Global NEST Journal, Vol 18, No 2, pp 392-401, 2016

THE COMPARISON OF PHOTO CATALYTIC DEGRADATION OF DISSOLVED ORGANIC CARBON (DOC) FROM WATER BY UV/TiO_2 IN THE PRESENCE AND ABSENCE OF IRON ION

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Received: 05/03/2016
Accepted: 13/04/2016
Available online: 18/05/2016

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ABSTRACT

Most of water sources throughout the world contain natural organic matter (NOM), which is the best description as a complex mixture of organic compounds. The effect of iron ion on removal efficiency of dissolved organic carbon (DOC) using UV/TiO_2 photo catalytic oxidation (TiO_2) was examined. In this quasi-experimental study, the different variables such as pH value, contact time, various concentrations of TiO_2, $FeCl_2$ on the removal efficiency of DOC by the UV/TiO_2 on raw water of Zayandehroud in Isfahan were studied. The results were analyzed by using Pearson correlation coefficient test and SPSS software. Removal efficiency DOC improved as the amount of catalyst was increased. Maximum removal efficiency was achieved during acidic conditions (pH=3) within 60 minutes of contact time. The removal efficiency of DOC by the UV/TiO_2 decreased with increase of contact time. The presence of iron ions increased the rate of DOC removal by the UV/TiO_2. Removal efficiency of dissolved organic carbon increased when ionic strength and initial concentration of Ferric Chloride was increased. Also, by adding particles of Ferric Chloride, Removal of dissolved organic carbon increased to 98% in comparison with absence of iron ion (78%).

Keywords: Dissolved organic carbon (DOC), Titanium dioxide nano particle, Photo catalytic oxidation, $FeCl_2$

1. Introduction

For protecting human health, the treatment processes of drinking water should be efficient as possible to hinder the anthropogenic compounds from entering drinking water. The main purpose of drinking water treatment plants using surface water as raw water are going to remove natural organic matter (NOM), turbidity, and microorganisms (Fent *et al.*, 2006). Many water sources throughout the world contain NOM, which is a complex mixture of organic compounds. NOM itself is harmless, however legislation requires disinfection of water in order that it remains fit for human consumption as it reaches the tap. It is the conversion of NOM into disinfection by-products (DBPs) when chlorine is used that can cause major problems (Krasner *et al.*, 1989). These by-products are varied but can be in the form of trihalomethanes (THMs), halo

Mansouri F., Kalankesh R.L. and Hasankhani H. (2016), The comparison of photo-catalytic degradation of dissolved organic carbon (DOC) from water by UV/TiO_2 in the presence and absence of iron ion, *Global NEST Journal*, **18**(2), 392-401.

acetic acids (HAAs) and many other halogenated compounds, some of these were identified in 1974. The THMs are of primary concern, because of tests that have shown some links between them and cancer in laboratory animals (Singer, 1999; Rodriguez *et al.*, 2000).

The first stage of D/DBP rule determines maximum contaminant level (MCL) and maximum contaminant level goals (MCLG) values for THMs. MCL and MCLG values for DBPs in the first stage of the rule are 0.08 mg l^{-1} and 0.06 mg l^{-1}, respectively (Qasim *et al.*, 2002). Techniques for NOM removal, such as coagulation and sand filtration, have been found to be inefficient in the elimination of pharmaceuticals (Vieno *et al.*, 2005; Stackelberg *et al.*, 2004). According to present knowledge, adsorption to activated carbon (either powered or granular), oxidation by ozone, and separation by membranes are the most promising methods for the elimination of pharmaceuticals (Hua *et al.*, 2006; Kim *et al.*, 2007).

UV/TiO_2 photo catalytic reactions are useful (Yang and Lee, 2006). The UV/TiO_2 method is a promising process for treatment and disinfection (Selcuk and Bekbolet, 2008). The use of TiO_2 is often due to its suitable chemical nature, non-toxicity, high stability, and relatively low cost that can be retrieved without considerable loss of its photochemical efficiency (Lin and Lin, 2007; Liu *et al.*, 2011; Ardestani *et al.*, 2014; Mansouri *et al.*, 2015). The advantage of TiO_2 is that it increases the concentration of hydroxyl groups on the surface and adsorbs water contaminants on the surface through an interaction with OH (Asuha *et al.*, 2010). The photo-reduction of DOC can be achieved via a photo catalytic process with a simplified mechanism as follows:

$$TiO_2+h\cdot v \rightarrow h+e^- \quad (1)$$

$$H_2O+h \rightarrow OH^-+H^+ \quad (2)$$

$$OH^{\bullet}+organics \rightarrow C_2+H_2O \quad (3)$$

$$H^++organics \rightarrow CO_2+H_2O \quad (4)$$

UV light illumination on TiO_2 produces hole–electron pairs (Eq. 1) on the surface of the photo catalyst. In the presence of degradable organic pollutants, the holes can produce ºOH radicals (Eq. 2), which can further degrade the organics to CO_2 and H_2O (Eq. 3). Of course, the holes can also directly oxidize the organic molecules reaction (Rodriguez *et al.*, 2000; Wang *et al.*, 2008). Semiconductor photo catalysis has been intensively investigated for its application to environmental pollutants degradation. It has been found that a variety of organic and inorganic pollutants can be oxidized or reduced by photo generated holes and electrons over semiconductors (Chen and Ray, 2001). Toyoda *et al.* (2004) observed that the crystalline of anatase was an important factor in order to get high photo catalytic activity for the decomposition of Methylene blue in water.

Lu *et al.* (2004) investigated the enhancement of β-Cyclodextrin ($C_{42}H_{70}$) on TiO_2 photo catalytic oxidation of Azo dyes and reduction of Cr (VI) in aqueous solutions, and proposed the mechanism as the formation of complexes of β-Cyclodextrin with the dyes and Cr (VI) anions on the TiO_2 surface. To our knowledge, there are no reported studies concerning the evaluation of the role of Iron ion in photo catalytic degradation of Dissolved Organic Carbon in water, particularly in the zayanderood water, so this paper is aim to study Comparing the removal of Dissolved Organic Carbon by UV/TiO_2 in the absence and presence of iron.

2. Materials and Method

The experiments were carried out on raw water of Zayandehroud in Isfahan, Iran. The raw water of Zayandehroud was sampled before entering Baba Sheikh Ali Water Treatment Plant and delivered to the laboratory at 4 °C. Glass materials and plastic bottles were washed with double-distilled water and exposed overnight to a 5% nitric acid solution. All the required materials were purchased from Merck Company in

Germany and Sigma-Aldrich Company. Solutions of required lower concentrations were prepared by diluting the stock solutions. Sodium hydroxide and hydrochloride acid was used for adjusting the pH.

2.1. UV/TiO_2 photocatalytic oxidation experiments

The experiments were carried out on water samples of Zayandehroud, Isfahan; Sampling was at random and in-depth the middle of the river water Iran. 500 ml of sample was collected on November, 20015. Autumn leaf fall contributes a large supply of Dissolved Organic Carbon at this time (Wood *et al.*, 1984). So we choose this season for sampling. Samples for chemical analyses were collected in polyethylene bottles immediately returned to the laboratory within 3 hours of Collection. Characterization of the water samples was undertaken according to the standard procedures. The concentration of DOC in the water was directly determined by using a UV-visible spectrophotometer at 254 nm (Schimadzu /UV-1800). The amount of water parameters as pH, hardness, Conductivity, Total Dissolved Solid, trihalomethanes and SO_4 concentration were also measured as per described methods. (Clescerl *et al.*, 1998).

Different parameters were examined including pH (3, 5, 7, and 9), contact time (15, 30, 45, 60, 75, 90, 105, 120, 135, and 150 min), initial concentration of TiO_2 nano particle (0.5, 0.75, 1, and 1.5 mg l^{-1}), and initial concentration of $FeCl_2$ (30, 70, 100 and 150 mg l^{-1}). Regards to, Ferric Chloride coagulant be used in the range of 50 to 200 mg per liter in water treatment in Isfahan, Therefore amount of Ferric Chloride is selected in this range. The experiments were carried out in a closed reactor equipped with cooling water circulation system using a magnetic stirrer with the speed of 500 r/min at 20±1 °C. In this study, the reactor for the photo catalytic oxidation was made of Plexiglas with effective volume of 1000 ml and dimensions of 21×15×10cm. A mercury UV source with beam intensity of 280W/cm^2 and maximum wavelength of 360nm was placed within 10cm of the reactor surface. To inhibit the effects of UV ray, the reactor was covered by an aluminum foil (Fig.1).

Figure 1. Experimental Setup of batch photo catalytic reactor

Every 15 minutes, 20 ml of the reaction mixture was taken and the sample was centrifuged for 15 minutes at 4000 r/min (model centrifuge-150), then the supernatant was filtrated with a 0.2 µ filter using PTEF in order to remove the catalyst particles. The amount of removed DOC was read using a UV spectrophotometer at wavelength of 254 nm (AWWA *et al.*, 1998). The experiments were performed as changing one parameter and keeping other parameters constant. During the experimental period, a total of five sets of tests were designed. The first set of tests was conducted under different experimental conditions including UV irradiation, photo catalyst while the secondary set of tests was carried out under the varied TiO_2 concentrations (0.5, 0.75, 1, and 1.5 mg l^{-1}) to identify the optimal catalyst dosage. The third set of tests was performed with various pH values (3, 5, 7, and 9). In order to determine the effect of contact time on DOC photo degradation the fourth set of tests was carried out by designing wide range of contact time (15, 30, 45, 60, 75, 90, 105, 120, 135, and 150 min). The fifth set of tests was carried out by adding Ferric Chloride particles ($FeCl_2$), (30, 70, 100 and 150 mg l^{-1}) with a different rang of concentration.

In all steps, experiments were carried out with beam intensity of 280W/cm^2 at maximum wavelength of 360 nm and a magnetic stirrer with the speed of 500r/min at constant temperature of 20±1°C. The amount of water parameters as pH, Hardness, Conductivity, Total dissolved solid, Turbidity, DOC concentration was also measured. According to (Clescerl *et al.*, 1998), DOC sorption capacity at each time was evaluated from Eq. (5).

$$qt=\frac{C_i\text{-}C_e}{M}\,V \tag{5}$$

Where V is the sample's volume in l, C_i is the initial solute concentration in mg l^{-1}, C_e is the equilibrium concentration in mg l^{-1} and M is the weight of TiO_2 nano particle in g. The DOC removal efficiency was calculated using Eq. (6).

$$\text{Removal efficiency}(\%)=\frac{C_0\text{-}C_t}{C_0}\times 100 \tag{6}$$

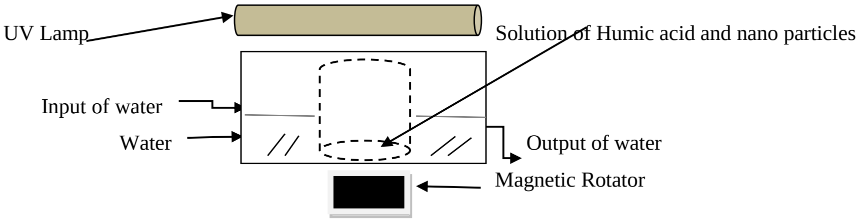
2.2. Statistical Analyses

The relationship between sorption coefficients for each set of samples was calculated by using IBM SPSS (Statistics Statistical Package for the Social) 16.00 Windows version and the obtained data were analyzed using for linear correlation and multiple regression.

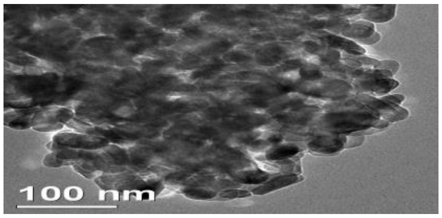
3. Results and discussion

3.1. Characteristics of the adsorbent

The figure 2a below shows a schematic of DOC removal photo catalytic pilot setup (Fig.1) and the Transmission Electron Microscopy (TEM) images of nano particles TiO_2 (Fig. 2b). Fig. 2b shows an average particle diameter in the range of 100 nm.



(a)



(b)

Figure 2. (a) Schematic of DOC removal photo catalytic pilot
(b)Transmission electron microscopy (TEM) of nano particle TiO_2

3.2 Tests for Chemical Quality of Water

The major resource of drinking water supply in Isfahan city is the surface water of Zayandehroud River and type of water treatment plant (named Babasheikh Ali) is a conventional system. Characteristics quality parameters of water before treatment in Isfahan water treatment plant (IWTP) such as, pH, Hardness, Conductivity, SO_4^2, Turbidity and Trihalomethanes are shown in Table.1.

Table.1 Average concentration of chemical quality parameters of Zayandehroud river raw water

Parameter	Unit	Max	Min	Mean ± SD
pH	-	7.7	7.5	7.6 ±0.0066
Conductivity	µs cm^{-1}	365	355	355.33±0.22
Ca^{2+}	mg l^{-1} CaCO3	84	80	82±2.5
Mg^{2+}	mg l^{-1} CaCO3	52.5	49	51.125±1.8
TH	mg l^{-1} $CaCO_3$	136	130	133.125±4.7
SO_4^{2-}	mg l^{-1}	31	30	30.66±0.22
TDS	mg l^{-1}	303.6	301.5	302.5±0.676
DOC	mg l^{-1}	1.6	1.4	1.5± 0.0066

3.2. Effect of adsorbent dosage

Fig.3 shows that the removal efficiency increased as the concentration of TiO_2 increased. Optimal concentration of TiO_2 catalyst for removal of DOC was 1-1.5 mg l^{-1}. Maximum removal of DOC (78%) was obtained with TiO_2 concentration of 1.5 mg l^{-1}. Statistical analysis showed a direct relationship between TiO_2 concentration on the removal of DOC by UV/TiO_2 with Pearson's correlation coefficient, r^2= 0.96.. This correlation was also found to be highly significant ($P<0.05$).

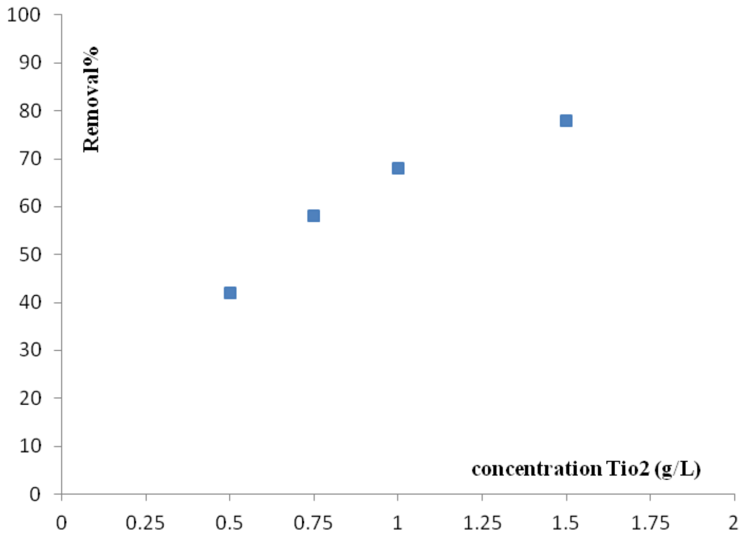


Figure 3. The effect of TiO_2 concentration on the photo degradation of DOC. Conditions: DOC=1.5mg mg l^{-1}, pH=3, Time=60min

With TiO_2 as catalyst for DOC removal, it favored adsorption sites on TiO_2 surface and production of free electrons in TiO_2 transmission band (Yang and Lee, 2006). increasing the removal efficiency in the higher catalyst concentration can be achieved by exposing the catalyst surface to the most active places, and the possibility of higher effect of UV radiation Hung *et al.*, in China (2008) one study on the decomposition of organic materials by Photo catalytic Oxidation of TiO_2 nano particles observe that they adjust the concentration of TiO_2 nano particles in the range of 1-0.1 g l^{-1} and the removal efficiency decreased with increasing catalyst (Huang *et al.*, 2008). Another study on Humic acid adsorption on TiO_2 nano particles shows that the removal efficiency decreased with increase in the concentration of TiO_2 nano particles and the optimal amount of TiO_2 nano particles the range of 1-0.5 g l^{-1} obtained (Wiszniowski *et al.*, 2002). The decrease of removal efficiency at the high TiO_2 dosage is probably due to light scattering resulting from the increased turbidity and the subsequent reduction in the UVA light penetration and the photo catalyst efficiency. This can be explained from the mixed results of various effects with increasing the catalyst dosage. As positive effects, the adsorption sites on the catalyst, as well as the generation of free electrons in the conduction band, should increase with larger dosage. The decrease of UV light penetration caused by the suspensions of photo catalyst particles could be the very possible explanation as the negative effect (Yang and Lee, 2006).

3.3. Effect of pH

The experimental results in Fig.4 show that under acidic conditions especially when pH=3, concentration of DOC decreased considerably. This indicates that the adsorption plays a significant role in photo catalytic degradation, so that, the photo catalytic reaction generally occurs on the surface.

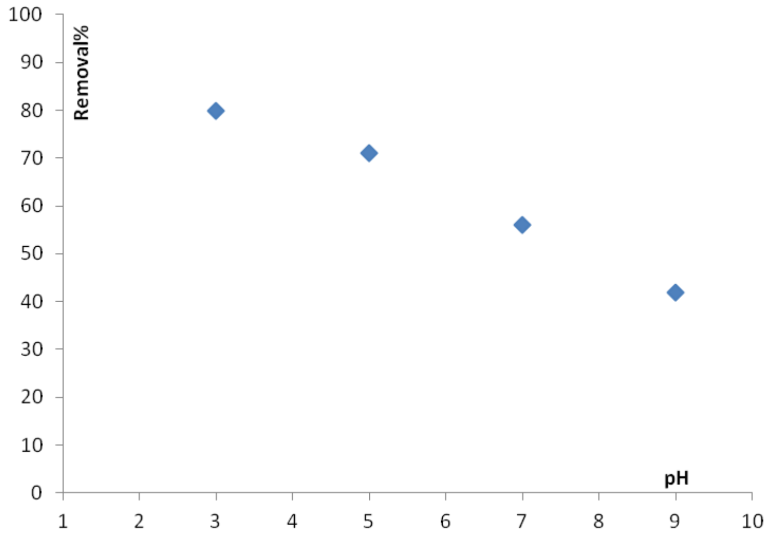


Figure 4. The effect of different amount of pH on the photo degradation of DOC.
Conditions: DOC=1.5mg l^{-1},TiO_2=1.5mg l^{-1}, Time=60min

Actually, the adsorption of H^+ and OH^- onto TiO_2 surface depends on the isoelectric point of zero charge of TiO_2 particles onto H^+ and OH^- (Marrison, 1980). The Isoelectric point of zero charge of TiO_2 is at pH=6.3 (O'Shea KE, 1995). When pH<6.3, positive charges of TiO_2—H^+ make a suitable surface for adsorption of DOC molecules with negative charge. However, when pH>6.3, TiO_2 surface is negatively charged ($TiO_2(OH)^-$) and produces unfavorable conditions for DOC molecules to get closer to each other (Bekbolet, 2002). The effect of pH on the photo degradation of DOC was studied by Fu *et al.* They reported that the reduction of DOC is more efficient in acidic environment than that in the alkalinous environment. (Fu *et al.*, 2006). Liu *et al.* (2008) in Australia showed that specific groups of organic compounds like carboxylic acids well adsorbed onto TiO_2 particles in acidic pHs, while other compounds like alcohol and long-chain saturated aliphatic compounds are not well adsorbed onto TiO_2 particles (Liu *et al.*, 2008). There was significant relationship ($P<0.05$) between different pH and the removal efficiency DOC process using UV/TiO_2. Based on statistical analysis and considering the Pearson's correlation coefficient, there was an inverse relationship (r^2= -0.99) between different pH on the removal of samples by UV/TiO_2. In fact, the efficiency of the process is decreased as pH increasing.

3.4. Effect of contact time

The experimental results in Fig.5 show that within 60 minutes of contact time, the oxidation rate reaches to its maximum and decreases as the contact time increases. The photo catalytic reaction occurs on the surface and adsorption plays a significant role in this reaction, the removal rate increases because the active sites on the adsorbent are unsaturated and concentration of the contaminant is high. Over 60 min of contact time, the active sites on the adsorbent become saturated and the adsorption rate decreases to the extent that during the interval of 135-150 min, desorption out of catalyst particles occurs. Furthermore, with the increase of contact time, hydroxyl radicals and paired electron-hole produced by photo catalytic process decrease. AL-rasheed & Cardine in England (2003) demonstrated under optimal conditions, in 1 hour, 95% of Humic acid removal efficiency achieve using Photo catalytic oxidation(rasheed, 2003). Based on the results, according to the Pearson's correlation coefficient, there was no significant relationship (P>0.05) between time of exposure and removal efficiency process using UV/TiO_2. Based on statistical analysis and considering the Pearson's correlation coefficient, there is no direct relationship (r^2=0.17) between time of exposure on the removal of samples by UV/TiO_2.

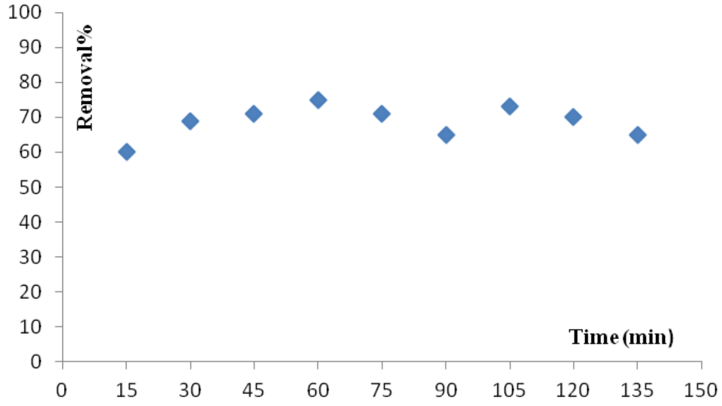


Figure 5. The effect of contact time on the photo degradation of DOC Conditions: DOC=1.5mg l^{-1}, TiO_2 = 1.5 mg l^{-1}, pH=3.

3.5. Effect of Iron ion

As shown in Fig.6, the presence of Fe^{2+} ion increases the rate of DOC adsorption onto TiO_2 particles. The reasons are that Fe^{2+} ions receive and neutralize the negative charges of TiO_2 and DOC & surface hydroxyl groups arising from photo catalytic oxidation and reduce the intermolecular repulsive force. On the other hand, in addition to the oxidation process Photo catalytic oxidation, coagulation process is performed by Iron ions then increases the efficiency of the process. There are a function of calcium ion bridging between the dissolved organic carbon in solution and the DOC adsorbed on the surface of TiO_2 (Yoon *et al.*, 1998).

Based on the results, according to the Pearson's correlation coefficient, there was significant relationship (P<0.05) between different concentrations of $FeCl_2$ and removal efficiency process using UV/TiO_2. Based on statistical analysis and considering the Pearson's correlation coefficient, there is direct relationship (r^2=0.998) between different concentrations of $FeCl_2$ on the removal of samples by UV /TiO_2.

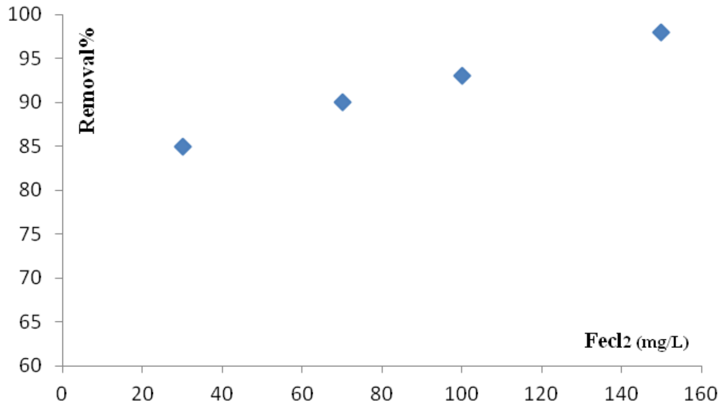


Fig.6. The effect of Fe^{2+} concentration on the photo degradation of DOC.
Conditions: DOC=1.5 mg l^{-1}, TiO_2 = 1.5 mg l^{-1}, pH=3, Time=60min.

3.6. Modeling of Adsorption Isotherms:

The equilibrium data were modeled with linearized Langmuir, Freundlich expressions. At first the experimental values of q_e and C_e are arranged with the linearized equations in order to determine the model parameters and the isotherms are reconstituted using the determined values. Linear correlation coefficients (R^2) calculated from linear regression analyses are the most extensively used criteria in evaluating good experimental data and linearized forms of isotherm Equations (Table 2). Reveals that the Langmuir isotherm yielded best-fits to the experimental data, probably due to the homogeneous and monolayer nature of surface sites involved in the Dissolved Organic Carbon uptake (Jonglertjunya and Lertchutimaku, 2012).

Table 2. Parameters of Langmuir and Freundlich for adsorption of Doc on TiO_2/UV

Langmuir ($1/q_e = 1/k_l Q_m (1/C_e) + 1/Q_m$)		**Freundlich ($\log q_e = (1/n)\log C_e + \log k_f$)**	
K_l	1.19	**K_f**	1.67
N	5.2	**Q_m**	2.21
R^2	0.67	**R^2**	0.97

3.7. Adsorption Kinetics

Adsorption kinetic is one of the most important factors for designing adsorption system and determine the residence time of the adsorbent in the adsorption process.

Table 3. Parameters of kinetic models for DOC adsorption onto UV/TiO_2

First-order kinetic $\log(q_e - q_t) = \log q_e - k_l t/2.303t$		**second-order kinetic ($1/q_t = 1/k_2 q_e (1/t) + 1/q_e$)**	
q_e (mg g^{-1})	651.6	**q_e (mg g^{-1})**	1250
k_1 (min^{-1})	0.0004	**k_1 (min^{-1})**	0.000457
R^2	0.15	**R^2**	0.99

Adsorption Kinetic depends on physical and chemical properties of the adsorbent. In this work adsorption kinetics of DOC on UV/TiO_2 were described with the pseudo-first-order model and pseudo-second-order model. It can be concluded that the pseudo second order kinetic model can produce better fitting to the experimental data of DOC photo catalytic adsorption. According to the calculated kinetic Parameters shown in Table.3

4. Conclusion

Experimental investigation in this study has demonstrated that Dissolved Organic Carbon can be degraded by UV radiation in the presence of TiO_2 photo catalyst in a photo catalysis reactor. The photo catalysis reactor can be considered as a convenient and efficient reactor for organic matters especially Dissolved Organic Carbon degradation. By examining the key factors including pH values, TiO_2 concentration, contact time and concentration of Ferric Chloride, it is clear that the increase of the Tio_2 dosage (catalyst concentration), Ferric Chloride and decrease of pH values and contact time can enhance the DOC removal. In addition, in the photo catalytic UV/TiO_2 process by adding particles of Ferric Chloride removal of the DOC improved, and reached up to 98%. The isotherm study indicates that adsorption data fit well with the Langmuir model. As well as the kinetic process was well predicted by pseudo second-order model.

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