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Study of the Adsorption of Dicarboxylic Acids on Titanium Dioxide in Aqueous Solution

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Abstract. The photodegradation processes using semi-conductor like TiO_2 as a catalyst, provide new methods for waste water treatment. In this method the step of adsorption of organic compounds on the semi-conductor surface could have a prominent influence. In this work we describe the results of the study of the dicarboxylic acids adsorption on TiO_2 (P25) in aqueous phase. The Langmuir model gives a good representation of the adsorption of the studied organic diacids. The maximum adsorption capacities are close to 7.10^{-5} mol/g for the four studied diacids. The diffuse reflectance infrared spectroscopy (IRFT-DRIFT mode) of loaded TiO_2 enables to demonstrate the formation of a dicarboxylate film on the semi-conductor surface.

Keywords: titanium dioxide, dicarboxylic acid, Langmuir, IRFT-DRIFT

Introduction

The photocatalytic degradation of organic compounds in aqueous suspension of TiO_2 is a promising and valuable method of water depollution (Pelizzetti et al., 1991). The principle of these reactions is the ejection of the electrons from the valence band to the conduction band by U.V. light. This induces the formation of the holes which migrate at the semi-conductor surface:

$$TiO_2 + h\upsilon \longrightarrow e^-_{\text{(conduction band)}} + h^+_{\text{(valence band)}}$$

The electron-hole pairs participate in the redox reaction at the semi-conductor surface, and the adsorption of organic pollutants could influence the mechanism of degradation (Robert and Weber, 1998). We observed that the degradation of dicarboxylic acids has a different behaviour than the classical degradation of monoacids (Robert and Weber, 1997). Noteworthy that a first step of adsorption is generally remarked for dicarboxylic acids, leading to more complex kinetics of degradation. In order to investigate the influence of the adsorptive step, we studied in this work the adsorption of 4 dicarboxylic acids on TiO_2 in aqueous solution. The adsorption on oxide surface has been also studied by diffuse reflectance infrared spectroscopy IRFT (DRIFT). This technique is particularly well adapted for surface analysis (Culler et al., 1984).

Experimental

Products

TiO_2 (P-25) from Degussa Corporation has an average particle size of 30 nm, a surface area of 50 m^2/g. Its prevailing cristallin form is anatase (70%) and its purity is superior to 99.8% (the principal impurities are SiO_2 and Al_2O_3). The highly dispersed TiO_2-P25 is manufactured by flame hydrolysis (Aerosil process). The pores with a diameter ranging between 2 and 4 nm predominate (Martin et al., 1997). The four diacids (oxalic, malonic, succinic and methylsuccinic) were obtained from Aldrich and their purity is superior to 99%.

Adsorption Experiments

The adsorption isotherms of the diacids on TiO_2 were studied in static mode at 293 K (Vinodgopal et al., 1996). The suspensions were prepared by mixing 100 ml of aqueous diacid solutions of various initial concentration C_i at natural pH (about 3–4) with a fixed weight (0.2 g) of Degussa P-25 TiO_2 (after mixing with TiO_2, the initial pH is not changed a lot). The suspensions were stirred up one hour in the dark and then filtered. This time was determined after preliminary experiments about the kinetic of adsorption. We determined the diacid remaining concentrations by measuring them with NaOH 4.10^{-3} M. The extent of equilibrium adsorption was determined from the decrease in the diacid concentration detected after filtration.

Diffuse Reflectance FTIR Experiments

DRIFT spectra of samples were recorded between 4000–600 cm^{-1} at a resolution of 2 cm^{-1} on a Bio-Rad FTS 185 spectrometer. Potassium bromide powder was used as a sample matrix and reference material (sample to KBr ratio 5/100 in weight). The diffuse reflectance FTIR spectrum of the reference compounds was obtained by mixing it with KBr powder (5% in weight). All samples were dried at 110°C under vacuum till constant weight before analysis. In order to eliminate the sloping baseline due to TiO_2 absorption, the baseline-correction procedure was carried out for samples after adsorption.

Results and Discussion

Adsorption Isotherms

For diacids (oxalic, malonic, succinic and methylsuccinic), we observe that they adsorb fastly onto TiO_2 particles from aqueous solution. In general after a few minutes an equilibrium is got. The adsorption isotherms for diacids in which n_s is the number of diacid μmoles adsorbed per gram of TiO_2, are plotted versus the equilibrium concentration of the diacid solution C_{eq} (see Fig. 1).

The number of diacid moles adsorbed per gram of TiO_2 (n_s) can be determined from the adsorption-induced decrease in the molarity (ΔC) and V, the volume of diacid solution: $n_s = (V\Delta C)/W$ where W is the weight of TiO_2 in grams.

The classical model of Langmuir (Langmuir, 1915) was tested on our results, and the parameters obtained after linearization (Stumm et al., 1981) of the following equation are given in Table 1.

Table 1. Parameters of the Langmuir equation for the diacids.

Diacids	n_s^0 (μmol/g)	K (1/mmol)	R^2
Oxalic	73	2.5	0.961
Malonic	72	1.9	0.962
Succinic	67	0.4	0.992
Methylsuccinic	62	0.2	0.989

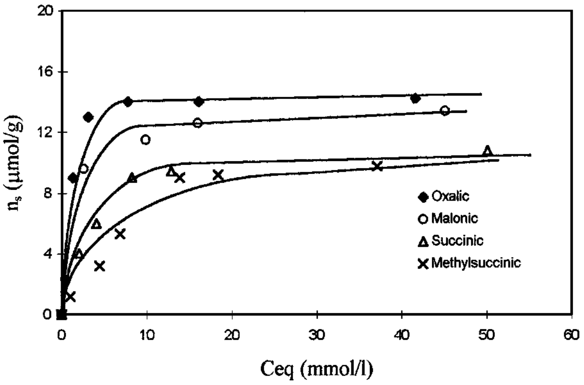


Figure 1. Adsorption isotherm for diacids on TiO_2, plot of the n_s (μmol/g) versus C_{eq} (mmol/l).

$$n_s = \frac{(n_s^0 K)}{(1 + KC_{eq})}$$

n_s: number of diacid adsorbed (μmol/g of TiO_2), C_{eq}: equilibrium concentration of acid remaining in solution (μmol/l), n_s^0: maximum adsorption capacity (mmol/g of TiO_2), K: adsorption equilibrium constant for the pair solute/TiO_2 (1/μmol).

We can consider that this model gives a good representation of the adsorption of diacids ($R^2 > 0.96$ in all cases).

The linearized Langmuir equation has enabled to obtain the maximum adsorption capacity n_s^0 and adsorption equilibrium constant for the pair solute/TiO_2, for each diacid. The maximum adsorption capacity n_s^0 decreases when the steric effect increases (Fig. 2).

This observation is very important to determine mechanism of the photocatalytic degradation. The recombining reaction of the photogenerated electron and hole is very fast (picosecond timescale) and the interfacial electron transfer is possible only when the donor or acceptor is preadsorbed before the photocatalysis. In aqueous suspension, OH^- and H_2O can behave as

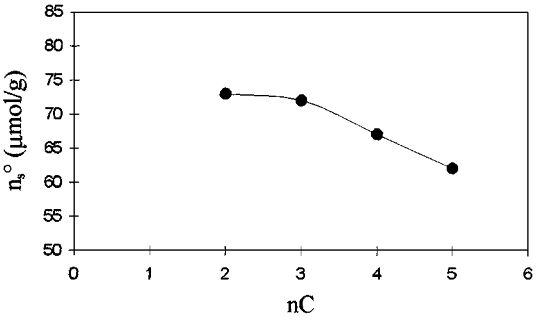


Figure 2. Steric effect of the diacids, plot of the n_s^0 (μmol/g) versus nC (number of carbon atom of the diacid).

hole traps, forming hydroxyl radicals adsorbed at the TiO_2 surface.

$$OH^- + h^+ \longrightarrow OH^0$$
$$H_2O + h^+ \longrightarrow OH^0 + H^+$$

The direct oxidation of the diacids adsorbed by photogenerated holes is possible at the semi-conductor surface. If the compound is very adsorbed this last way can be considered and if not the mechanism of degradation is preferentially the oxidation by photogenerated holes.

The results given in the Table 1 are consistent with results reported for other compounds such as aminobenzoic acid on TiO_2 (Cunningham et al., 1994) or EDTA (Madden et al., 1997).

Study of the Adsorption with DRIFT Spectroscopy

The analysis of the isolated TiO_2 loaded particles by DRIFT (in Fig. 3, we showed the case of the methylsuccinic acid) shows the appearance of the band at 1590 cm^{-1} clearly associated with the carboxylate bands.

It is logical to propose that the decrease of the acid concentration in aqueous phase is associated with the formation of dicarboxylate film:

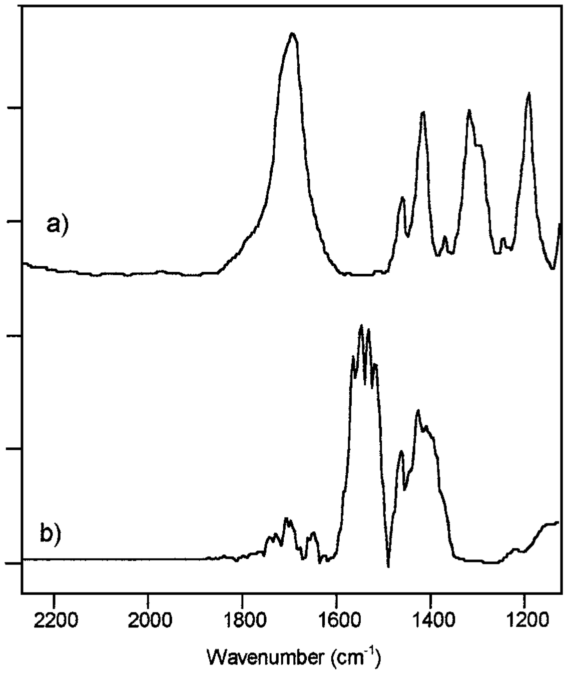
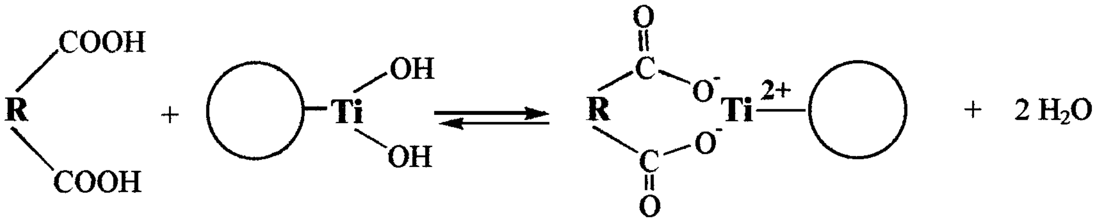


Figure 3. Diffuse reflectance adsorption spectra (DRIFT) of methylsuccinic acid in KBr (a) and acid adsorbed on TiO_2 by direct addition in KBr (b).

Due to the very low variation of $[H_3O^+]$ the pH change cannot be observed experimentally in our conditions. This hypothesis is sustained also by the study of the adsorption of diacids, showing a characteristic behaviour of Langmuir adsorption (this model is correct for the monolayer adsorption). Consequently the diacids are chemisorbed in monolayer of dicarboxylate at the TiO_2 surface.

Conclusion

From our experimental results we can conclude that the Langmuir model gives a good representation of the adsorption of diacids on TiO_2. We have shown that the adsorption is a function of the steric effect of the diacids: oxalic > malonic > succinic > methylsuccinic. The photodegradation mechanism depends on the



adsorption capacities. However for the diacids the n_s^0 values are very comparable. So the mechanism is probably the same. The results based on infrared spectroscopy in DRIFT mode suggest the formation of a dicarboxylate film on the TiO_2 surface. The carboxylate films have a quick kinetic of formation (a few minutes).

Nomenclature

n_s	Number of diacid moles adsorbed per gram of TiO_2 (μmol/g)
n_s^0	Maximum adsorption capacity (μmol/g)
C_{eq}	Equilibrium concentration of diacid (μmol/dm^3)
V	Volume of diacid solution (dm^3)
W	Weight of TiO_2 (g)
K	Adsorption equilibrium constant (dm^3/mmol)

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