The use of TiO$_2$ as catalyst in thin film fixed bed reactor for the treatment of landfill water

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Abstract: The main purpose of this study is the use of TiO$_2$ as catalyst in thin film fixed bed reactor (TFBR) for the treatment of landfill water with the high initial concentration of recalcitrant organic matter. The effectiveness treatment process was determined by the evaluation of the influence of the experimental parameters such as the pH on the Chemical Oxygen Demand (COD) and NH$_4^+$ concentration. The experimental assays were performed by varying the pH value from 5 to 6. The results obtained after treatment using this process was relevant. Indeed, a decrease of about 92% of the COD was achieved at pH maintained at 5. Moreover, the value of the BOD$_5$/COD ratio obtained indicated that the water obtained after treatment are favorable for biological treatment. However, the NH$_4^+$ concentration was not affected by this process and remained at its high value.

Keywords: TiO$_2$/UV; TFBR; Landfill water; BOD$_5$/ COD ratio; NH$_4^+$.

Introduction

Until today, landfill disposal is still the most method practiced in the world for municipal solid waste management, and the inevitable consequence of such operation is the production of leachate water. It was estimated that one ton of waste would produce 0.2 m^3 of water [1,2]. This water is rich in organic compounds, ammonium, heavy metal and inorganic chlorinated compounds, which may cause serious pollutions to groundwater and surface waters. Indeed, many reports on the contamination of the groundwater by landfill water have been published [3]

To achieve a satisfactory removal of pollutants from landfill water, several types of treatments have been adopted [4,5]. Biological processes have been found to be prone to toxic compounds that inactivate waste-degrading microbes. Moreover, conventional chemical and physical methods are not destructive, but transfer only the pollutant from one phase to another.

Advanced oxidation processes (AOPs) have been reported as one of the most powerful methods to degrade a variety of refractory compounds [6]. This performance can be attributed to the role of a highly reactive radical intermediate such as free hydroxyl radical (°OH) which can rapidly degrade aromatic, chlorinated and phenolic compounds. This radical can be produced using several processes like UV/O$_3$, UV/H$_2$O$_2$, O$_3$/H$_2$O$_2$, UV/TiO$_2$. Once the reaction of the free radical is initiated during the treatment, a series of oxidation reactions occurs in the solution and the radicals rapidly react with the organic compounds and mineralize it to CO$_2$ and H$_2$O.

Heterogeneous photocatalysis using TiO_2 as catalyst has been recognized as a principal AOP[7]. This catalyst is widely used in many environmental processes for example in the treatment and the disinfection of wastewater[8,9,10,11], in the air pollution remediation[12,13] and for self-cleaning materials[14]. The usefulness of the TiO_2 in the mineralization of bacterial cell mass and pathogenic microorganisms has been studied[15,16]. Moreover, it was also applied in medicinal research[17]. These large applications of TiO_2 are due to its chemical stability, non-toxicity and mainly to its high photocatalytic activity[18]. This catalyst is employed in combination with UV radiation or sun-light to initiate the generation of °OH radicals. The photocatalysis process based on TiO_2 catalyst can be explained by the following scheme (Figure 1).
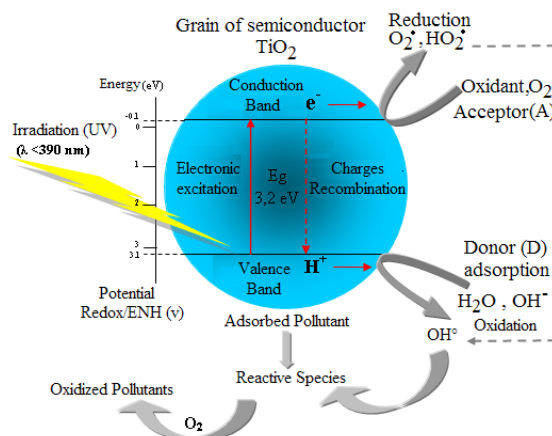

Figure1. Schematic presentation of the heterogeneous photocatalysis processes which occur after irradiation of the semiconductor particle[20,21].

TiO_2 is the most widely used semiconductor in photocatalytic degradation of organic pollutants due to its suitable band-gap energy (E_{bg}) of 3.05 eV over a wide range of pH. E_{bg} is the energy difference between two bands, the valence band (VB), which has a manifold of electron energy levels filled with electrons and the conduction band (CB), which has many higher energy levels that are largely vacant. This band gap also defines the sensitivity of the semiconductor to irradiation by photons at different wavelengths[19]. Under the irradiation, an electron (E) of the valence band is promoted towards the conduction band. The photogenerated electrons and holes (e^-/h^+) can be drained towards the surface of the material where species of the liquid phase can be adsorbed. After that the following reactions can occur: the reduction of an electron acceptor A at the surface by a photogenerated electron and the oxidation of an electron donor D at the surface by a photogenerated hole. Water can thus be dissociated in radical hydroxyl °OH. The organic compounds, as for them, can react in two manners: either they react directly with the photogenerated hole or electron at the surface of TiO_2, or they react indirectly via the reactive species such as the radical hydroxyl and superoxyde at the surface of TiO_2.[19,20,21]

The aim of this work was to apply the TiO_2 adsorbed in thin film for the treatment of landfill water in thin film fixed bed reactor.

Experimental Section

Oued Smar landfill; site information

Oued Smar landfill has been in operation from 1978 to 2011, so, methanogenic conditions are dominant in the landfill as the age of waste is more than 10 years. The landfill is located

at about 13 km of the center of Algiers and covers approximately 37.5 ha and the amount of wastes received was 1600 to 4 000 tons/day. The area of the site profits from a local climate of Mediterranean type semi-wet where precipitations annual averages range between 700 and 800 mm. The landfill has been closed, on reaching its useful life.

Materials

Leachate samples were obtained in three separate visits. 50 liters of landfill water which reached from the drainage pipeline were collected in January and February 2009. In June 2009, 20 liters were collected from the same sampling points. Collected samples were mixed to obtain a representative leachate sample. Samples intended for the treatment with TiO_2/UV system were filtered to minimize particulate effects in oxidation reactions, then, it was distributed in polyethylene bottles of 1.5 L and stored at temperature of freezing.

Reactor

The photo-reactor scheme is shown in Figure 2, with the following dimensions: length = 80 cm, width = 31 cm and height = 30 cm. Three UV lamps (medium-pressure mercury vapor lamp, 125 W, OSRAM) are fixed on the cover. This design allows varying the number of the UV lamps and the distance between the support of the catalyst and the UV lamps. The slope of inclination and the flow can also be modulated. The aeration and the agitation of the water are ensured by the air pump.

From several supports purposed for TiO_2 immobilization, TiO_2-loaded paper sheets have been proposed, where the catalyst can be immobilized in paper fibers via two general approaches coating process and wet-end addition[22]. In our study, the catalyst (TiO_2) is deposited on a paper not woven developed by Ahlstrom Paper Group Research and Competence Center[23,24]. The support made up of TiO_2-PC500 (20 g/m^2), fibres celluloses 60%, synthetic fibres (20%) and inorganic binding agent comprises colloidal silica dioxide (SiO_2) (20%). The binder (SiO_2) acting as binder among the catalyst agent and the support, and protective the fibres against UV radiation.
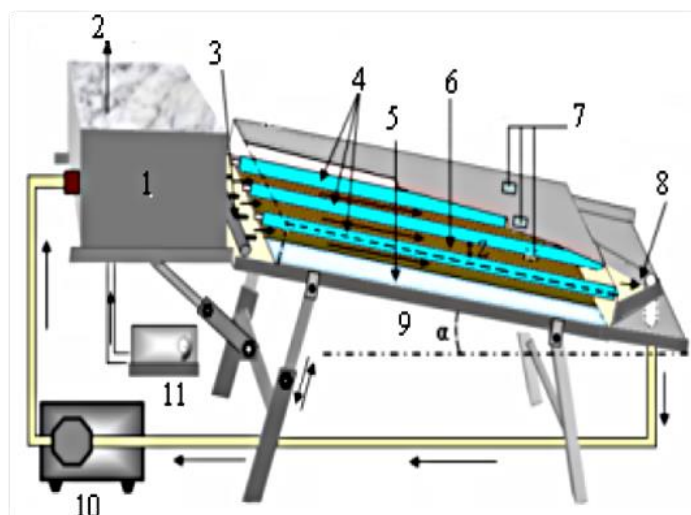

Figure 2. photoreactor. tank (1), taking sample (2), distributor with valves (3), UV lamps (4), glass plate (5), TiO_2 coated (6), electric current supply (7), collector (8), pump of recirculation (10), air pump (11)

This support was placed on the glass plate with 30 cm of width and 50 cm of length. Onto its surface, streams a thin blade of water. The good distribution of water on the surface of the support was ensured by eight dispensers, fitted with valve placed on the tank.

Experimental procedure

Experiments were carried out at three pH values; leachate's natural pH, pH 5 and pH 6 (with and without controlled pH). The pH was controlled by using 1 M H_2SO_4 solution. All others parameters are maintained constant. The slope of inclination of the reactor was fixed at 10° and the flow was fixed at approximately 1 mL. s^{-1}. At regular time intervals (each 3 hours), a sample was taken out from the tank in order to determine its COD, BOD_5/COD ratio and NH_4^+ value.

Analytical determinations

Standard methods were used to characterize the water. COD was determined by closed reflux and colorimetric method following the analytical procedure (5220 D: Closed Reflux, Colorimetric Method at 600 nm). BOD_5 was measured by incubation during 5 days at 20 °C using Oxitop bottles. Heavy metals in water were measured with flame atomic absorption, using AA spectrophotometer (Perkin-Elmer Co., Model 5000), according to the Standard Methods[25]. All chemicals products used were of analytical grade.

Results and Discussion

Characterization of the landfill waters

Chemical characteristics of untreated water sample are summarized in Table 1. These results reported recently[27] by our team research show a low value of BOD_5/COD ratio, low concentrations of heavy metals, slightly basic pH value and high contents of NH_4^+, thus the landfill water collected from the municipal waste of Algiers was stabilized as reported by Bodzek et al.[26]. The contents of heavy metal (mg L^{-1}) of the collected samples follow the following sequence: Fe > Cr > Cu > Cd. Hence, the pollution potentials of the Fe from landfill water should be extremely high. In general, the heavy metals in the water sample were in low concentration. These results were in accordance with a previous work[28].

Table1. Water landfill characteristics.

Parameter (unit)	Values
pH	7.6 - 8.4
Conductivity (mS/cm)	12.85 -14.63
COD (mg L^{-1})	28200 -34200
BOD_5 (mg L^{-1})	3850 - 3685
BOD_5 /COD	0.10 - 0.13
NH_4^+ (mg L^{-1})	3145.4 - 3625.7
Cl^- (mg L^{-1})	2584 - 4076
Cd (mg L^{-1})	< 0.002
Cu (mg L^{-1})	< 0.003
Cr (mg L^{-1})	0.13 - 0.31
Fe (mg L^{-1})	3.29- 4.88

Photocatalytic treatment of landfill water

First, the influence of UV light was investigated. An experiment was carried out without UV light. Figure 3. shows the COD removal (mg. L^{-1}) as a function of time. After 18 hours of treatment, the concentration in COD remains practically constant. This experiment was carried out in order to determine the reduction of the COD obtained by means of the adsorption phenomenon on the catalyst support and thus the photo oxidation process performance may be determined exactly.
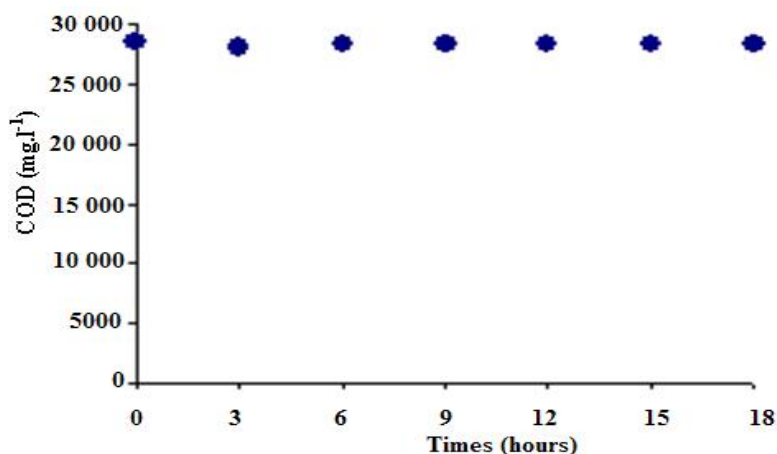

Figure 3. COD removal (mg. L^{-1}) as a function of time exposition on catalytic support without UV light.

Table. 2, summarizes the results from the essays carried out at different values of pH. The best removal efficiency (92 %) was achieved at pH maintained at 5. In these conditions, the duration of treatment was the shortest (30 hours). These results indicated that acidic condition could enhance the photocatalytic oxidation and the adsorption of the organic substance on the surface of the catalyst, which promote the formation of hydroxyl radicals with the highest oxidative power [29,30]. However, at the end of the treatment, the COD value has not reached the authorized value of 120 mg. L^{-1} and must then discharged to a municipal wastewater treatment facility.

Table.2. COD removal efficiency (%) and reaction time vs. pH values. Reaction conditions: natural pH of water leachate (a), pH adjusted before treatment to 6 (b), pH maintained during treatment to 6 (c), pH adjusted before treatment to 5 (d), pH maintained during treatment to 5 (e). CDO_0: value before treatment, COD_f: value after treatment.

pH	Reaction duration (h)	COD_0	COD_f	COD removal efficiency
a	45	28950	4450	84
b	54	29450	3200	89
c	48	30700	7450	76
d	39	25700	3700	86
e	30	30700	2450	92

The curves of COD removal were illustrated in Figure 4. From COD curves, it can be observed that for lower pH (pH 5), the influence of heterogeneous photocatalysis on the elimination of the COD has the most pronounced influence. These results may be due the increasing concentration of the ionized organics forms, and to the charge of TiO_2 (at this pH, catalyst is positively charged). Under these conditions, adsorption on the surface of the

catalyst was strongly favoured by the attraction forces between the organic molecules and TiO_2. A degradation of the organic matter could be also realized in the solution, by the $°OH$ radicals released in the solution. This can be argued by the increase of the pH discussed later.

Moreover, some researchers reported that photocatalytic oxidation under acidic conditions proceeded through the intermediary of free $°OH$ radicals present in the solution, rather than on the surface of TiO_2[31,32]. As the pH increases, TiO_2 surface acquired a negative charge, thus the adsorption of organic species and their degradation would become more difficult and take more time. Another explanation to elucidate the slowness of the process at high pH (6 and 7), the reaction of hydroxyl radicals with carbonate or bicarbonate ions leads to the formation of $CO_3^{°-}/HCO_3^{°-}$ radical anions. However, the dissolved carbon dioxide which reacts with water to produce the carbonate species HCO_3^- and CO_3^{2-} could scavenge the hydroxyl radicals or holes produced on TiO_2 surface[33] and then reduces the degradation of the organic maters by the oxidation process.
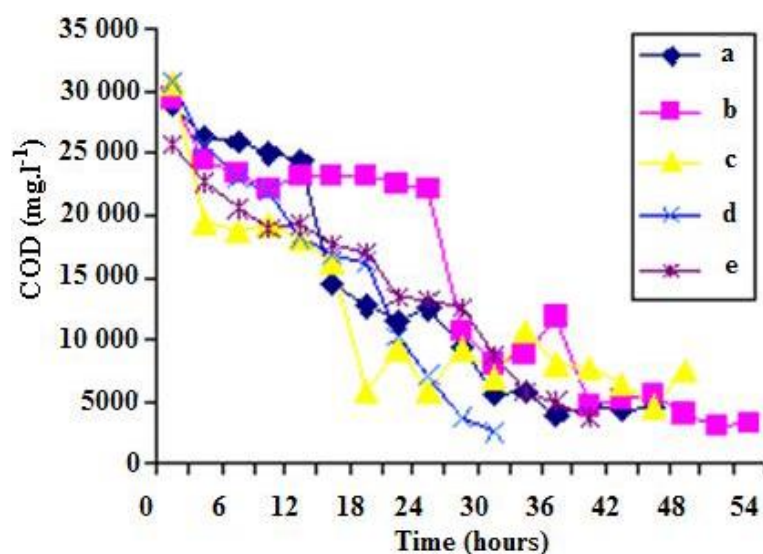

Figure 4. Kinetic Curves of COD removal at different pH values.
natural pH of water leachate (a), pH adjusted initially to 6 (b), pH maintained to 6 (c), pH maintained to 5 (d), pH adjusted initially to 5 (e)

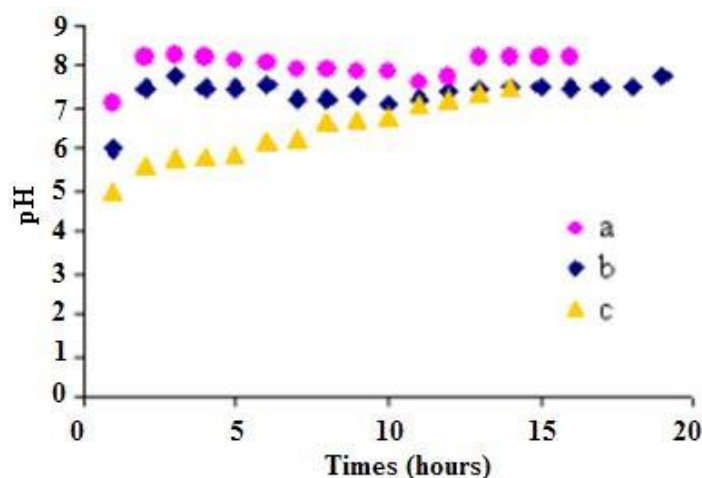**Evolution of the pH during the treatment**

Figure 5. Change of the pH during the treatment.
Essays conditions: natural pH of water (a), pH adjusted initially to 6 (b), pH adjusted initially to 5 (c).

The pH values of the photocatalytic samples were measured as a function of the reaction time. From the Figure 5, one can have observed that pH variation in relation with treatment time took place during the application of extended reaction times, particularly in the case of treatment carried out at pH 5. However, for shorter reaction periods, around 3 hours after the launching of the experiment, the pH value change significantly and this for all types of treatment.

The increase in the pH values is the direct result of the production of the hydroxyl radicals. The stability of the pH observed is due to the production of these oxidants and their consumption for the degradation of the chemical species. Hydroxyl radicals being produced uninterrupted and the limited formation of acidic by-products, explains the increase of the pH values until reach a plateau in the range of pH 8.

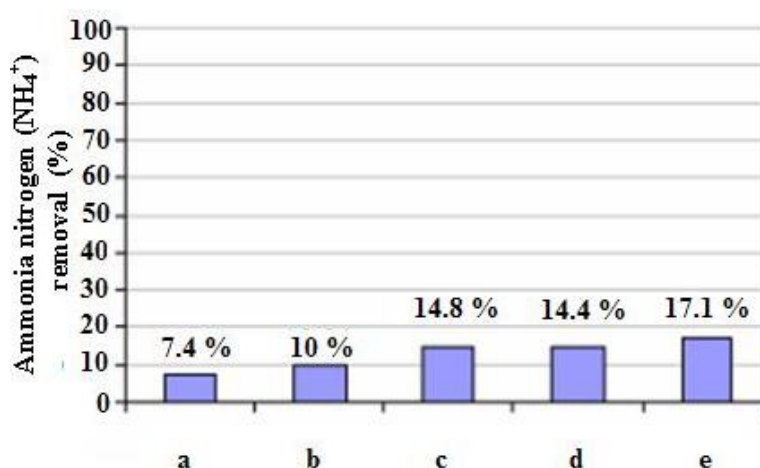**Photocatalytic degradation of ammonia nitrogen (NH_4^+)**

Figure 6. Ammonia nitrogen (NH_4^+) removal efficiency (%) at various experimental conditions:
pH maintained at 5 (a), pH adjusted initially to 5 (b), pH maintained to 6 (c), pH adjusted initially to 6 (d), natural pH of leachate water (e).

The results obtained, presented in Figure 6, indicate that the reduction of NH_4^+ was not exceeding 17% at various experimental conditions. On another hand the photocatalytic degradation of ammonia nitrogen at various pH values show an increase in NH_4^+ removal at higher pH values. utilized in this work. These performances may be explained by the several studies [34,35] on the photocatalytic degradation of ammonia nitrogen (NH_4-N) using TiO_2. These authors studied the influence of the pH on photocatalytic degradation of NH_4^+ and found that higher rate of degradation was obtained at pH alkaline.

The adsorption of organic components and the parameters that have the greatest effect on adsorption were also studied. Richard and Benagana, (1996)[19], have been studied the kinetics degradation of fenuron and concluded that the pH effect on the degradation of fenuron can be explained by differences in adsorption with changing pH. Because the point of zero charge of TiO_2 (pH_{PZC}) is between a 5.6 and 6.4 [19,36], at pH lower than pH_{PZC} of TiO_2, the surface is positively charged and molecules are attracted to the surface by their electronegative component. Hence, at higher pH values it would mostly be present in Ti-O$^-$ form. Therefore, adsorption of cationic NH_4^+ species on the anionic TiO_2 surface is strongly enhanced.

In similar studies, Cho et al.[37] used Photocatalytic process for the degradation of the landfill leachate containing refractory matters and nitrogen compounds and reached yields of COD abatement of 80% but without elimination of ammoniacal nitrogen at pH = 4. However, at pH 12, they removed only 20% of the COD but they reached a rate of ammoniacal nitrogen abatement of 16%.

Conclusion

In this study, TiO_2 catalyst in thin film fixed bed reactor for the treatment of landfill water was successfully applied. It was experimentally proven that UV light is the most important parameter in catalysis reaction involving TiO_2. The treatments of the landfill water were carried out using different pH's values. It was shown experimentally that the oxidation of the organic species was strongly depends on the pH. The treatment carried out at pH maintained at 5 during 30 hours allowed to obtain the highest COD removal efficiency (92 %), whereas acidic and neutral pH had no significant effect on NH_4^+ elimination. Indeed, only 17 % removed from the water at pH 7. These results are attributed to the fact that adsorption on the support is the dominant factor affecting the degradation of the ammoniac nitrogen. Therefore, TiO_2 may have a promising future as catalyst in water treatment with a higher content of organic matter.

Acknowledgements

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