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Adsorption of Aqueous 4-Chlorobiphenyl and Treatment with UV-Illuminated Titanium Dioxide

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The research of 4-chlorobiphenyl in aqueous solution was conducted in two parts. The first part of the study explored the adsorption of 4-chlorobiphenyl onto glass. When the initial concentration of 4-chlorobiphenyl was below 25 μg/L, the sample concentration became undetectable after 24 h. With respect to 4-chlorobiphenyl adsorbed onto glass, the adsorption rate constant k was 18 μg/h L, the adsorption equilibrium constant K was nearly 10^{-3} μg/L using the Langmuir first-order reaction model, and the monolayer saturated density, using the BET model, was 1200 μg/m^2. In the second half of this study, the photocatalytic oxidation (UV/TiO$_2$) of 4-chlorobiphenyl was investigated using its adsorption characteristics. The UV/TiO$_2$ process decreased the 4-chlorobiphenyl concentration (initial concentration = 500 μg/L) by 77% within 120 min. The ratio between the TiO$_2$ adsorption rate constant and the UV/TiO$_2$ process degradation rate constant was 1/10^5. © 1997 Academic Press

Key Words: **4-chlorobiphenyl; glass; adsorption; photocatalytic oxidation; UV/TiO$_2$ process; Langmuir first-order reaction.**

INTRODUCTION

Polychlorinated biphenyls (PCBs) are among the most widespread pollutants in the global ecosystem (1, 2), especially in sludge at river bottoms (3, 4), and have recently been widely discussed in literature (4–7). 4-Chlorobiphenyl is a PCB, which has very low solubility and a tendency to adsorb onto solid surfaces (4, 8). Brown *et al.* were the first to show that PCBs exist in Hudson River sediments because the substances are continually adsorbed from aqueous solution to sludge and are partly dehalogenated by anaerobic bacteria (9). The adsorption behavior of cationic and nonionic surfactants on oxide surfaces in the solution and interface has recently been widely probed in literature (10–14). Because glass is composed mainly of oxides and its surface is hydrophobic relative to many other oxides such as TiO$_2$ (15), PCB solutions should have a tendency to adsorb onto glass. We studied the adsorption behavior of 4-chlorobiphenyl to quantify its loss through adsorption during experimental processes. In this paper, we also present a detailed study of 4-chlorobiphenyl, which is a PCB, to explore concentration instability, to discover the factors affecting sample inaccuracy, to attempt to efface this adverse effect, and to probe the adsorption and desorption behavior of 4-chlorobiphenyl at the TiO$_2$ (anatase)/solution interface. Moreover, we used the adsorption characteristics to investigate the photocatalytic degradation of 4-chlorobiphenyl with titanium dioxide suspension in a glass reactor and 77% of 4-chlorobiphenyl was oxidized after 120 min. In traditional treatment of water or wastewater, finding efficient methods for the degradation of contaminants which are like 4-chlorobiphenyl is pressing because some contaminants are bioaccumulative and their toxicity causes the inhibition of microorganism function in the treatment process. In addition, retreatment or disposal is needed after phase transfer. Because of this and increased awareness of toxic organic substances, modern water or wastewater treatment technologies, such as UV/H$_2$O$_2$ and UV/TiO$_2$, which are called advanced oxidation processes (AOPs), are continuously being developed to destroy organic impurities. Under suitable operational conditions, the mineralization of pollutants is fast. The UV/TiO$_2$ process, an emerging technology for treating toxic organic contaminants (16–21) is a heterogeneous photocatalytic process in which the illumination of an oxide semiconductor, usually the anatase form of titanium dioxide, produces photoexcited electrons (e^-) and positively charged holes (h^+). The illuminated surface in the aqueous phase is widely regarded as a producer of hydroxyl radicals (22), which become extremely powerful oxidizing agents (e.g., $h^+ + OH^- \rightarrow \cdot OH$), and these and other highly oxidizing initial products of this indirect photochemistry go on to attack oxidizable contaminants.

MATERIALS AND METHODS

Sample Preparation

4-Chlorobiphenyl (Chem Service Co., S.G. grade 99+%) was chosen as the model compound. Methyl alcohol (Merck, G.R. grade) containing 4-chlorobiphenyl was used as stock solution (50 mg/L), which was diluted with deionized water (Milli-Q SP) to the required concentration before use. All other agents used were of Merck, G.R. grade.

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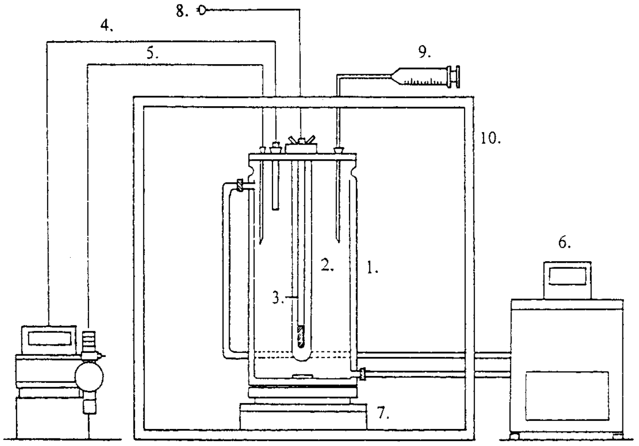
Before the UV/TiO_2 process was performed, TiO_2 (Degussa, P25) was repurified in the laboratory to remove impure substances which could easily affect adsorption results. Purification was accomplished by modification of procedures for purifying γ-Al_2O_3 (23). First, $HClO_4$ was added to deionized water containing TiO_2 to maintain the pH below 2 (Radiometer Copenhagen PHM 85). After stirring, the TiO_2 solution was left to precipitate overnight until the solid–liquid interface became clearly defined. The supernatant was discarded, and deionized water was added to the precipitate. These steps were repeated until the pH of the solution returned to that of deionized water. The precipitated TiO_2 was then placed into a reverse osmosis membrane, and deionized water was changed repeatedly until electrical conductivity equaled that of deionized water. The resulting TiO_2 slurry was dried in an oven at 103°C until it reached constant weight. The dried product was then ground into powder, and TiO_2 preparation was completed.



1. Glass Photocatalytic Reactor
2. Quartz Tube
3. UV-Light
4. pH Meter
5. pH Control System
6. Temperature Control System
7. Stirrer
8. Power Supply
9. Sampling Port
10. Stainless Steel Case

FIG. 1. Schematic of UV/TiO_2 experimental setup.

Analytical Methods

4-Chlorobiphenyl was analyzed by modification of Standard Method 6431 (24) and EPA Method 608 (25) on GC (Hewlett Packard 5890 Series II Plus) with a fused silica capillary column (HP 5, 30 m × 0.32 mm i.d., and 3.0 μm film thickness) and electron capture detector (ECD). Analysis involved microextraction of 4-chlorobiphenyl from 10 mL of sample using 5 mL of *n*-hexane. The mixture was mechanically shaken for 20 min, followed by the addition of 2 g of Na_2SO_4 to control ionic strength. The GC analytical method used was the splitless method with the opening of the valve set at 1 min later than injection. The temperatures of the injection port and the ECD were 270 and 330°C, respectively. The oven temperature program was controlled by Chemstation (HP, 1989). The analytical peaks did not overlap. To ensure the accuracy of the results, all detailed analyses strictly followed the QA/QC suggested by Standard Method 6020 (23).

Experimental Method and Design

An experiment was conducted to explore the adsorption phenomenon of aqueous 4-chlorobiphenyl onto vials. 10 mL various concentrations of 4-chlorobiphenyl were placed separately in amber glass bottles (Kimble, A203) to keep out light. $NaNO_3$ was added to maintain ionic strength at 0.1 N, and temperature was controlled at 4 or 20°C. After the solution was completely removed for extraction, each bottle was turned over to drip-dry for about 10 min and then rinsed with a small amount of deionized water. The desorption of 4-chlorobiphenyl from glass was conducted with 10 mL of 12 N NaOH for 10 h. The experiments explored the effects of pH, temperature, 4-chlorobiphenyl concentration, and adsorption time. Adsorption and desorption experiments of 4-chlorobiphenyl from TiO_2 were the same as those for glass and explored the effects of TiO_2 concentration, the interactions between TiO_2 and glass, and the mass balance of the system.

In addition, the photocatalytic degradation of 4-chlorobiphenyl with titanium dioxide suspension in a glass batch reactor was investigated. The photoreactor was illuminated with a 500 W UV fluorescent tube (Oriel 6285, mercury lamp). Under light irradiation, extremely powerful oxidizing agents like $\cdot$OH were produced and reacted with organic contaminants.

Figure 1 displays an UV/TiO_2 experimental reactor in which the synthetic sample was supplemented with $HClO_4$ or/and NaOH, which were used as sources in the pH controller (Toho Kagaku, PET 300A). The photoreactor was a double-layer glass batch reactor (Iwaki Code 7740) with an extradiameter of 12 cm, interdiameter of 10 cm, and height of 23 cm. In the center of the photoreactor, there was a double-layer quartz tube for placing a UV tube. Cooling water was recycled between both these double layers. A stirrer (FG Fargo MS 203) was placed at the bottom of the photoreactor for mixing.

RESULTS AND DISCUSSION

Quality Assurance and Quality Control (QA/QC)

QA/QC of the analytical methods are important for proving the accuracy and usefulness of the experimental data (26). In our paper, analysis of 4-chlorobiphenyl was conducted using used modified Standard Method 6431 (24) and EPA Method 608 (25). The modification involved microextraction of 4-chlorobiphenyl using *n*-hexane followed by analysis of 4-chlorobiphenyl on GC. This method not only saved experimental time but also retained accuracy. The

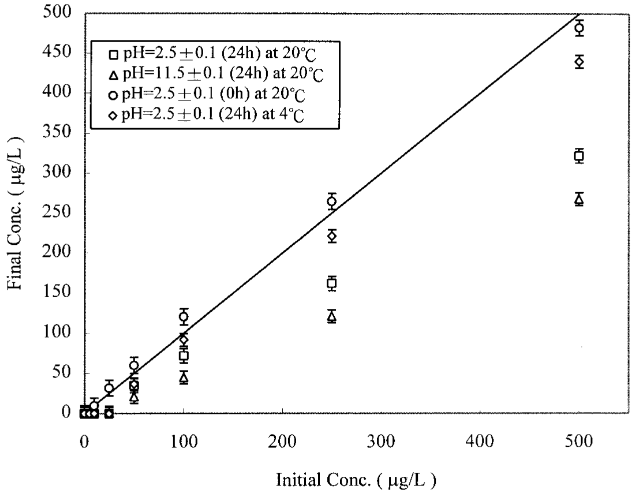


FIG. 2. Variation of final 4-chlorobiphenyl concentration after adsorption onto glass (methanol = 1%).

MDL value, the best of which should be as small as possible, in our paper was 0.9 μg/L, which is small enough and similar to other published data (27).

Adsorption Effects on Glass

All experiments in this section were performed at a total ionic strength of 0.1 N ($NaNO_3$). In Fig. 2 (20 and 4°C), we found that temperature is an important factor in controlling 4-chlorobiphenyl adsorption onto glass. ΔH of adsorption, which is >0 (usually), causes adsorption of 4-chlorobiphenyl to increase with increasing temperature. Results infer that the surface charge on oxide originates from adsorption and desorption of proton and hydroxyl ions and is governed by the solution temperature. This phenomenon is also observed in the adsorption of cadmium onto oxides (28).

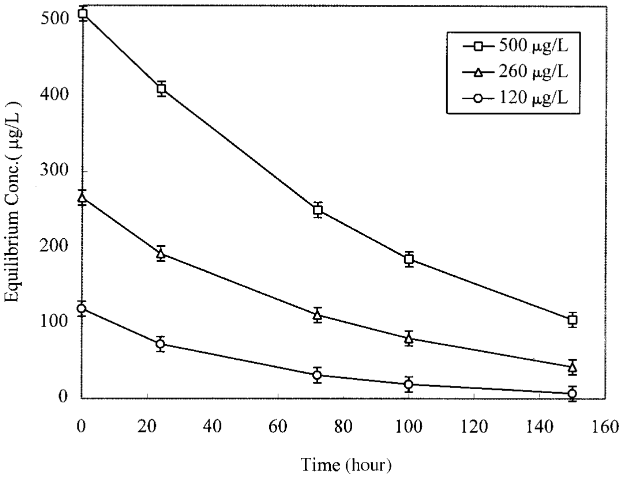


FIG. 3. Adsorption of 4-chlorobiphenyl onto glass with different initial 4-chlorobiphenyl concentration at pH 2.5 ± 0.1 (methanol = 1%, 100 h, 20°C).

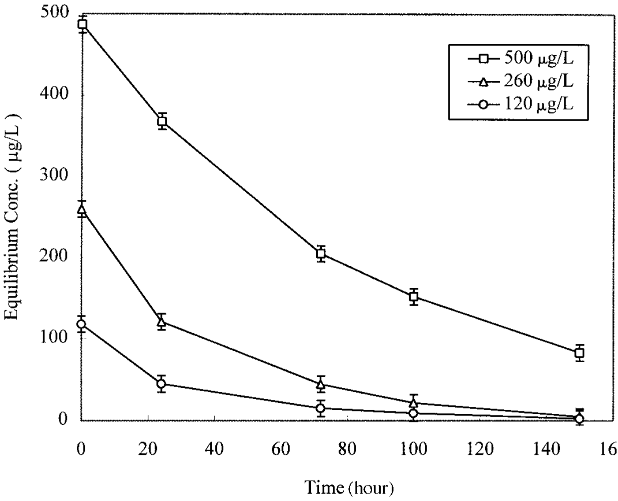


FIG. 4. Adsorption of 4-chlorobiphenyl onto glass with different initial 4-chlorobiphenyl concentration at pH 11.5 ± 0.1 (methanol = 1%, 100 h, 20°C).

All experiments were conducted in closed systems in amber glass bottles without mass transfer. Because the vapor pressure of 4-chlorobiphenyl is below 0.1 mmHg at 38°C and its boiling point is 280°C (offered by Chem Service), vaporization was expected to be negligible in this solution. In addition, various concentrations of 4-chlorobiphenyl in our experiments were lower than the saturated concentration of 1190 μg/L (29) without extrasaturation. It was demonstrated that the decrease of 4-chlorobiphenyl from water was due to its adsorption on glass. This was also demonstrated by desorption experiments and evidenced by mass balance results of the system.

In Fig. 2, the line indicates the concentration of 4-chlorobiphenyl without adsorption. Variation of pH is an important property of solids and is closely related to the adsorption reaction. This may be attributed to the surface charge and surface acidity. The acidity of the surface sites of oxides is driven by electrostatics and is mainly governed by three structural parameters (30):

1. the coordination number of the hydroxyl group,
2. the change on the cation(s), and
3. the coordination number of the cation(s).

Furthermore, structural properties of surface OH groups have been discussed with heterogeneous catalysis and colloid physics (31). A better explanation is that glass is dominated by the coordination number of the pH-dependent hydroxyl groups of the glass oxides. Because high pH causes the glass surface to become hydrophilic-like and causes 4-chlorobiphenyl to become partially positively-charged, adsorption of 4-chlorobiphenyl increases with increasing pH. From Fig. 2, it is suggested that aqueous 4-chlorobiphenyl be stored below 4°C at pH lower than 2.5 and be analyzed on GC within 24 h.

Results of concentration effects from Figs. 3 and 4 show that the final concentrations of 4-chlorobiphenyl, at initial

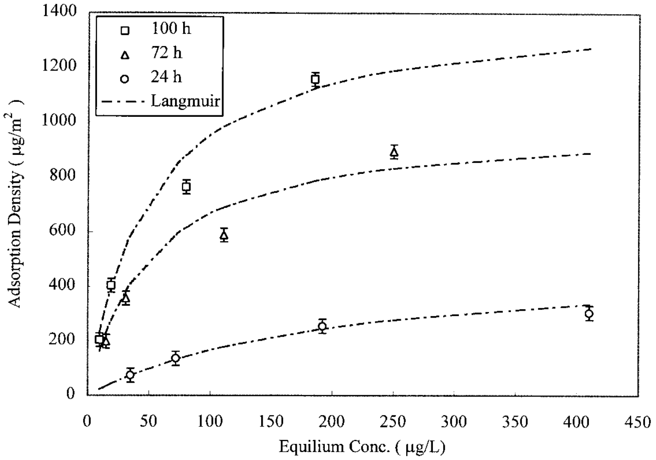


FIG. 5. Variation of adsorption density (Γ) on glass with different 4-chlorobiphenyl equilibrium concentrations at pH 2.5 ± 0.1 (methanol = 1%, 20°C).

concentrations of 500, 260, and 120 μg/L, were 20.6%, 15.8%, and 5.9%, respectively, at pH 2.5 ± 0.1 and 17.0%, 1.9%, and 2.3%, respectively, at pH 11.5 ± 0.1. It could be inferred that the concentration gradient increased the forces driving adsorption, and it was demonstrated again that pH was closely related to adsorption.

Adsorption Models

The adsorption rate constant and adsorption equilibrium constant were calculated by adsorption models using data from Figs. 3–6. Langmuir and BET isotherms were used to describe the adsorption behavior.

Using Langmuir model simulated adsorption, the *R* square decreases from 0.998 to 0.988 with increasing equilibrium time from 24 h to 100 h. Therefore, adsorption of 4-chlorobiphenyl molecules onto glass surface sites, forming a monolayer within 24 h, was simulated successfully. The *b* (adsorption constant), which was the result of Langmuir simulation, was maintained at about 10^{-2} (μg/L) from 24 to 100 h at both pH 2.5 ± 0.1 and 11 ± 0.1. The *a* (monolayer saturation density), simulating the Langmuir isotherm, maintained at about 1400 (μg/m^2).

The simulated results of the Langmuir isotherm (100 h) are

$$\Gamma = \frac{28.52[C]}{1 + (2 \times 10^{-2})[C]}, \text{ at pH } 2.5 \pm 0.1, \qquad [1]$$

$$\Gamma = \frac{60[C]}{1 + (3 \times 10^{-2})[C]}, \text{ at pH } 11.5 \pm 0.1, \qquad [2]$$

where [*C*] is the concentration of 4-chlorobiphenyl in water (μg/L), Γ represents the amount of 4-chlorobiphenyl adsorbed onto glass (μg/m^2).

The BET model produced better results than the Langmuir model in excess of 24 h. The R^2 increased from 0.976 to 0.994 with increasing equilibrium time from 24 to 100 h, and monolayer saturation density was 1200 μg/m^2 by BET isotherm. Results revealed that adsorption of 4-chlorobiphenyl onto glass did not produce a monolayer after 24 h, and, therefore, was a slow process. Although the changes of R^2 in the Langmuir and BET isotherms were insufficient and the values remained at above 0.97, the Langmuir isotherms were more useful for modeling adsorption onto glass because the glass was usually saturated with aqueous 4-chlorobiphenyl in experiments like Figs. 5 and 6.

Using the Langmuir isotherm to calculate the adsorption rate constant and the equilibrium constant is important for this research. First, the assumption is made that the maximum adsorption possible is that of a complete monolayer. In other words, the model assumes that there are *N* sites of glass and that each 4-chlorobiphenyl molecule is adsorbed by one site. The reaction is written as

$$C + G \underset{k_d}{\overset{k_a}{\rightleftharpoons}} C\text{–}G, \qquad [3]$$

where *C* is 4-chlorobiphenyl in water, *G* represents glass surface sites, *C–G* is 4-chlorobiphenyl adsorbed onto glass, and k_a and k_d are adsorption and desorption constants.

$$\text{Adsorption rate} = k_a[C][G], \qquad [4]$$

$$\text{Desorption rate} = k_d[C\text{–}G], \qquad [5]$$

$$[G] = N(1 - \theta), \qquad [6]$$

$$[C\text{–}G] = N\theta, \qquad [7]$$

where [*G*] is the concentration of empty sites and θ is surface coverage. At steady state,

$$k_a[C]N(1 - \theta) = K_d N\theta \qquad [8]$$

can be rearranged to

$$\theta = \frac{k_a[C]}{k_d + k_a[C]}. \qquad [9]$$

Assuming that $K = k_a/k_d$ is an adsorption equilibrium constant,

$$\theta = \frac{K[C]}{1 + K[C]}. \qquad [10]$$

It is further assumed that the relation between the reaction rate and surface coverage of reaction is a first-order reaction.

TABLE 1
Simulation of Langmuir First-Order Reaction for Adsorption onto Glass (20°C)

	pH 2.5 ± 0.1			pH 11.5 ± 0.1		
C_i[a] (μg/L)	k (μg/h L)	K (μg/L)	R_2	k (μg/h L)	K (μg/L)	R_2
500	17.27	7.08×10^{-4}	0.9989	18.52	1.13×10^{-3}	0.9833
260	43.67	2.85×10^{-4}	0.9888	18.55	1.38×10^{-3}	0.9948
120	17.36	1.06×10^{-3}	0.9958	161.29	7.17×10^{-5}	0.9883

[a] Initial concentration: 508.5, 265.5, and 118.5 μg/L (pH 2.5 ± 0.1), and 487.1, 260.4, and 117.5 μg/L (pH 11.5 ± 0.1), respectively.

Consequently, the following equation is called a Langmuir first-order reaction:

$$r = -\frac{d[C]}{dt} = k\theta = \frac{kK[C]}{1 + K[C]}, \qquad [11]$$

where k is an adsorption rate constant. The values of k (about 18 μg/h L), K (on the order of 10^{-3} μg/L), and R^2 (>0.985) are summarized in Table 1. Results showed that k and K were constants under experimental conditions. That is, k and K simulated from the Langmuir first-order reaction were independent of initial 4-chlorobiphenyl concentration and pH.

When the initial concentration of 4-chlorobiphenyl was below 25 μg/L, we found that the sample concentration became undetectable after 24 h. Thus, actual water phase concentrations could have been underestimated in previously published data and may be inaccurate. Mass balance of the glass system was accomplished to demonstrate that adsorption onto glass was the only factor which decreased the concentration of 4-chlorobiphenyl (Table 2). It is acceptable that the total recoveries of the glass system are 82.2%–93.2% and that desorption was accomplished with 12 N NaOH.

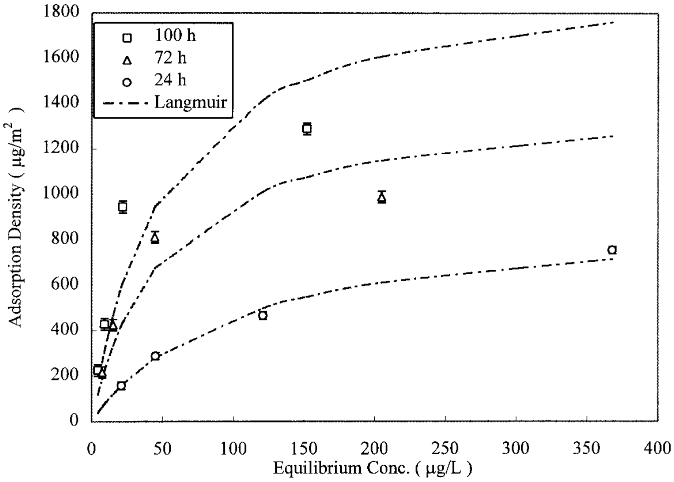


FIG. 6. Variation of adsorption density (Γ) on glass with different 4-chlorobiphenyl equilibrium concentrations at pH 11.5 ± 0.1 (methanol = 1%, 20°C).

Adsorption onto Hydrous Titanium Dioxide

The experimental results showed that increasing the concentration of TiO_2 really leads to a lower concentration of 4-chlorobiphenyl (aqueous) but decreases adsorption density (Fig. 7). Since the specific area of TiO_2 (P25) is about 43 m^2/g (BET), the adsorption density of each unit of TiO_2 area decreases as a consequence of equilibrium.

$$C + T \underset{k_d}{\overset{k_a}{\rightleftharpoons}} C\text{–}T, \qquad [12]$$

where C is 4-chlorobiphenyl in water, T represents TiO_2 surface sites, C–T is 4-chlorobiphenyl adsorbed onto TiO_2, k_a and k_d are adsorption and desorption constants, and $k_a/k_d = K$ represents the equilibrium constant. The simulation value of K is about 10^{-5} (μg/L), as shown in Table 3, and the specific area of TiO_2 is 43 m^2/g (BET). When $[T]$ equals 10^5, 5×10^5, and 10^4 (μg/L), the calculated results are 250, 83.33, and 45.45 (μg/L) for aqueous solutions at equilibrium and 26.5, 8.8, and 4.8 (mmol/m^2) onto TiO_2, respectively. Assuming that the TiO_2 intersurface contains a large number of ineffective holes, the TiO_2 surface effective area decreases through monolayer adsorption so the adsorption density of each unit of TiO_2 area decreases as a consequence of equilibrium.

TABLE 2
Mass Balance of the Adsorption System[a]

pH	C_i (μg/L)	C (μg/L)	C_g (μg/L)	C_{tal} (μg/L)	C_{tal}/C_i (%)
2.5 ± 0.1	60.6	15.1	41.5	56.6	93.2
	118.5	31.0	74.6	105.6	89.1
	265.5	111.0	122.7	233.7	88
	508.5	250.2	186.5	436.7	85.8
11.5 ± 0.1	58.2	7.5	45	52.5	90.2
	117.5	15.2	88.5	103.7	87.9
	260.4	44.5	169.2	213.7	82.2
	487.1	205	205.8	410.8	84.4

[a] C_i = initial concentration, C = solution concentration, C_g = desorption concentration from glass, and $C_{tal} = C + C_g$, equilibrium time = 72 h.

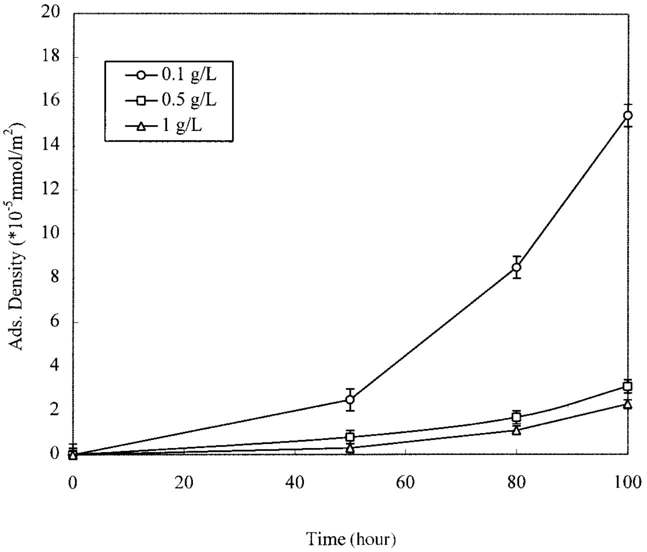


FIG. 7. Variation of adsorption density (Γ) on TiO_2 with time (4-chlorobiphenyl initial concentration = 500 μg/L, methanol = 1%, pH 3 ± 0.1, 72 h, 20°C).

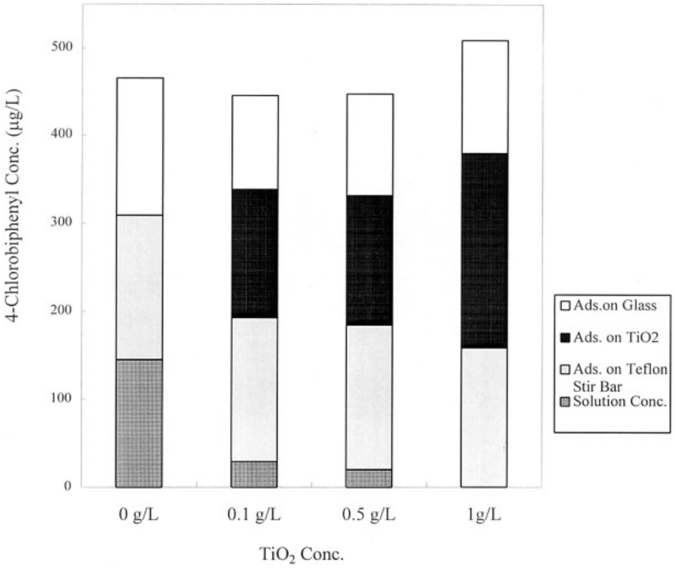


FIG. 8. Mass balance of the system (4-chlorobiphenyl initial concentration = 500 μg/L, methanol = 1%, pH 3 ± 0.1, Teflon stir bar length = 20 mm, stirring rate = 600 rpm, 100 h, 20°C).

In addition, (data not shown in this paper) the adsorption density, which was maintained at about 600 μg/m^2, onto glass was independent of TiO_2 concentration for 72 h. The mass balance results in Fig. 8 leads to the conclusion again that adsorption is an important factor for the decrease of 4-chlorobiphenyl in water. In the results, the adsorption of 4-chlorobiphenyl onto Teflon was assessed, showing that more 4-chlorobiphenyl adsorbed onto Teflon than onto glass. Thus, using Teflon containers or stir bars in the sampling process should be avoided.

Nonaqueous organic liquids can increase 4-chlorobiphenyl solubility but retard adsorption onto hydrous TiO_2. The presence of an organic liquid or cosolvent can reduce the adsorption of hydrophobic organics like 4-chlorobiphenyl onto solids by enhancing solute–solvent interactions. Fig. 9 indicates that the results of adsorption in different solvents demonstrated that the presence of cosolvents such as methanol and acetone affected adsorption through a cosolvent effect. Methanol is a protic solvent with hydrogen bonding character, but acetone, which is less polar than methanol, is a dipolar aprotic solvent that cannot act as a hydrogen bond donor (32). Results display a decreased amount of 4-chlorobiphenyl on hydrous TiO_2 when methanol and acetone existed in the solution. Acetone (1%) appeared to inhibit adsorption to an extent sightly greater than methanol (1%), as shown in Fig. 9.

The adsorption density on hydrous TiO_2 increased with increasing pH (Fig. 10). The phenomenon was similar to that observed in adsorption onto glass. With respect to adsorption onto solids, free energy (ΔG_{ads}) is a summation of various adsorption energy components and can be expressed as the sum of individual contributions (33):

$$\Delta G_{\mathrm{ads}} = \Delta G_{\mathrm{e}} + \Delta G_{\mathrm{i}} + \Delta G_{\mathrm{c}} + \Delta G_{\mathrm{id}} + \Delta G_{\mathrm{hb}} + \Delta G_{\mathrm{hp}}, \qquad [13]$$

TABLE 3
Simulation of Langmuir First-Order Reaction for Adsorption onto TiO_2 (20°C)

pH	k (μg/h L)	K (μg/L)	R^2
3 ± 0.1	1.406	1.85×10^{-5}	0.9712
7 ± 0.1	0.497	6.94×10^{-5}	0.9743
11 ± 0.1	3.258	1.59×10^{-5}	0.9861

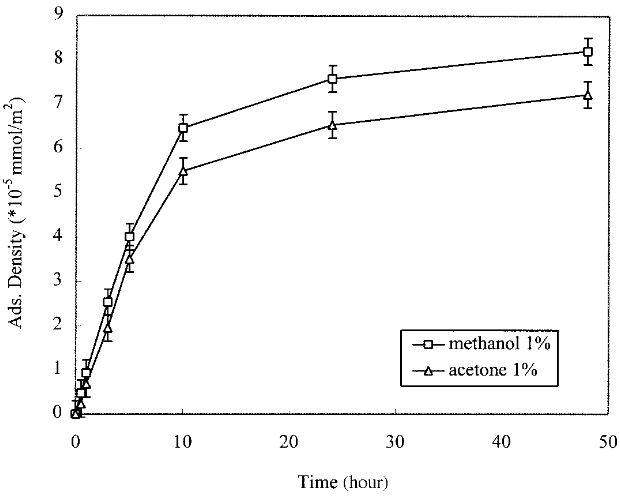


FIG. 9. Variation of adsorption density (Γ) on TiO_2 with time using different solvents (4-chlorobiphenyl initial concentration = 500 μg/L, pH 3 ± 0.1, 20°C).

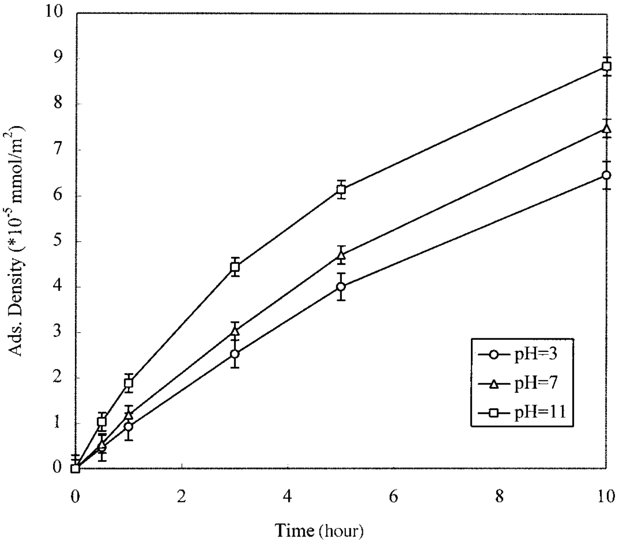


FIG. 10. Variation of adsorption density (Γ) on TiO$_2$ with time at different pH (4-chlorobiphenyl initial concentration = 500 μg/L, methanol = 1%, 20°C).

where the subscripts e, i, c, id, hb, and hp represent the energy of electrostatic interactions, ion exchange, coordination by surface metal cations, ion–dipole interactions, hydrogen bonding, and hydrophobic interactions, respectively.

Since 4-chlorobiphenyl is a deionizable compound, ΔG_e and ΔG_i are negligible. Coordination by surface metal cations is not important because the organic ligand is not as good an electron donor as water (31). Ion–dipole interactions with nonionic adsorbate are also expected to be negligible in the solution. Thus, the adsorption energy of 4-chlorobiphenyl onto hydrous TiO$_2$ may have been caused primarily by hydrophobic interactions, hydrogen bonding, or both.

The addition of organic solvent to water enhances interactions between 4-chlorobiphenyl and the solvent, resulting in a decrease in adsorption density. A similar effect was also observed in the adsorption of substituted phenols onto hydrous CdS (34), and organic acids on soil (35), which may be attributed to the difference in proton affinity and ion solvation of these solvents. Thus, less polar solutions, due to the hydrophobic driving force, may be favorable for adsorption. Adsorption behavior in solvents may be predicted by the partitioning of hydrophobic compounds onto solids.

Using the Langmuir first-order reaction model, the results of simulation from Fig. 10 are summarized in Table 3. The reaction rate constant k was 3.3 μg/h L at pH 11 ± 0.1, and the adsorption equilibrium constant K was nearly 10^{-5} μg/L at two pH-controlled values. Both constants were lower than those calculated for adsorption onto glass.

UV/TiO$_2$ Process for Treating 4-Chlorobiphenyl

Using the 4-chlorobiphenyl characteristic of being easily adsorbed onto solids, treatment of 4-chlorobiphenyl with UV-illuminated TiO$_2$, called an AOP, was studied. First, 4-chlorobiphenyl was adsorbed onto hydrous TiO$_2$, and then TiO$_2$ was illuminated with UV light of wavelength <365 nm. Degradation of 4-chlorobiphenyl began when the adsorption of bandgap radiation excited an electron into the conduction band. Powerful oxidizing agents like ·OH (36) were produced and reacted with 4-chlorobiphenyl adsorbed onto hydrous TiO$_2$ surfaces.

The background tests are summarized in Table 4. Adsorption onto glass and TiO$_2$ surfaces and direct degradation by UV light were, respectively, about 7%, 7%, and 3% after 120 min. With respect to the background test results, the degradation of 4-chlorobiphenyl was promoted by using photocatalytic degradation over illuminated TiO$_2$. Figure 11 gives the results of comparision between the UV/TiO$_2$ process and adsorption. In the UV/TiO$_2$ process, 77% of 4-chlorobiphenyl was degraded by photocatalytic treatment within 120 min, and degradation was shown to be greater than adsorption. Data from the UV/TiO$_2$ process were also calculated by the Langmuir first-order reaction, resulting in a degradation rate constant k of 4.8 μg/s L and an adsorption equilibrium constant K on the order of 10^{-5} μg/L. The ratio between the TiO$_2$ adsorption rate constant (from Table 3) and the UV/TiO$_2$ degradation rate constant, both simulated by the Langmuir first-order reaction, was $1/10^5$. Degradation of 4-chlorobiphenyl was much greater than its adsorption, but its adsorption behavior allowed degradation to be achieved within a shorter period of time.

CONCLUSIONS

This paper explored the adsorption of 4-chlorobiphenyl onto glass in order to quantify its loss due to adsorption during experimental processes. Adsorption onto glass caused

TABLE 4
UV/TiO$_2$ Background Tests

	Glass[a]		TiO$_2$[b]		Direct UV light[c]	
min	pH 3 C/C_i[d]	pH 11 C/C_i	pH 3 C/C_i	pH 11 C/C_i	pH 3 C/C_i	pH 11 C/C_i
0	1	1	1	1	1	1
10	0.98	0.93	0.95	0.92	1	0.98
30	0.95	0.92	0.90	0.89	1	0.97
60	0.94	0.92	0.92	0.90	0.98	0.98
120	0.94	0.93	0.93	0.92	0.97	0.96

[a] 4-Chlorobiphenyl adsorbed onto glass

[b] 4-Chlorobiphenyl adsorbed onto TiO$_2$. The values given for the TiO$_2$ adsorption experiments were calculated by subtracting the amount of 4-chlorobiphenyl adsorbed onto glass from the total amount absorbed experiments.

[c] Treatment of 4-chlorobiphenyl with only UV illumination. The values given for the direct UV light experiments were calculated using the same method as *b*.

[d] C and C_i are the same parameters as in Table 4, and C/C_i displays the ratio of the remainders.

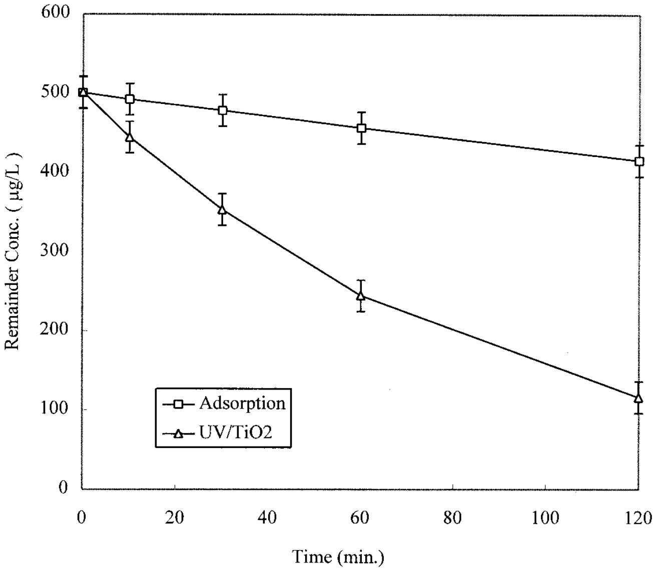


FIG. 11. Comparison of the UV/TiO_2 process and adsorption (TiO_2 + glass) (4-chlorobiphenyl initial concentration = 500 μg/L, methanol = 1%, pH 3 ± 0.1, 20°C, UV light intensity = 10 mW/cm^2).

an adverse effect on sample accuracy. Mass balance of the glass system demonstrated that adsorption onto glass was the only factor that decreased the concentration of 4-chlorobiphenyl. Thus, the actual water phase concentrations could have been underestimated in previously published data. In summary, it is suggested that aqueous 4-chlorobiphenyl be stored below 4°C at pH lower than 2.5 and be analyzed on GC within 24 h. With respect to 4-chlorobiphenyl adsorbed onto glass, the adsorption rate constant k was 18 μg/h L, the adsorption equilibrium constant K was on the order of 10^{-3} μg/L using the Langmuir first-order reaction model, and the monolayer saturated density, using the BET model, was 1200 μg/m^2. The Langmuir and BET models are good for modeling adsorption onto glass. In addition, the results of adsorption onto TiO_2 surfaces infer that hydrogen bonding and/or hydrophobic interactions are the main forces. The UV/TiO_2 process decreased the 4-chlorobiphenyl concentration (initial concentration = 500 μg/L) by 77% after 120 min. The ratio between the TiO_2 adsorption rate constant and the UV/TiO_2 process degradation rate constant was $1/10^5$. In summary, the degradation of 4-chlorobiphenyl is much greater than its adsorption, but its adsorption behavior allowed degradation to be achieved within a shorter period of time.

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