

Selective Photocatalysis of Dimethylnaphthalene by Means of β -Cyclodextrin Molecular Recognition Sites

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Abstract

Heterogeneous photocatalysis using titanium dioxide is a non-selective technique used for the degradation of target molecules such as dimethylnaphthalene. This work presents a novel approach for selective photocatalysis implementing molecular recognition sites (MRS) placed in the vicinity of titanium dioxide which attract target molecules and shuttle them to the surface of titanium dioxide, where they are more rapidly and selectively degraded. The photodegradation rate of dimethylnaphthalene was studied under two variables: surface area and kinetics of titanium dioxide, as well as the presence of MRS. While improvement under zero order kinetics was not noteworthy, it was discovered that presence of MRS in conjunction with first order kinetics significantly improves the degradation rate of dimethylnaphthalene.

Introduction

Photocatalysis is a technique used for the degradation of target molecules by means of creating OH[•] radicals through ultraviolet radiation. Heterogeneous photocatalysis, then, incorporates the use of a catalyst characteristic of a different phase than that of the degraded material. Titanium dioxide is known to be an efficient photocatalyst that, by the same token, is inexpensive, non-toxic, chemically stable, and accessible. A key characteristic of titanium dioxide is its high surface area, which allows the rate of reaction to increase, as the efficiency of a photocatalyst is proportional to its surface area. The process of photodegradation on the surface of titanium dioxide, initiated by ultraviolet illumination that generates electron-hole pairs, forms OH[•] radicals when photogenerated holes interact with adsorbed water¹.

It is acceptable to assume that the rate of photodegradation on titanium dioxide is of the form:

$$(1) \text{ Rate} = \frac{kK[S]}{1+K[S]}$$

where *Rate* = rate of photodegradation,

[*S*] = concentration of the target molecule (dimethylnaphthalene),

K = equilibrium constant between the surface of titanium dioxide and dimethylnaphthalene,

and *k* = reaction constant.

When the concentration of the target molecule is very low, the rate can be approximated to be a first order rate:

$$(2) \text{ Rate} = kK[S]$$

In this case, the coverage of the titanium dioxide surface is partial and is proportional to the concentration of the target molecule in the bulk.

However, when the concentration of the target molecule is very high, the rate becomes zero order:

$$(3) \text{ Rate} = k$$

Here, the coverage is thorough, and the bulk concentration has no influence on the rate of degradation; only the constant of the reaction has such an influence.

In the process of using photocatalytic reactions to chemically degrade a contaminant, the problem arises that such reactions have low selectivity. Selectivity controls a reaction in such a way that one target molecule can be adsorbed preferentially by the system and become decomposed more rapidly. Research in the field of selective photocatalysis is relatively novel, but selectivity of TiO_2 has previously been achieved in several ways: modifying surface conditions or pH, imprinting the target molecule into the TiO_2 particle, adding zeolites, and more². This work presents a different approach to selective heterogeneous photocatalysis based on molecular recognition sites (MRS) located in the vicinity of titanium dioxide (see figure 1). The target molecule is attracted by the MRS and then shuttled towards the titanium dioxide by surface diffusion, where it is degraded.

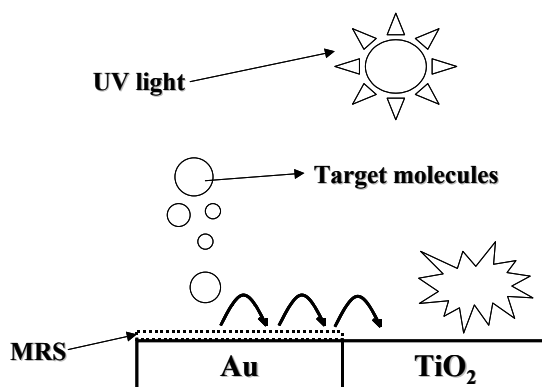


Figure 1: The general concept.

Some work has previously been published on this subject, using β -cyclodextrin as a molecular recognition site and 2-methyl-1,4-naphthoquinone (MNQ) as a target molecule³. It has been shown that the presence of β -cyclodextrin improves the photodegradation rate of MNQ by approximately 200%, and that selective preference to the MNQ can be achieved over a second contaminant (benzene) through use of MRS. Another system developed by the same research group uses mercaptoundecanoic acid as a molecular recognition site and diisopropyl methylphosphonate as a target molecule.

This particular work deals with a system in which β -cyclodextrin is used as a molecular recognition site, and the target molecule is dimethylnaphthalene. Dimethylnaphthalene is a compound that is a common contaminant of marine environments, due to the frequency of oil spills during oil transport. It has a good affinity to β -cyclodextrin, because of their compatible sizes and shapes (see figure 2).

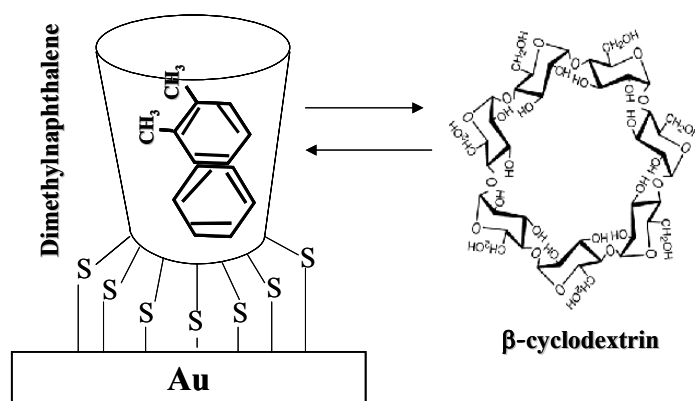


Figure 2: The chemical relationship between dimethylnaphthalene and β -cyclodextrin.

Methods And Materials

Four hybrid substrates of titanium dioxide and gold (prepared according to Haick et al.⁴) were used in two correlated experiments: one with a thiolated β -cyclodextrin coating and one without. The synthesis used to produce thiolated β -cyclodextrin was as described by Rojas, et al.⁵. Prior to the coating, the substrates were cleaned thoroughly in a commercial UV-Ozone cleaner (Jelight Ltd, UVO model 42-220) for 10 minutes. The coating of β -cyclodextrin on the substrates was accomplished by direct immersion into the 1 mM solution of thiolated β -cyclodextrin in dimethylsulfoxide (DMSO) and water (60/40v/v). This formed an organic self-assembled monolayer on the gold stripes on the substrate surface.

A 0.2 μ M solution of dimethylnaphthalene was made in equal volume parts of water and propanol. 15 mL of this solution were illuminated at 254 nm in a reactor (7 cm diameter) with four substrates at room temperature for 20 hours at an intensity of 750 μ W/cm². The reactor was covered with a quartz lid and sealed. The kinetics of the reaction were studied by UV-VIS spectroscopy (Perkin-Elmer, Lambda 40).

Results

In order to analyze the effect of β -cyclodextrin on the degradation of dimethylnaphthalene, all parameters other than the presence of the β -cyclodextrin monolayer were held constant. The data was compiled using the UV-VIS spectrometer; a representative image of the progression of dimethylnaphthalene degradation is shown in figure 3.

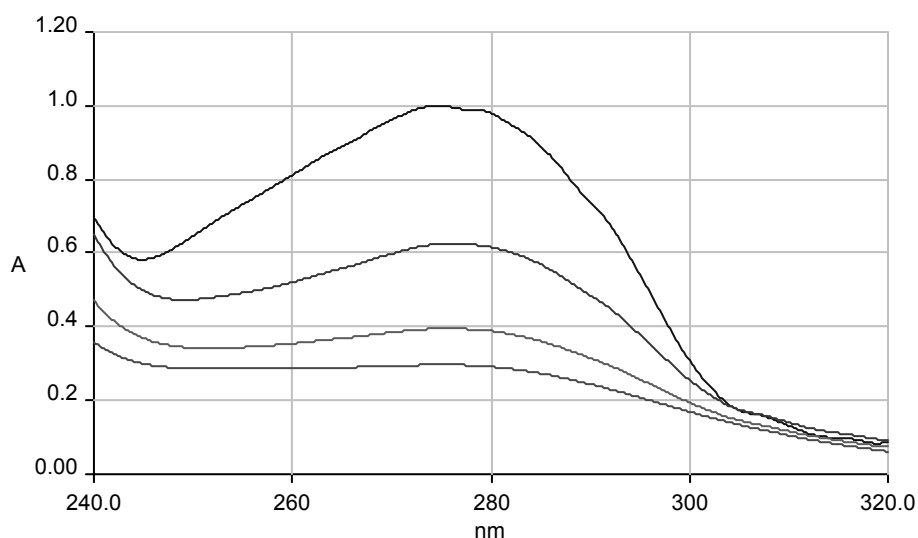


Figure 3: absorbance peaks of dimethylnaphthalene under degradation

A calibration curve was built in order to find a direct correlation between ultraviolet absorbance of dimethylnaphthalene and its concentration.

$$(4) C = 0.000000203A - 0.000000005$$

where C = concentration of dimethylnaphthalene in Molar
and A = the absorbance.

The effect of titanium dioxide as a photocatalyst of dimethylnaphthalene can be seen in figure 4.

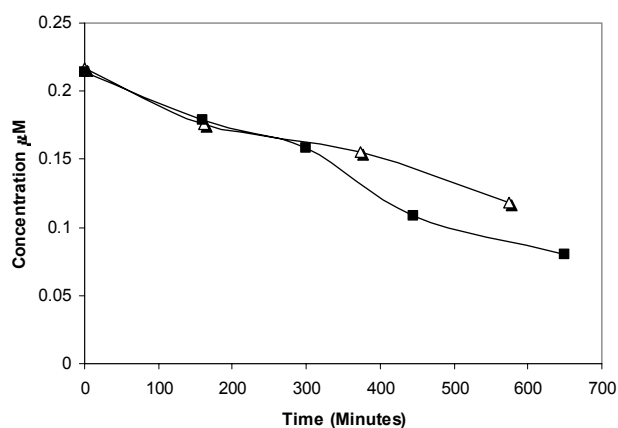


Figure 4: The effect of 3 titanium dioxide substrates on the degradation of dimethylnaphthalene. Δ Degradation of dimethylnaphthalene under ultraviolet illumination without substrates. \blacksquare Degradation of dimethylnaphthalene with three titanium dioxide substrates.

The rate of photodegradation of dimethylnaphthalene using three titanium dioxide substrates was calculated to be twice as fast as that without substrates when approximated as a linear reduction. Moreover, this linear reduction remains at a similar rate with hybrid substrates of gold and titanium dioxide. It was also noted that when four substrates were

placed in the reactor, the curve of the photodegradation was dramatically altered. While the curve in trials with three substrates remained constantly linear, it became exponential with the addition of a fourth substrate, as seen in figure 5.

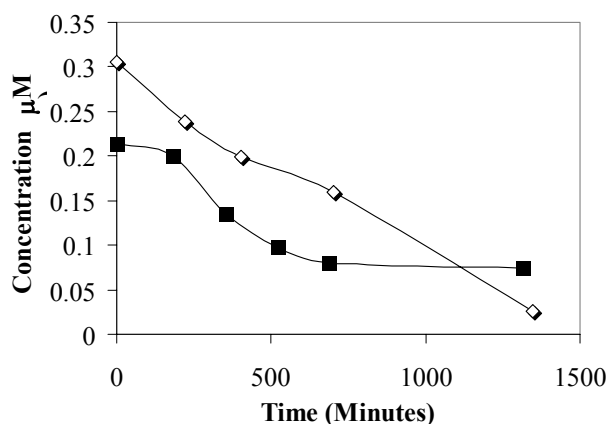


Figure 5: The photodegradation of dimethylnaphthalene: ◇ Three substrates of titanium dioxide and gold, ■ Four substrates of titanium dioxide and gold.

Thus, it can be noted that throughout 23 hours, the degradation of dimethylnaphthalene using three substrates is more efficient than that using four.

The photodegradation of dimethylnaphthalene using three titanium dioxide and gold substrates (with and without β -cyclodextrin), then, can be seen in figure 6.

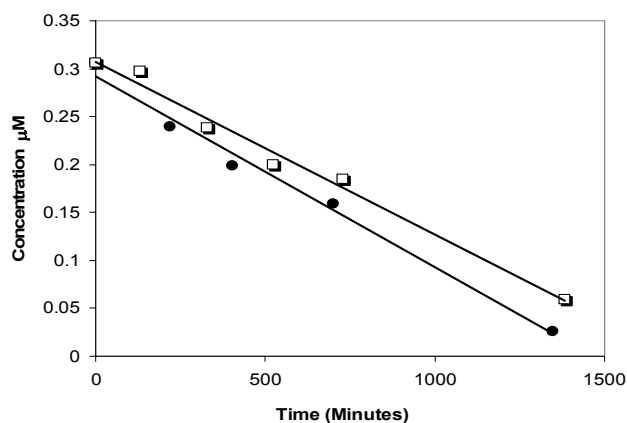


Figure 6: The photodegradation of dimethylnaphthalene: □ Three substrates of titanium dioxide and gold, ● Three substrates of titanium dioxide, gold, and β -cyclodextrin monolayer

After approximately 23 hours, it can be seen that more than 90% of the dimethylnaphthalene has been degraded in both experiments. Both experiments also reflect a linear behavior. The rate of degradation of dimethylnaphthalene was increased by 10.6% with the presence of β -cyclodextrin.

When four substrates were placed in the reactor, the results of illumination varied, as seen in figure 7.

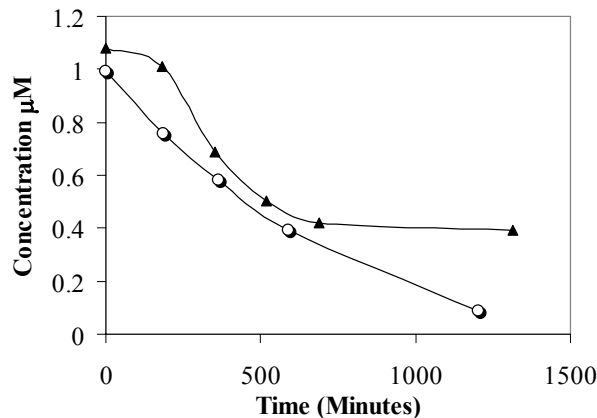


Figure 7: The photodegradation of dimethylnaphthalene: ▲ Four substrates of titanium dioxide and gold, ○ Four substrates of titanium dioxide, gold, and β -cyclodextrin monolayer.

Both experiments appeared to behave more exponentially than linearly. It can be seen that at low concentrations, substrates without β -cyclodextrin ceased to degrade the remaining molecules of dimethylnaphthalene, while the β -cyclodextrin coated substrates continued to degrade the material. It was calculated that the rate of degradation of dimethylnaphthalene under these conditions was increased by 139.9% (under the assumption of exponential behavior), also because of β -cyclodextrin.

Discussion

Titanium dioxide improves the photodegradation of dimethylnaphthalene, which can be seen according to figure 4. The improvement is not drastic because of the small surface area of titanium dioxide and its low efficiency, which can be assumed by its inability to degrade dimethylnaphthalene under higher frequencies. When three substrates of titanium dioxide were placed in the reactor, the rate of photodegradation was very similar to that of three substrates of titanium dioxide and gold (on which titanium dioxide covers only half the surface area). Because the kinetics of the photodegradation are of zero order, the reduction of the surface area of titanium dioxide will have little effect of the rate, as dimethylnaphthalene is absorbed on the surface of titanium dioxide. As long as the surface of titanium dioxide is fully covered with the dimethylnaphthalene, it will be degraded at the same rate. On the other hand, when surface area is increased with the addition of a fourth substrate, the kinetics are dependent on concentration as they are shifted towards first order.

Figure 5 depicts the larger efficiency of the photodegradation of dimethylnaphthalene due to the implementation of three wafers. Because titanium dioxide has a low affinity to dimethylnaphthalene, the rate of photodegradation is slowed when it becomes dependant on this factor (first order reactions). Thus, when surface area of titanium dioxide is increased with a fourth wafer, the rate is slower than that with only three, despite the larger surface area.

Figure 6 demonstrates the photodegradation of dimethylnaphthalene under two conditions: with and without β -cyclodextrin. The kinetics of the photodegradation are approximately zero order for both conditions. The improvement due to the β -cyclodextrin is only 10%, because of the independence of the rate of photodegradation on the concentration of dimethylnaphthalene.

In figure 7, the same two conditions are exhibited for four substrates instead of three. The kinetics of these reactions were approximately first order, as they were more exponential than they were linear. In this situation, β -cyclodextrin helped to account for the difference in coverage by dimethylnaphthalene on the surface of the titanium dioxide, allowing it to degrade at a similar rate than that of a zero order reaction, where affinity is not the limiting factor. Thus, with β -cyclodextrin and four substrates, optimal results may be achieved as affinity does not limit the reaction and surface area is increased to further speed it up.

Conclusions

Rate of photocatalysis is often dependent on surface area. The apparent change from zero to first order kinetic behavior is a direct result of additional titanium dioxide. When the reaction pertains to first order kinetics, it is inferred that the concentration of dimethylnaphthalene is low, as when the reaction is of zero order the concentration of dimethylnaphthalene is usually significantly higher.

When β -cyclodextrin was added to the system of titanium dioxide and gold, molecules of dimethylnaphthalene were seen to degrade much more quickly, as its affinity with dimethylnaphthalene helped increase the selectivity and the efficiency of the reaction. For a zero order reaction, the improvement was only 10% because the role of β -cyclodextrin in helping to coat the titanium dioxide in dimethylnaphthalene is already accomplished due to the already higher concentration of the solution. On the other hand, for a first order reaction the improvement was approximately 140%, since the β -cyclodextrin was able to increase the coverage of dimethylnaphthalene on the surface of titanium dioxide.

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