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Remediation of pesticide contaminated soil using TiO_2 mediated by solar light

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Abstract

Heterogeneous photocatalytic degradation of the pesticide Diuron (Nortox, 3-(3,4-dichlorophenyl)-1,1-dimethylurea) was carried under laboratory conditions to evaluate the potential use of this technology for in situ remediation. Soil samples were spiked with three Diuron concentrations (10, 50 and 100 mg kg^{-1}), loaded with catalyst TiO_2 and exposed to solar light (22°S and 47°W, with an averaged intensity of 2 mW cm^{-2} measured at 365 nm). Different catalyst loads (0, 0.1, 0.5, 1 and 2% w/w) were tested in Diuron contaminated soil (100 mg kg^{-1}) for up to 120 h of exposure. Both the catalyst and the Diuron concentration show no influence on the kinetics of the pesticide degradation. The effects of water (10% w/w) and $Ca(OH)_2$ (0.1% w/w) were also evaluated. Water increases the degradation rates, whereas the rise in the pH due to $Ca(OH)_2$ addition shows no measurable effect on the degradation. The photocatalytic treatment using TiO_2 combined with solar light is shown to be very efficient in the destruction of Diuron in the top 4 cm of contaminated soil, with the degradation rate markedly dependent on the irradiation intensity.

Keywords: Diuron; TiO_2; Soil decontamination; Photocatalysis; Sunlight

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1. Introduction

In the last decade, pesticide contamination in tropical countries [1] has been a major concern throughout the world. Although developing countries are normally ranked among the top agrochemical consumers, there is very little data available to support a realistic inventory of environmental contamination in these countries, compared to data available for temperate climates. Nowadays, Brazil figures in third place among the leading world pesticide markets. In 1998, more than US$ 2 billion was spent on agrochemicals, and US$ 1 billion on herbicides alone [2].

Herbicides are the most extensively used type of pesticides in agriculture. Due to their limited biodegradability, high vapor pressure and high lipid affinity (K_{ow}), haloaromatic herbicides are considered a persistent class of chemicals and the uncontrolled or accidental disposal of such compounds in soil may pose a threat to human health. The herbicide Diuron Nortox is widely used to control a large number of weed species in a variety of crops in Brazil, and is considered as highly toxic and persistent when applied in high dosages to the soil. The structural formula of this pesticide is shown in Fig. 1.

There are numerous technologies potentially used for soil remediation and deactivation processes of hazardous wastes, mainly centered on biological and chemical treatments [3–5]. However, the American Environmental Protection Agency (USEPA) has

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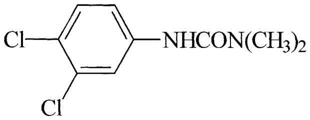

Fig. 1. Structural formula of Diuron.

proposed in situ treatment as a potentially safe and economical method of soil cleanup [6,7]. There have been numerous studies exploring the use of soil bioremediation in situ, since it appears to cause less impact to the environment. Nonetheless, considering that some waste components can be toxic to the microorganism consortium normally used in this remediation process, long periods of time may be necessary to achieve the target concentration of the contaminants in the soil. In this case, the choice of a chemical treatment based on the use of strong oxidants, such as H_2O_2 and $KMnO_4$, may provide a suitable means of destroying xenobiotic contaminants over time periods shorter than the ones required for biological treatment, leaving byproducts that are ubiquitous in the environment.

Heterogeneous photocatalysis has been successfully tested as an emerging technology for the decontamination of industrial effluents [8]. Unlike non-destructive traditional methods, like volatilization or adsorption onto a solid phase, this process has the advantage of destroying the organic compounds by redox reactions on the catalyst surface. The mechanisms of this process have been described in detail elsewhere [8,9].

As expected, as a photon mediated process that, in this particular case, explores the use of solar light, radiation intensity has to be considered as a key parameter when evaluating the process efficiency, which means that, mainly in tropical countries, soil remediation using photocatalysis is very dependent upon the season of the year. Another parameter that will influence the extent of degradation is the characteristics of the soil. In this porous medium, the presence of a carrier is necessary to bring together the substrate onto the catalyst surface and this is normally achieved by increasing the amount of water in this medium. Additionally, water molecules can further react in the surface of the catalyst by oxidation in the hole (h^+) and generate $^\bullet OH$ radicals, thus increasing the rate of degradation. The pH is another important parameter, and the presence of an alkaline coadjutant, such as $Ca(OH)_2$, can modify not only the surface charge in the catalyst, but also determine the predominant species of the substrate, controlling the extension of adsorption, thus potentially affecting the kinetic of degradation.

The feasibility of using heterogeneous photocatalysis in the treatment of highly contaminated soil was recently demonstrated [1]. The present paper describes the investigation of some key environmental parameters that can alter the degradation rate of Diuron in contaminated soils when using a photocatalytic treatment combining TiO_2 and solar light.

2. Experimental

2.1. Materials

Titanium dioxide (Degussa, P25, nanoporous, 70:30% anatase:rutile mixture) with a Brunaur–Emmett–Teller (BET) surface area of $50 \pm 15\,m^2/g$, and an average particle size of 21 nm [10] was used as received. The formulated pesticide Diuron (80%), a commercial Nortox product, was used without any purification. Acetonitrile (HPLC grade) was an Aldrich product and methanol (HPLC grade) purchased from Grupo Química, both filtered (0.45 μm) and degassed by sonication (15 min) before being used as mobile phase in HPLC. Sandy soil was just sieved (1 mm). Propanone (PA) was purchased from Cromato Produtos Químicos.

2.2. Soil contamination and irradiation

The experiments were carried out on a laboratory scale, where 50 g of sandy soil held in Petri dishes were contaminated with Diuron dissolved in 20.0 ml of propanone. Sandy soil was provided by EMBRAPA (Jaguariuna, São Paulo), and presented 0.9% carbon, 98.1% sand, 1.0% silt, and 1.0% clay. The pesticide spike was made in duplicate for each concentration of Diuron, and in one of them the catalyst was incorporated in the soil, whereas the catalyst-free sample acted as a control. The plates were exposed to sunlight, normally from 9 a.m. to 4 p.m., covered after exposure and kept in the dark in the laboratory. Thus all the graphs showing irradiation time refers to the summation of sunlight exposure on sequential days. To follow Diuron degradation, 2.0 g samples of soil were collected after 20 or 30 h of solar irradiation and analyzed for the pesticide. The catalyst load was made by adding the desired amount of TiO_2 in the pesticide spiked soil, followed by manual shaking for 30 min in a 500 ml closed stainless steel reactor. All the experiments described were carried out over a period of 24 months, at least eight times under different solar intensities, and the results shown in this paper represent the average performances obtained in different runs carried out at different seasons of the year.

To study the optimum concentration of catalyst in the destruction of the pesticide, five plates were prepared with contaminated soil (100 mg kg^{-1} Diuron). In each plate, 0; 0.1; 0.5; 1.0 and 2.0% of TiO_2 (w/w) were incorporated into the soil and submitted to the treatment. The influence of pesticide concentration was also assessed through the contamination of six soil samples with 10, 50 and 100 mg kg^{-1} of the pesticide (in duplicate), followed by the incorporation of 1% (w/w) of the catalyst.

The influence of humidity and $Ca(OH)_2$ (as a pH controller) in the photocatalytic degradation of Diuron was also assessed. To increase the humidity (an additional increment of 10% (w/w) of water to the natural humidity of 14%), contaminated soil samples (with and without catalyst) were sprayed with ultra-pure water and weighted until the mass increase indicated the selected humidity. So, when humidity adjustment is mentioned, it is assumed that the soil received an extra load of 10% (w/w) of water. The addition of lime ($Ca(OH)_2$) to bring the soil pH to more alkaline conditions was carried out by simple weighing of the correct amount of the reagent and mixing to the soil as described for the addition of TiO_2.

To study the seasonal influence of light in the degradation of the target compound, the same experiments using contaminated soil (100 mg kg^{-1}), with and without TiO_2 (1% w/w), were performed at different times during the year. Sun light intensity was monitored using a Cole-Parmer radiometer at 365 nm. This wavelength was selected because it is very close to the TiO_2 bandgap. Preliminary experiments using covered plates containing contaminated soils and TiO_2 showed that degradation did not exceed 7% of the total amount of Diuron present in the soil after 120 h, confirming that destruction is photodependent.

Considering that solar light penetrates only few centimeters of the soil surface, one should expect the photocatalytic treatment to be effective only in the top layer of the soil, assuming that no further action will be taken (such as soil mixing followed by new catalyst additions). In this context, an experiment was carried out to evaluate the rate of destruction as a function of soil depth. Three dark plastic cylinders (5.0 cm in diameter and 15 cm high) containing the contaminated soil in the presence of TiO_2 (1% w/w) and humidity (10% w/w) were irradiated with sunlight during 0, 20 and 40 h. The soil cylinder was sliced at every 0.5 cm down to 2 cm and at 1 cm intervals from 2 cm down to 8 cm (10 slices in total). Each slice was analyzed for the pesticide.

2.3. Soil extraction and HPLC analysis

An aliquot of 2.0 g of exposed soil was extracted with 10 ml of acetonitrile using a Branson 2210 sonication bath for 6 min, followed by mechanical shaking for 2 min. The extracts were filtered using 0.45 μm millipore syringe filter and analyzed using a Varian 9010 high performance liquid chromatography having a Varian 9050 UV detector, fitted with a 100 mm × 4.6 mm stainless steel column packed with Hypersyl ODS. The mobile phase used was acetonitrile:water (50:50 v/v) at a flow rate of 0.5 ml min^{-1}, and UV detection was at 251 nm.

3. Results and discussion

Fig. 2 shows the results obtained for the degradation of the target compound when the concentration of Diuron spiked in the soil varied between 10, 50, and 100 mg kg^{-1} using 1% (w/w) of TiO_2 and exposed to sunlight. Degradation follows a pseudo-first order kinetics with a half-life around 10 h, independent of the three different pesticide concentrations. In the absence of catalyst, only 10–20% of the contaminant has degraded after 50 h of solar irradiation, with this degradation being more noticeable at lower loads of the pesticide. Pesticide destruction observed in the absence of the catalyst may be due to both photolysis and thermal decomposition, since the soil temperature reached up to 45 °C during solar exposure. The results also allow to conclude that, at these levels of contamination, loading the contaminated soil with 1% of catalyst was enough

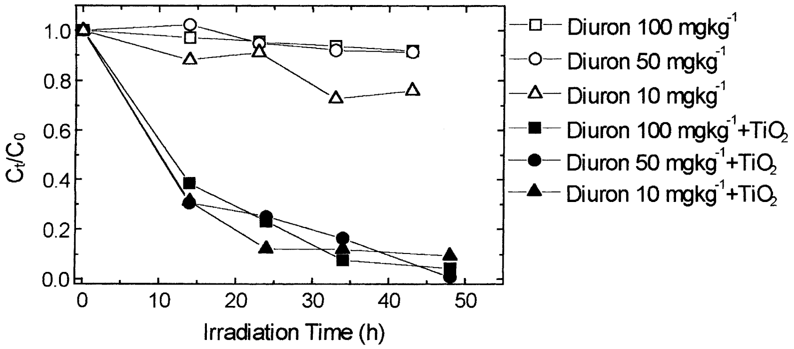

Fig. 2. Influence of Diuron concentration on the photocatalytic degradation in soil in the presence and in the absence of TiO_2.

to reach efficiencies above 99% for the degradation.

When the pesticide contamination in the soil was fixed at 100 mg kg^{-1}, changes in the concentration of TiO_2 from 0.1 to 2% (w/w) has no significant effect in the rate of Diuron degradation, as presented in Fig. 3. These results differ from the ones obtained for pesticide contaminated water, where spikes of TiO_2 from 0.01 to 0.04% (w/w) in a 50 mg l^{-1} solution of Malathion [11] showed an exponential dependence of the degradation rate as a function of the TiO_2 load. A similar behavior was also observed for a 100 mg l^{-1} solution of Carbetamide [12] in the presence of the solid form of the catalyst. In the case of the soil, the results show that even low loads (0.1%) provide enough catalyst surface area to promote maximum rates of Diuron destruction. Despite the results shown in Fig. 3, catalyst load was selected as 1% for all subsequent experiments, to provide a very consistent margin of safety.

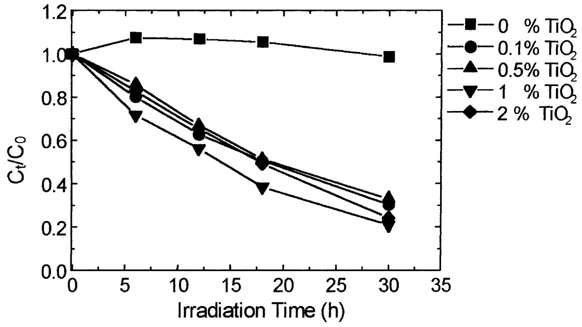

Fig. 3. Influence of TiO_2 load on the photodegradation of Diuron (100 mg kg^{-1}) in soil.

Fig. 4 clearly shows that rise in the soil pH from adding $Ca(OH)_2$ does not significantly alter the

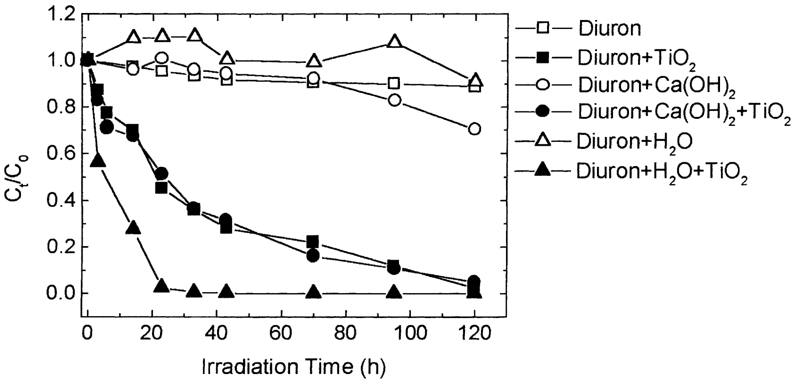

Fig. 4. Influence of humidity and $Ca(OH)_2$ on the photocatalystic degradation of Diuron in soil in the presence and in the absence of TiO_2.

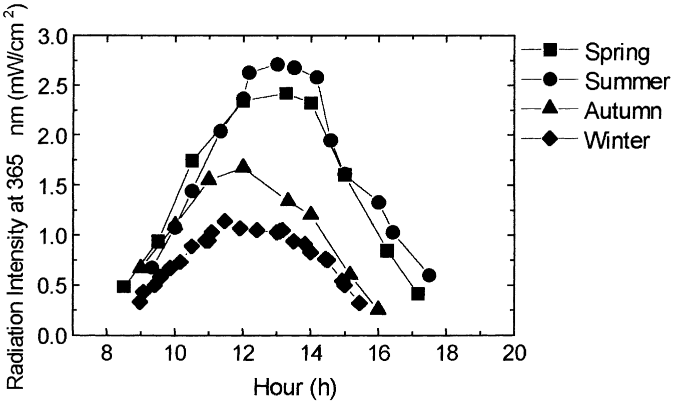

Fig. 5. Incident solar light intensity variation during the day in different seasons of the year, measured at 365 nm in Campinas city.

photocatalytic degradation of Diuron when compared to soil that received no lime. On the other hand, when the humidity increases, the degradation rate also increases. Under the background humidity observed for the soil, the Diuron half-life ($t_{1/2}$) was about 20 h, dropping 50% ($t_{1/2} \sim 10$ h) when the soil became more saturated with water. This result shows that, in this particular case, the limiting mechanism for pesticide degradation using heterogeneous photocatalysis is more likely related to suitable conditions of transporting the substrate to the catalyst surface, or increasing the mobility of the target compound, although the hypothesis of using water as an additional source of OH radicals cannot be ruled out. Usually, experiments of photocatalytic degradation in soil performed in laboratories are carried out in an aqueous slurry (4), where the half-life of the target compound can reach values of a few minutes [13]. However, one has to consider that such an experimental set up may not be feasible when using in situ decontamination.

Solar intensity seems to be a key parameter in both the extension and the kinetics of Diuron photodegradation. As presented in Fig. 5, light intensity reaching the surface of the soil in Campinas (22°S, 47°W) differs markedly from summer (February) to winter (August). These measurements were carried out almost daily (280 data points) during the whole year. In the summer, the maximum light intensity (I_{max}) measured

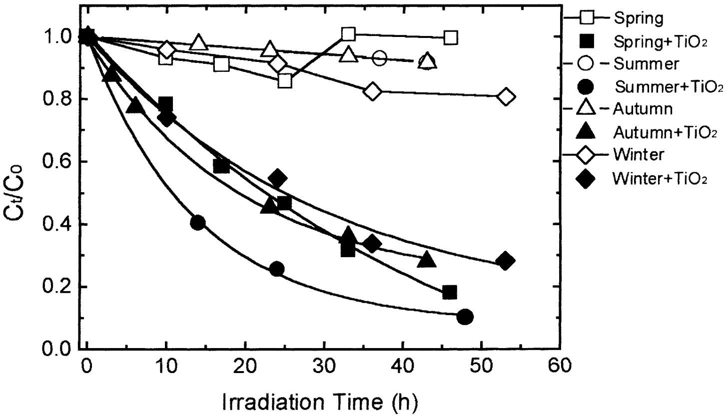

Fig. 6. Degradation rates of Diuron in soil in different seasons of the year.

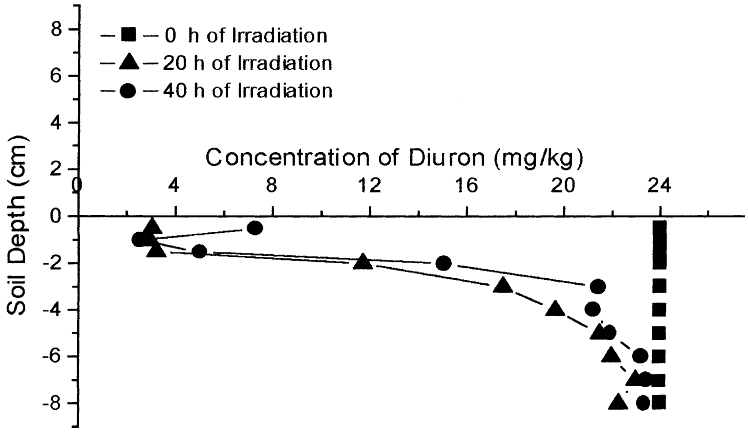

Fig. 7. Photocatalytic degradation of Diuron in soil at different depths.

was 2.7 mW cm^{-2}, resulting in a $t_{1/2}$ of 10 h (as seen in Fig. 6), while in the winter the maximum intensity was almost three times lower, presenting an I_{max} of 1.0 mW cm^{-2}, which corresponds to a $t_{1/2}$ of 24 h. It is interesting to note the inversely proportional relationship between light intensity and $t_{1/2}$ in this case.

As already mentioned, soil remediation using TiO_2 coupled to solar light, as described in these experiments is a process of limited application, since it acts only in the uppermost layer of the soil. As presented in Fig. 7, the profile of Diuron degradation in a contaminated soil (24 mg Diuron/kg of soil) illuminated from the surface shows that after 40 h of illumination the concentration of the pesticide in the top 1 cm of soil was slightly above 2 mg kg^{-1} (or around 90% degradation), with a sharp decrease in the degradation process in the soil column below 3 cm. At 8 cm depth, degradation of the pesticide reached values around 5% of the original spike in this same time interval.

In all the experiments mentioned above, no subproducts were detected using the experimental conditions arranged for HPLC quantification of the parent compound. However, when using GC-MS, two different intermediates were detected after 20 h of solar exposure. With the help of the NIST library, these compounds were identified as 1,2-dichloro-4-isocyanate benzene and 3,4-dichloro benzenamine. After 40 h exposure to solar light, 3,4-dichloro benzenamine is no longer detected, and the isocyanato compound drops to around 10% of the concentration present at the end of 20 h.

4. Conclusion

It has been demonstrated that the combination of TiO_2 with solar light can destroy a recalcitrant pesticide such as Diuron (12) present in soils, leading to intermediates that were also degraded after being exposed for up to 120 h. The process is fast, and the pesticide half-life rarely exceeded 25 h under optimized conditions. As expected, solar intensity was an important parameter to control the degradation, and the higher the soil humidity, the better the destruction yield.

Despite the fact that the destruction was limited to the first 4 cm of contaminated soil, it is worth mentioning that no efforts were made to mix the soil to increase the destruction rate by exposing deeper fractions of the contaminated soil to solar light and TiO_2, which would be the expected management procedure for in situ remediation. However, in the case of surface contamination, such as the ones observed in the handling area of the pesticide, or even at the production site, the proposed advanced oxidation technology (AOT) seems to be very suitable, since the estimated costs of this process, comprising only the spreading of the catalyst over the contaminated area, are far more attractive than any other conventional technology.

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