Degradation of Humic Acid by Titanium Dioxide Catalyst

RIUNGU N. J., Department of Biomechanical and Environmental Engineering, J. K. U. A. T., P.O. Box 62,000-00200, Nairobi, Kenya
HOME P. G., Department of Biomechanical and Environmental Engineering, J. K. U. A. T., P.O. Box 62,000-00200, Nairobi, Kenya
NDEGWA G. M., Department of Biomechanical and Environmental Engineering, J. K. U. A. T., P.O. Box 62,000-00200, Nairobi, Kenya

Abstract
The presence of humic acid (HA) in water has for long posed a challenge for treatment. Its presence in water during treatment such as disinfection by chlorination leads to formation of disinfection by-products (DBPs) that may be carcinogenic. It forms complexes with heavy metals present in water and also causes membrane fouling during membrane application for water treatment. HA should hence be removed from water before chlorination or membrane filtration as this would lead to longer membrane life with minimum operational cost and also reduce the health hazards associated with DBPs. This paper compares the efficiency of two forms of Titanium dioxide (TiO₂) catalysts; TiO₂, solution form (TiO₂, s) and TiO₂, powder form (TiO₂, p). Of major interest was their ability to degrade humic acid both in presence and absence of UV radiation.

TiO₂, s showed higher degradation efficiency than TiO₂, p both in presence and absence of UV radiation, an observation that was attributed to the differences in surface area between the two catalyst when at same concentration. Degradation efficiency was seen to be affected by initial catalyst loading and type of catalyst. It was seen that use of TiO₂ is a promising method degradation of organic contaminants.

1.0 INTRODUCTION

Humic substances make up a large portion of organic matter found in natural environments with a typical concentration in the range of 0.1 to 200 mg/L dissolved organic carbon (Kinniburgh et al., 1996). Humic acid (HA) is a key component of humic substances (Stevenson, 1994) and they are a complex mixture of organic compounds. The removal of humic substances from water has been a challenge. In many countries, the HA is eliminated from water before chlorination by coagulation with aluminium sulphate and filtration. However, coagulation presents two main disadvantages which are maintenance of residual sludge with high aluminium concentration and treated water needs high quality monitoring of aluminium. The recommended aluminium concentration is 0.2 g/L (Wiszniewski et al., 2002). The conventional treatment process can remove only 10–50% of the TOC (Wiszniewski et al., 2002).

Photocatalysis using semiconductor catalysts such as TiO₂ is a promising method for removing humic substances and other organic compounds from water. The process can degrade the majority of the organic molecules, without additional chemicals except the photocatalyst (e.g. titanium dioxide). The basic process of photocatalysis consists of ejecting an electron from the valence band (VB) to the conduction band (CB) of the TiO₂ semiconductor creating a h⁺ hole in the VB (Wiszniewski et al., 2002) that occur due to the UV irradiation of TiO₂ with an energy equal or superior to the band gap (>3.2 eV). The photocatalyst absorbs efficient photons from UV light, producing strong oxidants including OH⁻ radicals that decompose organic compounds adsorbed on the catalyst surface. Numerous organic contaminants including herbicides, pesticides, and halophenols have been reported to be efficiently removed from polluted water using this method (Bertelli and Selli, 2006; Toepfer et al., 2006; Parra et al., 2004; Hoffmann et al., 1995). Recently, TiO₂-based photocatalysis has been reported to effectively remove humic acid (Fang et al., 2005; Li et al., 2002; Tay et al., 2001) and NOM (Fu et al., 2006; Le-Clech et al., 2006; Doll and Frimmel, 2005). No studies have been made to compare the effectiveness of the solution and powder form of the TiO₂ catalyst.
This research addresses the destructive removal of humic acid in aqueous medium by photocatalytic oxidation process using two types of catalyst; TiO$_2$ Degussa p-25 (in powder form) and titanium dioxide solution (TiO$_2$), (C380 from TIPE Company, China). The influence of operating parameters like TiO$_2$ and humic acid concentration on degradation of humic acid were investigated.

2.0 EXPERIMENTAL WORK

2.1. Membranes
Three kinds of flat sheet commercial UF membranes were used for this work. These are;
- PS100H-A PSu UF membrane supplied by Microdyn-Nadir GmbH with the following characteristics according to manufacturer, PSu top layer, polypropylene support layer and a cut-off of 100 kg/mol.
- C100H- A regenerated cellulose membrane with a cut-off of 100 kg/mol supplied by Microdyn-Nadir GmbH.
- C30H- a regenerated cellulose membrane supplied by Microdyn-Nadir GmbH with a cut-off of 30 kg/mol.

2.2 Chemicals
Humic acid sodium salts was supplied by Sigma–Aldrich company. Two types of catalyst were used for this work. TiO$_2$ Degussa p-25 (in powder form with 70% anatase, 99.8% purity) having a BET surface area of 50±15 m$^2$/g and an average particle size of 30 nm and titanium dioxide solution (TiO$_2$), (C380 from TIPE Company, China) with primary particle size 6-8 nm, agglomeration index in water of approximately 3-4, a TiO$_2$ concentration of 0.85% by weight and a BET surface area of 150±30 m$^2$/g.

2.3 Photocatalytic degradation
Humic acid was used to simulate the organic matter in natural waters. Photocatalytic degradation was investigated using two types of catalyst discussed in section 2.2. The photocatalytic degradation of humic acid (100 mg/L) was carried out in a 1 L cylindrical Pyrex reaction vessel. To study the effect of catalyst concentration, 0.17 g/L, 0.34 g/L and 0.5 g/L catalyst concentration was used at the natural pH of the solution pH 6.5 respectively for both catalyst types. The degradation was investigated in presence and absence of UV light for all catalyst concentrations. When studying effect of UV light on degradation of humic acid, the reaction vessel was illuminated from the top and continuous stirring of the suspension was provided by means of a magnetic stirrer. The light source was a 15 W low pressure mercury lamp with a major emission of 254 nm. Prior to analysis, TiO$_2$ was removed from the reaction medium by filtration through 0.45 µm Millipore membrane filter.

Total organic carbon (TOC) was analyzed with a Shimadzu Total organic carbon Analyzer TOC-5050A. The UV absorbance of humic acid was measured at a wavelength of 280 nm with a Cary IC UV-VIS spectrophotometer. The absorption spectrum of the feed was scanned at a wavelength range of 190 nm-600 nm.

2.4 Calculations
The TOC in the samples was analyzed using a Shimadzu TOC-5050A total organic carbon analyzer. To compare the two catalysts in terms of their ability to degrade the humic acid, their rates of reaction were evaluated. According to Huang et al., 2008 reaction rate constant is evaluated using the formula;

\[ k_a = \frac{\ln \left( \frac{C}{C_0} \right)}{t} \]

Where $k_a$ denotes the reaction rate constant and $C_0$ is the initial concentration of the substrate and $C$ the concentration of the substrate at time $t$. This equation is true when there is first order reaction. Most of researchers have said that the decomposition of HA on TiO$_2$ is a first order reaction (Li et al., 2002, Huang et al., 2008). This means that logarithm of concentration vs. time is a straight line and the slope of this line is reaction rate constant (Huang et al., 2008).

3. RESULTS AND DISCUSSION

3.1. Results of experiments in batch photo reactor

3.1.1 Degradation of humic acid by catalyst
Photo catalytic (TiO$_2$) experiments were performed using the photo reactor described in section 2.3, to evaluate the effectiveness of TiO$_2$ and TiO$_2$/UV treatment for HA removal. Degradation of 100 ppm HA feed solution was investigated using 17 ppm and 34 ppm of both TiO$_2$, s and TiO$_2$ p. The experimental results are shown on figure 2.
Fig. 2; Ratio of remaining TOC with time in photocatalytic degradation of 100 ppm HA by TiO$_2$.

After addition of catalyst, experimental results showed a slight decrease in TOC followed by an increase in TOC concentration before continuous reduction of TOC was obtained. The slight decrease was caused by adsorption of HA on the surface of catalyst. The increase in TOC was due to the release of intermediate oxidation products from the surface of the TiO$_2$ catalyst to the bulk solution. Similar findings were reported by Huang et al., 2008 and Choo et al., 2008 who noted that the HA adsorbed on the surface of catalyst was oxidized and transformed into intermediate oxidation products more hydrophilic than the original HA. The continuous decline in the TOC that followed indicated the mineralization of the intermediate products of humic acid to carbon dioxide and water, an observation also made by Huang et al., 2008 and Uyguner et al., 2005. UV absorbance showed a continuous decrease in values as the experiment proceeded. Uyguner et al., 2005 noted this decrease in specific absorbance values was caused by degradation of humic acid to less UV absorbing compounds through a series of intermediate products and their consequent reaction.

### 3.1.2 Effect of catalyst concentration

Table 1 shows the reaction rate constants during the photocatalytic oxidation, using different doses of TiO$_2$ catalysts. The initial concentration of HA was 100 ppm. It has been reported that the efficiency of photocatalytic activity of TiO$_2$ depends on its dosage and that as the dosage increases, the rate of oxidation increases (Huang et al., 2008). This is largely due to the higher surface area and hence greater NOM removal via adsorption on catalyst surface at higher TiO$_2$ doses.

However, on further increase of dosage, the turbidity of the suspension increases reducing the effective UV irradiation which negatively affects the reaction rate. From table 1 below, it can be seen that when catalyst concentration was increased from 0.17 g/L to 0.34 g/L, the reaction rate constants increased almost double in all cases. This was caused by an increase in surface area of the particles thus providing high efficiency of surface trapping of photon-generated electrons and holes, thus increasing the probability of photocatalytic degradation on the catalyst surface. A further increase from 0.34 g/L to 0.50 g/L showed a slight increase in the constants which could have been caused by increased solution turbidity due increase in number of suspended particles that reduce UV penetration into the solution.

TiO$_2$ concentration is known to have a direct impact on the amount of light transmitted to the suspension and therefore on the rate of photon uptake by TiO$_2$. The negligible improvement in TOC removal with TiO$_2$ concentrations above 0.34 g/L can be explained by weakening UV light penetration into the bulk suspension, counteracting the effect of increasing catalyst surface area.
3.1.3 Effect of UV irradiation on reaction rate constant

Degradation of HA was investigated in presence and absence of UV irradiation at catalyst concentration of 0.17 g/L, 0.34 g/L and 0.50 g/L respectively. The UV lamp was a 15 W low pressure lamp with a major emission of 254 nm. Complete mixing was enhanced by means of a magnetic stirrer. The experiment was carried out for 6 hrs with samples taken for analysis of TOC and absorbance on hourly basis. From the values in table 1, it can be seen that for both catalysts, the reaction rates for all concentrations were much higher with UV illumination than in absence of UV light. This is because the catalyst produces electrons and holes by ultraviolet radiation which makes it possible to form the hydroxyl radicals that have strong oxidizing power. These help in degradation of humic acid and destruction of toxins.

3.1.4 Effect of catalyst type on HA degradation

From the results shown on table 1 TiO$_2$, s achieved higher reaction rate constants than TiO$_2$, p except at concentration of 0.34 g/L without UV lamp. This could have been because of surface area. At same catalyst concentration, TiO$_2$, s has a higher surface area than TiO$_2$, p. Due to increased surface area; more sites are available for reaction for the solution catalyst. It has been noted in previous studies that photocatalytic process mainly occurs on the photocatalyst surface and not in the bulk solution (Li et al., 2002) hence the higher the surface area the faster the reaction rate. TiO$_2$, s is also more stable than TiO$_2$, p and this too could be a reason for its higher degradation rates.

4. CONCLUSION

The degradation of HA was affected by catalyst type, concentration and UV radiation. TiO$_2$, s catalyst showed higher removal efficiency than TiO$_2$, p. This was mainly attributed to an increase in surface area for TiO$_2$, s catalyst than TiO$_2$, p particles when at same concentration. For both catalysts, presence of UV radiation at wave length of 254 nm seemed to offer higher degradation rates than in its absence. For all cases, the rates increased when catalysts concentration was increased to 0.34 g/L from 0.17 g/L almost doubling the rates but showed less increase when the catalyst concentration was increased from 0.34 g/L to 0.50 g/L.

Use of Titanium Dioxide catalyst was seen as an efficient way of degrading organic matter from water and the solution form of the catalyst proved to be better due to increased surface area for trapping of the pollutants.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support of the CIMO-NSS scholarship funds.

REFERENCES


---

**Table 1: Comparison of reaction rate for two types of TiO$_2$ (solution and powder). Absorbance measurements are at wavelength of 280 nm.**

<table>
<thead>
<tr>
<th>Concentration of TiO$_2$ (g/L)</th>
<th>Reaction rate</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TiO$_2$, p</td>
<td>TiO$_2$, s</td>
<td>TiO$_2$, p</td>
<td>TiO$_2$, s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO UV</td>
<td>UV on</td>
<td>NO UV</td>
<td>UV on</td>
<td>NO UV</td>
<td>UV on</td>
<td>NO UV</td>
</tr>
<tr>
<td>0.17</td>
<td>0.0006</td>
<td>0.010</td>
<td>0.0005</td>
<td>0.025</td>
<td>0.0008</td>
<td>0.012</td>
</tr>
<tr>
<td>0.34</td>
<td>0.010</td>
<td>0.023</td>
<td>0.0076</td>
<td>0.047</td>
<td>0.0096</td>
<td>0.023</td>
</tr>
<tr>
<td>0.50</td>
<td>0.0059</td>
<td>0.039</td>
<td>0.0067</td>
<td>0.052</td>
<td>0.0076</td>
<td>0.0424</td>
</tr>
</tbody>
</table>


