

# Fotocatálise aplicada no estudo da descoloração e remoção da DQO dos percolados de aterro sanitário

## Photocatalysis applied in the studies of decolorization and COD removal of landfill leachate

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### Resumo

Neste artigo foi utilizado o processo fotocatalítico para a descoloração e remoção da DQO do chorume sobre a suspensão  $\text{TiO}_2$  em solução aquosa e irradiado com luz UV. Alguns parâmetros experimentais foram estudados para determinar a eficiência do processo. Os comportamentos da descoloração e remoção da DQO foram acompanhados por métodos espectrofotométricos e os resultados obtidos indicaram que o processo pode ser usado como um pré-tratamento ao processo convencional.

**Palavras-chave:** fotocatalise heterogênea. dióxido de titânio. Chorume. Descoloração. Remoção de DQO.

### Abstract

In this paper photocatalysis processes on titanium dioxide suspension in aqueous solution illuminated with UV light are described for decolorization and Chemical Oxygen Demand (COD) removal of landfill leachate. Several operational parameters to achieve optimum efficiency are presented. The properties of the decolorization and COD removal were enhanced and studied by spectrophotometer methods. The results indicate that the process can be used as a pretreatment to the conventional processes.

**Key words:** Heterogeneous photocatalysis. Titanium dioxide. Leachate treatment. decolorization. COD removal.

### Introduction

Population growth added to the consumption of manufactured goods in urban areas have increased the generation of solid waste that, in most of cases, are destined to landfills. In these locations, leachates are generated which have an environmental impact

due to their potential for contamination. In landfills, leachate is generated by the chemical and microbial decomposition of solid waste and the passage of rainwater. When drained from the landfill, leachate resulting from combining the two sources carries dissolved and suspended materials posing a high

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potential for contamination. The percolated liquid can reach the surface hydric collections as well as infiltrate the soil to reach groundwater, affecting their quality and therefore the ecosystem (IM et al., 2001; KJELDSSEN et al., 2002).

The impact produced by leachate on the environment is directly related to its decomposition stage. Leachate generated at a new landfill, where it receives a good amount of rainwater, is characterized by an acidic pH, high Biochemical Oxygen Demand (BOD), high value of Chemical Oxygen Demand (COD) and various potentially toxic compounds. Over the years, there has been a significant reduction in biodegradability of the waste. In this condition, the ratio of BOD/COD results in lower values, which means less capacity for leachate retrogradations. This is explained by the fact that under these conditions, there is an accumulation of substances in the leachate that hinder biological degradation, such as fulvic and humic acids, originating from decomposition of vegetable material. These compounds also contribute significantly to the dark color of the leachate.

The method most employed in leachate treatment is a biological process; these materials have characteristics very similar to those found for domestic sewage. However, difficulty often occurs for such biological treatment of leachate. The flow and organic loading are highly variable, requiring a large area for implementation, low efficiency for stabilized or poorly biodegradable and very often the effluent does not fit in the standards established by legislation.

Generally, conventional wastewater treatment removes significant levels of BOD but the environmental standards for COD, N and color are not attained. Consequently, establishing a treatment method is very challenging due to the need of achieving a better biodegradability and possibly a complete destruction of organic pollutants contained in the leachate (BEKBOLET et al., 1996).

Since there are no economically viable processes that could allow reduction of all environmentally relevant parameters of the leachate matrix, several studies have proposed the use of an integrated process. Among them are the physicochemical process of coagulation/flocculation that, applied as a pretreatment, aims to improve the efficiency of subsequent biological treatment (SLETTEN et al., 1995; SILVA et al., 2004). Recently, an advanced oxidation process has been integrated with a conventional biological process (KOH et al., 2004; LOPEZ et al., 2004).

Aiming at developing a promising means for the treatment of leachate, this work is based on using some principles of heterogeneous catalysis to achieve an effective degradation of landfill leachate from Londrina City, Brazil.

The use of methods that lead to a higher degradation rate, producing environmentally friendly products, is a major goal of the methods referred to as "Advanced Oxidation Processes" (AOPs). These methods are based on the formation of hydroxyl radicals, which being highly reactive agents may even promote the mineralization of organic compounds (NOGUEIRA; JARDIM 1998).

Using AOPs, Cho; Hong e Hong (2002) evaluated the removal of COD samples from landfill leachate with a correlation of BOD/COD < 0.1. For that a system containing 16 lamps of 8W, radiating at 254 nm, pH 4.0, 3 g L<sup>-1</sup> of TiO<sub>2</sub> and continuous bubbling of oxygen was used. After 4 and 8 h of irradiation, approximately 50% and 70% of COD reduction were obtained, respectively. At pH 8.6, after 4 h of irradiation under the same conditions as the previous experiment, a COD reduction lower than 20% was obtained. After 8 h of irradiation, approximately 25% of COD reduction was obtained. Cho; Hong e Hong (2004) studied the endpoint of photocatalytic degradation for samples of leachate from Kimpo - South Korea. For their process a semi-batch system was used, with continuous bubbling of oxygen, 2 lamps

radiating at 254 nm, with 3g L<sup>-1</sup> of TiO<sub>2</sub> and pH at 4.0. After 5 and 10 h of irradiation, 52% and 56% of COD reduction were obtained, respectively. To evaluate the efficiency of photoelectrocatalysis for a sample of leachate, Moraes e Bertazzoli (2005) used a low-pressure mercury vapor lamp with the sample immersed in a quartz flask with continuous bubbling of oxygen, at a natural pH of 8.0. After 60 min of irradiation, a COD reduction of 34 to 40% occurred, and after 90 min it reduced by approximately 48%.

The aim of this work was to define the experimental parameters that promote the degradation of the landfill leachate from Londrina region, through the photocatalysis of TiO<sub>2</sub> particles in suspension, thus making this process effective for decontaminating these recalcitrant systems. To understand the factors governing the leachate degradation using TiO<sub>2</sub>, a systematic study was performed on the experimental parameters affecting the decolorization and COD reduction of the local landfill compounds.

## Experimental

### *Samples*

For the experiments, the samples of leachate were collected from Londrina's landfill and then stored in the refrigerator. After filtration, the samples were diluted with ultrapure water and the pH was adjusted with H<sub>2</sub>SO<sub>4</sub> or NaOH using a pH meter. In this work, all reagents were analytical grade and used without further purification.

### *Irradiation Chamber*

The leachate photodegradation experiments were performed in an irradiation chamber (homemade), similar to that described in the literature (SANTANA; BONANCEA; TAKASHIMA, 2003). Aliquots of 300 mL, containing TiO<sub>2</sub>, were placed in glass beakers of 1000 mL capacity under stirring

and irradiated with a mercury vapor lamp of 125 W, being at a distance of 10 cm above the solution.

### *Decolorization Analysis*

To determine the percentage of decolorization of the samples, before the irradiation, they were diluted and the pH was adjusted with acid or base. After being filtered, their absorbances were determined. After irradiation, the samples were filtered again to eliminate the titanium dioxide, and the delta absorbances were determined.

In order to determine the spectral region of leachate maximum absorption for further decolorization measures, scans were made at wavelengths between 300 and 800 nm at various concentrations; however, an absorption band was not observed. Thus, it was decided to make the absorbance measurements of samples at 410 nm because at this wavelength the color change from brown to yellow is observed.

A calibration curve was required to verify the percentage of leachate decolorization. For this procedure, leachate samples were used in a range of concentration of 0.2 to 50 %. A good correlation was observed.

### *COD Analysis*

COD measurements were performed by closed reflux colorimetric method according to *Standard Methods* (Method 5220 D). The digestions were performed on samples of digestive block (Hack). Borosilicate tubes were used with the dimension of 16 x100 mm. The absorbance readings for the COD determination were performed in a Hach spectrophotometer.

To determine the COD by colorimetric method, solutions containing potassium dichromate (reagents digested) were used at concentrations 0.03472 mol L<sup>-1</sup> or 0.00347 mol L<sup>-1</sup>. The most concentrated solution was applied to analytes with COD above 50 mg O<sub>2</sub> L<sup>-1</sup>, while the less concentrated solution

was applied to analytes with COD between 5 and 50 mg O<sub>2</sub> L<sup>-1</sup>.

Due to the leachate having a strong brown color, it was necessary to make dilutions of samples to achieve greater efficiency in the photocatalytic process. For degradations, dilutions were made in the ratios 1:20, 1:10, 2:10 and 3:10. The COD of sample at 1:10 ratio was 249.75 mg L<sup>-1</sup> and could be determined by the COD curve made with the most concentrated K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, which was named as high range. However, after degradation of 24 h, the COD removal was high, so its determination was made with the lower dichromate concentration, named as low range.

To more accurately determine the leachate concentration corresponding to the lowest detectable range, with respect to equipment and in relation to the linearity of the method, it was necessary to obtain a calibration curve using the low range standard. The digestion reagent used for this procedure was that containing potassium dichromate 0.0034 mol L<sup>-1</sup>. Dilutions of crude leachate were 1, 2, 3, 4 and 5% in ultrapure water.

## Results and Discussion

The results obtained for the decolorization and COD removal of diluted leachate samples, irradiated in solution with the presence of TiO<sub>2</sub> particles, using different experimental parameters on the photocatalytic process, are presented below. For all decolorized samples absorbances were measured initially and following the photocatalysis. COD determinations of the samples were performed before the photocatalytic process and via the reagent of digestion for low range afterwards.

### *Influence of time and TiO<sub>2</sub> concentration in samples decolorization*

Table 1 lists the data relating to leachate decolorization and COD removal after the dilution 1:10. Time of irradiation and TiO<sub>2</sub> concentration

were varied but the initial pH of the solution was adjusted to 3.0. The reason to keep the pH at 3.0 for solutions, before irradiation, was under the assumption that the nature of the species in the leachate should be, in most, anionic species. At this pH, higher absorption by TiO<sub>2</sub> should occur because in pH below the point of zero charge it is expected that the surface of titanium dioxide would be positively charged, which favors the adsorption of the leachate. Despite this preliminary assessment, some exploratory experiments in basic medium were also performed, whereas the leachate could be positively charged species. Thus, the basic pH would have a pH above the point of zero charge of TiO<sub>2</sub>, favoring a negatively charged surface and the positively charged species adsorption on the particles of titanium dioxide. From this experiment, low decolorization of leachate was obtained in basic medium. Thus, work in acid medium (pH 3.0) was chosen early as the standard. The results indicated that better efficiency of the leachate treatment can be explained by the adsorption of the compounds on the surface of the semiconductor, which has a direct influence on the efficiency of the photocatalytic process.

It was also verified by exploratory experiments that over 8 hours of irradiation, in any condition of TiO<sub>2</sub> concentration, the results of the final absorbances of the samples are very close to the value of the blank, i.e., a complete decolorization of the samples occurs. Therefore, it was considered that for exposure durations above 8 hours, the concentration of TiO<sub>2</sub> cannot be considered a significant parameter for the study of leachate samples with 1:10 dilution.

**Table 1** - Percentage of decolorization and COD removal of leachate as a function of  $\text{TiO}_2$  concentration and irradiation time in leachate samples with 1:10 dilution.

$[\text{TiO}_2]$ ( $\text{g L}^{-1}$ )	t (h)	$\text{pH}_i$	$\text{pH}_f$	$A_i$ (a. u.)	$A_f$ (a. u.)	D (%)	$\text{COD}_i$ ( $\text{mgO}_2\text{L}^{-1}$ )	$\text{COD}_f$ ( $\text{mgO}_2\text{L}^{-1}$ )	R (COD) (%)
1.0	2	3.0	3.0	0.236	0.114	51.69	278.1	249.65	10.23
1.0	4	3.0	3.0	0.236	0.087	63.13	278.1	241.86	13.03
1.0	8	3.0	2.6	0.236	0.019	91.94	278.1	186.25	33.02
2.0	2	3.0	3.1	0.177	0.039	77.96	171.87	117.90	31.40
2.0	4	3.0	3.2	0.177	0.011	93.78	171.87	94.58	44.97
2.0	8	3.0	3.1	0.356	0.002	100.00	249.75	97.25	61.06

\*Absorbance of the blank: ultrapure water +  $\text{TiO}_2$ , about 0.001 a.u.;  $[\text{TiO}_2]$  =  $\text{TiO}_2$  concentration; t = irradiation time;  $\text{pH}_i$  and  $\text{pH}_f$  = initial and final pH, respectively;  $A_i$  and  $A_f$  = initial and final absorbance, respectively; D = Percentage of leachate decolorization;  $\text{COD}_i$  and  $\text{COD}_f$  = initial and final COD, respectively; R (COD) = Percentage of COD removal of leachate.

**Source:** author

It was observed in Table 2 that increasing decolorization was achieved by decreasing the leachate concentration.

The percentage of decolorization for the 1:10 dilution was 16.76%, higher than that found for the 2:10 dilution and, in turn, 53.49% higher than that obtained for the 3:10 dilution after 4 h of irradiation and at pH 3.0 for all samples. For natural pH (8.4), the same tendency was observed. The 1:10 dilution showed a percentage of decolorization 14.74% higher than found for the 2:10 dilution and 36.01% higher than 3:10 dilution. Thus, it was verified that the initial leachate dilution has been a limiting factor to the decolorization efficiency. This is due to strong brownish color of the leachate, which reduces the incidence of radiation on the photocatalyst and inhibits the action of the same on the sample (BEKBOLET et al., 1996).

From the results in Table 2, it was observed that for the 1:10 dilution and 4 h of irradiation, the difference of COD removal was significant between conditions of the natural pH (8.4) and 3.0. This demonstrates the influence of pH on experiments, and it is considered the effect of zero charge potential of  $\text{TiO}_2$ . For 2:10 and 3:10 dilutions at both pH values (3.0 and natural), the COD removal declines considerably due to the strong leachate coloring affecting the efficiency of the photocatalyst.

#### *Influence of pH on the decolorization of the samples*

In Table 3 is shown data related to decolorization and COD removal of the leachate as a function of pH, while keeping leachate 1:10 dilution and  $\text{TiO}_2$  concentration of  $2.0 \text{ g L}^{-1}$  constant, with irradiation time of 2, 4 and 8 h.



**Table 3** - Decolorization and COD removal of leachate as a function of pH, keeping the same leachate dilution (1:10), TiO<sub>2</sub> concentration (2.0 g L<sup>-1</sup>) in different irradiation time.

t (h)	pH <sub>i</sub>	pH <sub>f</sub>	A <sub>i</sub> (a. u.)	A <sub>f</sub> (a. u.)	D (%)	COD <sub>i</sub> (mgO <sub>2</sub> L <sup>-1</sup> )	COD <sub>f</sub> (mgO <sub>2</sub> L <sup>-1</sup> )	R(COD) (%)
2	1.0	1.0	0.153	0,042	72.55	226.25	181.25	19.88
4	1.0	1.0	0.153	0,033	78.43	226.25	181.25	19.88
8	1.0	1.0	0.153	0,007	95.43	226.25	166.25	26.52
2	3.0	3.1	0.177	0,039	77.96	171.87	117.9	31.40
4	3.0	3.2	0.177	0.011	93.78	171.87	94.58	44.97
8	3.0	3.1	0.356	0.002	100.00	249.75	97.25	61.06
2	8.4	8.4	0.326	0.196	39.87	346.25	293.23	15.31
4	8.4	8.4	0.326	0.096	70.55	171.87	145.25	15.48
8	8.4	8.6	0.326	0.034	89.57	346.25	182.29	47.35

\*Absorbance of the blank: ultrapure water + TiO<sub>2</sub>, about 0.001 a.u.; [TiO<sub>2</sub>] = TiO<sub>2</sub> concentration; t = irradiation time; pH<sub>i</sub> and pH<sub>f</sub> = initial and final pH, respectively; A<sub>i</sub> and A<sub>f</sub> = initial and final absorbance, respectively; D = Percentage of leachate decolorization; COD<sub>i</sub> and COD<sub>f</sub> = initial and final COD, respectively; R (COD) = Percentage of COD removal of leachate.

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t (h)	pH <sub>i</sub>	pH <sub>f</sub>	A <sub>i</sub> (a. u.)	A <sub>f</sub> (a. u.)	D (%)	COD <sub>i</sub> (mgO <sub>2</sub> L <sup>-1</sup> )	COD <sub>f</sub> (mgO <sub>2</sub> L <sup>-1</sup> )	R(COD) (%)
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\*Absorbance of the blank: ultrapure water + TiO<sub>2</sub>, about 0.001 a.u.; [TiO<sub>2</sub>] = TiO<sub>2</sub> concentration; t = irradiation time; pH<sub>i</sub> and pH<sub>f</sub> = initial and final pH, respectively; A<sub>i</sub> and A<sub>f</sub> = initial and final absorbance, respectively; D = Percentage of leachate decolorization; COD<sub>i</sub> and COD<sub>f</sub> = initial and final COD, respectively; R (COD) = Percentage of COD removal of leachate.

**Source:** author

It was observed in Table 3 that for samples irradiated at lower times than 8 h there is a strong influence of pH on decolorization of the samples. For pH values of 1.0 and 3.0, higher decolorizations were observed relative to the data obtained for the pH 8.5. For the pH 3.0, higher decolorization was observed than at pH 1.0 for all irradiation times studied. This fact was quite significant when compared at the time of 4 hours. At this duration it was observed that decolorization at pH 3.0 was 15.35% higher than at pH 1.0. At pH 1.0, for the times of 2 and 4 h, decolorizations of 72.55 % and 78.43% were observed, respectively, which indicates that even with doubling the irradiation time, the difference of the decolorization percentage between them was only 5.88%. For the pH 3.0 at these same durations the difference was 15.82% higher, which points out that efficiency of decolorization at pH 3.0 was higher than for pH 1.0.

The contribution of acidic medium towards more efficient decolorization can be better understood by

considering the precipitation of humic substances in this pH. Tauchert et al. (2006) obtained 20% of decolorization and 39% of COD removal after precipitation of humic substances from the leachate in acid medium. Already in basic medium, the carbonate and bicarbonate ions, which are present in leachate due to its high alkalinity with respect to those ions, act as abductors of the hydroxyl radical, which may reduce the efficiency of the photocatalytic process (CHO; HONG; HONG, 2004; KURNIAWAN; LO; CHAN, 2006).

As shown in Table 3, for irradiation time of 2 h, the decolorization at pH 3.0 was 38.09% higher than at the natural pH; however, for irradiation duration of 4 h, this difference relative to natural pH was 23.23% and in 8 h of irradiation decreased to 10.43%.

The results also indicate higher COD removal in acidic medium for any irradiation time. However, while at pH 3.0, COD removal was higher than

natural pH and pH 1.0. At the time of 4 h, the COD removal at pH 3.0 was 25.09% higher than at pH 1.0 and 29.49% higher than natural pH. At the 8 h period of irradiation, the COD removal at pH 3.0 was 34.54% higher than at pH 1.0 and 13.71% higher than that for the natural pH sample.

Considering these results from the experiments of leachate decolorization, considering the difficulty of acidifying and subsequently neutralizing this effluent for disposal, it was decided to optimize the experimental parameters in natural pH.

#### *Influence of the nature of UV radiation on the leachate decolorization*

This study was conducted to determine the effect of the nature of the exciting radiation on the photocatalytic process by monitoring the decolorization and COD removal of leachate samples. To do so, the data obtained previously for the irradiation samples using the mercury vapor lamp bulb was compared with the data obtained

for the samples irradiated by a mercury vapor lamp without the bulb protector.

Consideration was given to the TiO<sub>2</sub> crystalline form anatase, which has a bandgap at 386 nm while the rutile crystalline form has one at 410 nm (SANTANA et al., 2007). To photo-excite a semiconductor, energy near or above the bandgap values is necessary. The mercury vapor lamp without the bulb protector has higher emission intensity between 185-400 nm and the one containing the bulb protector presents emission between 300-546 nm. Thus, the emission of light more intense at the range of UV wavelength should more easily excite the anatase form than the rutile, which could have greater activity on the decolorization of the samples.

Table 4 lists the results of decolorization and COD removal of the leachate as a function of the nature of the UV radiation and exposure duration, under the conditions previously fixed at times of 2, 4 and 8 h using the lamp without the bulb protector.

**Table 4** - Percentage of decolorization and COD removal of leachate as a function of UV and time irradiated keeping the TiO<sub>2</sub> concentration (2.0 g L<sup>-1</sup>), dilution (1:10), in natural pH and using a lamp without bulb.

t (h)	pH <sub>i</sub>	pH <sub>f</sub>	A <sub>i</sub> (a. u.)	A <sub>f</sub> (a. u.)	D (%)	COD <sub>i</sub> (mgO <sub>2</sub> L <sup>-1</sup> )	COD <sub>f</sub> (mgO <sub>2</sub> L <sup>-1</sup> )	R (COD) (%)
2	8.4	8.4	0.326	0.187	42.63	346.25	298.27	13.85
4	8.4	8.4	0.326	0.072	77.91	346.25	251.25	27.44
8	8.4	8.7	0.326	0.000	100.00	346.25	133.75	61.37

\*Absorbance of the blank : ultrapure water + TiO<sub>2</sub>, about 0.001 u.a.; D = fraction of dilution (leachate. : ultrapure water); pH<sub>i</sub> and

pH<sub>f</sub> = pH initial and final, respectively; A<sub>i</sub> and A<sub>f</sub> = initial and final absorbance, respectively; D = Percentage of leachate decolorization; COD<sub>i</sub> and COD<sub>f</sub> = initial and final COD, respectively; R (COD) = Percentage of COD removal of leachate.

**Source:** author



It was noticed that under the studied conditions, comparing the results of Table 4 and Table 3, a higher decolorization occurs when the lamp without the bulb protector is used for the irradiation, with a gain of 2.76%, 7.36% and 10.43% at durations of 2, 4 and 8 h, respectively.

With the same comparison, for times of 2 and 4 h of irradiation, no increase of COD removal was noticed; however, for the 8 h irradiation sample there is a gain of 14.02% when using the lamp without the bulb protector.

## Conclusions

Comparison of decolorization and COD removal of samples under the same conditions for the photocatalytic experiments indicated that the decolorization is not a parameter that correlates directly with COD removal. For an irradiation duration of 8 h at natural pH, where the decolorization was 89.57%, the COD removal was only 47.35%. This is due to the high organic content of these materials, demonstrating the resistance of being degraded.

With the use of the lamp without the bulb protector, it was possible to obtain higher COD removal, about 61.37%. It was observed that the best results for the COD removal were comparable to those found in the literature, but COD removals in significant amounts in short periods as 60 and 90 min was not achieved.

These facts demonstrate that photocatalysis is an alternative to pretreatment, improving the decolorization and the degradation of the residual organic products present in the raw leachate for later remediation using conventional methods. This can be made possible due to the small reduction in the pH of the waste during the photocatalytic process; it may increase efficiency, for example of the biological treatments that provide reduction of organic loads and demonstrate removal of color, leading to an increased efficiency of the biological

treatment that is susceptible to the variations of organic content and demonstrate a limited efficiency for color removal.

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