the characteristics of the plug flow reactor. The flow rates used in this study were large enough to keep the catalyst in suspension, and to promote good mass transfer between the reactants. When a small amount of PAC (0.05g/L) was added, a complete removal of DOC was observed after 250 and 300 min operation times. The addition of 0.05 g/L of PAC adsorbent to the recirculated continuous reactor facilitated better organic removal than titania photocatalyst alone. DOC removal was further increased to 75% within 30 min of operation.

The membrane photocatalysis hybrid system was used to separate catalyst from the effluent. The membrane flux was very low and fouling was high when TiO_2 was tried to be filtered through MF filter. To facilitated TiO_2 separation, (i) pH adjustment and (ii) flocculation of TiO_2 slurry were used. Although the use of pH adjustment achieved effective improvement to membrane operation, it was 15% less effective than applying a pre-treatment of flocculation of TiO_2 slurry. Photocatalysis and flocculation pre-treatment processes before MF/UF also resulted in high (over 90%) DOC removal, surpassing those achieved with mixed TiO_2 and PAC photocatalyst.

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Nomenclature

a	: isotherm constants
b	: constant related to the binding energy of adsorption (L/mg)
BV	: bed volume
C	: concentration in bulk solution, mg/L
C_b	: desired concentration of adsorbate at breakthrough (mg/L)
C_e	: equilibrium concentration (mg/L)
C_{ef}	: effluent adsorbate concentration (mg/L)
C_{if}	: influent adsorbate concentration (mg/L)
C_o	: initial concentration (mg/L)
Ct	: final concentration (mg/L)
d	: depth of adsorbent's bed (m)
D_x	: dispersion coefficient in x direction (m^2/s)
DOC	: Dissolved organic carbon concentration (mg/L)
EBCT	: empty bed contact time
k	: apparent photodegradation rate constant (min^{-1})
K_{Ad}	: the adsorption coefficient
K_d	: linear equilibrium partitioning coefficient (L/mg)
k_f	: external film mass transfer coefficient of organic, m/s
K_F	: Freudlich constant indicative of the adsorption capacity
K_S	: the Monod half velocity coefficient
k_s	: particle phase mass transfer coefficient (1/s)
m	: amount of adsorbent (g)
M	: Weight of adsorbent (g)
n	: experimental constant indicative of the adsorption intensity
n_T	: effective porosity (dimensionless)
p_s	: solid density of the particles (mg/L)

q_t	: amount of adsorbate at any time t, (mg/g)
q_e	: amount of adsorbate at equilibrium (mg/g)
q_m	: saturated maximum adsorption capacity (mg/g)
qs	: adsorbed phase concentration at the external surface of adsorbent particle (mg/g)
Q	: volumetric flow rate (L/min)
R	: radius of adsorbent particle, m
r	: correlation coefficient
t	: service time of column (h)
T	: temperature
u	: velocity of the fluid (m/s)
V	: throughput volume (L)
ε_b	: bed porosity
α	: dispersivity (m)
z	: bed depth, (m)

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