

# Photocatalyzed degradations on a TiO<sub>2</sub>-coated quartz crystal microbalance. I. Adsorption/desorption processes in the degradation of phenol and catechol

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The photocatalyzed degradation of phenol and catechol was re-examined to assess their adsorption/desorption behavior on a TiO<sub>2</sub>-coated (sol-gel technique) quartz crystal microbalance (QCM) sensor. The QCM senses changes in mass occurring during the photodegradation, which of necessity implicates photoinduced adsorption and desorption of molecules of the original substrate and its degradation intermediates. The temporal loss of spectral features of the benzene ring with irradiation time was monitored by fluorescence spectroscopy. The increase in the quantity of TiO<sub>2</sub> deposited on the QCM sensor scaled linearly with the number of dip-coatings (five). Water adsorption on QCM in the dark was relatively independent of pH. Adsorption of the organic substrates was pH dependent since the surface charge of TiO<sub>2</sub> varies with pH. Thus, both phenol and catechol tended to be adsorbed more at neutral pH 7 than at the other pHs examined and within the concentration range of substrate 0 to 0.012 mM. For phenol, adsorption reached near saturation around 0.007 mM in the order pH 7 > pH 9 > pH 5. Catechol showed a similar behavior except at the higher concentrations (around 0.010 mM). Mass changes occurring during the photodegradation of phenol and catechol on the TiO<sub>2</sub>-coated QCM sensor surface are reported.

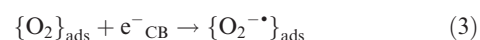
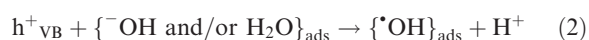
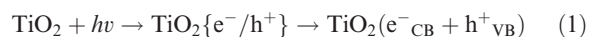
## Introduction

The extensive literature on heterogeneous photocatalysis to degrade a large variety of organic compounds in decontamination and detoxification treatment efforts of an aquatic environment has shown that photodegradation dynamics are governed by various experimental factors: (a) the wavelengths of illumination (Hg light sources, Xe light sources, solar irradiance, simulated sunlight – among others) (b) the magnitude of the light irradiance (*i.e.*, number of photons emitted by the source) (c) the particle size and thus the surface area of the photocatalyst particles; (d) the crystallinity and *quality* of the photocatalyst used (for TiO<sub>2</sub>, anatase *versus* rutile) (e) co-catalysts present with TiO<sub>2</sub> (as dopants or otherwise); (f) the concentration and nature of the organic substrate(s); (g) the concentration of dissolved molecular oxygen in the heterogeneous system; (h) the extent of adsorption of the substrates on the TiO<sub>2</sub> photocatalyst surface (a function of the zeta potential  $\zeta$ ); (i) the acidity (pH) of the dispersion; (j) the presence of anions and/or cations; and (k) the presence of additional oxidizing agents (*e.g.*, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>). Despite these factors, studies on the adsorption and desorption of substrates on the photocatalyst surface have been relatively few; however, see ref. 1.

The present article addresses the issues of adsorption and desorption of substrates and intermediates produced during the photodegradation of phenol and catechol using a TiO<sub>2</sub>-coated quartz crystal microbalance (QCM) sensor to measure mass changes occurring with irradiation time. This sensor is a well-known mass-measuring device since the resonance frequency is closely dependent on the deposition of a given

mass of solvent and substrate on the platinum electrode of the QCM. It is a nanogram-sensitive weighing device, which consists of a piezoelectric quartz crystal in the form of a sandwiched disk between a pair of vapor-deposited electrodes. When these electrodes are connected to an electronic oscillator, the crystal oscillates in a very stable manner at its resonant frequency as a result of the piezoelectric effect. If a thin and rigid film of the photocatalyst is deposited evenly over one or both electrode surfaces in such a way that it is not lost from the surface during oscillation, then the resonant frequency decreases proportionally with the mass of the film. Both adsorption and desorption events occurring on the TiO<sub>2</sub> film surface may be rate-determining factors in the overall degradation of the substrates and intermediates.<sup>2,3</sup>

Valence band (VB) holes are strongly oxidizing and the conduction band (CB) electrons are strongly reducing whenever they are photogenerated on a semiconductor particle surface such as titanium dioxide (reaction 1). In aqueous environmental applications, the most important adsorbates are water, molecular oxygen and the pollutant substrates.



Although the VB holes can react directly with the substrates, their initial reaction with water molecules are likely more significant because the concentration of H<sub>2</sub>O molecules far

exceeds the concentration of polluting substrates. Accordingly, oxidation of the surface-bound hydroxyl ions and water by the VB holes generate the highly oxidizing  $\cdot\text{OH}$  radicals (reaction 2), which can rapidly attack surface-adsorbed organic substrates indiscriminately and preferentially. These  $\cdot\text{OH}$  radicals are the most important oxidizing species formed by  $\text{TiO}_2$  photocatalysis. Reduction of adsorbed molecular oxygen by the CB electrons produces superoxide radical anions  $\text{O}_2^{\cdot-}$  (reaction 3), which to some extent suppress electron/hole recombination. In acidic media ( $\text{pH} < 4$ ), these anions produce the less oxidizing  $\cdot\text{OOH}$  radicals (reaction 4) that can also participate in the overall degradation of substrates.

Whether the above-mentioned strongly oxidizing species and substrates are located on the  $\text{TiO}_2$  surface (Langmuir–Hinshelwood pathway) or close to the surface and/or in the bulk solution will presumably affect the dynamics of the photooxidation. We revisit the photooxidative degradation of phenol and catechol focusing on these assumptions and on the adsorption/desorption events on the  $\text{TiO}_2$ -coated QCM sensor. Previous studies<sup>4</sup> have shown that catechol is strongly chemisorbed in the dark on the  $\text{TiO}_2$  surface forming surface catecholate complexes as evidenced spectroscopically and by the resulting yellow color of the dispersion.

## Experimental section

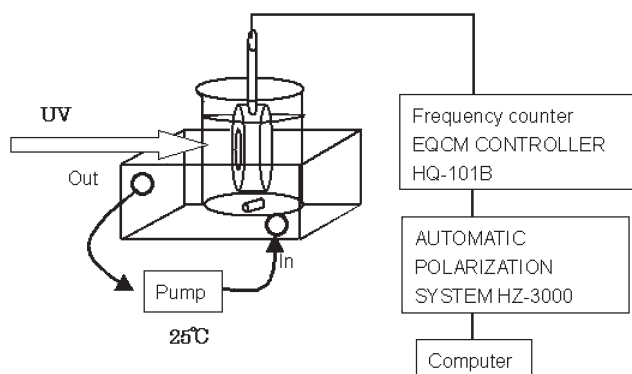
### Reagents and chemicals

Phenol, catechol, and titanium tetraisopropoxide,  $\{\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4\}$ , were used as received from the Wako Chemical Co. Ltd. Highly deionized water was used throughout. Coating  $\text{TiO}_2$  on the platinum QCM sensor was carried out using a sol–gel technique described below.

### The QCM sensor and its properties

The nanogram-sensitive  $\text{TiO}_2$ -coated QCM sensor device consisted of a HQ-101B QCM controller, a HZ-3000 automatic polarization system, and a HQ-304A mass sensor having a 6 MHz AT-cut piezoelectric quartz plate made by Hokuto Denko Co. Ltd. (Tokyo, Japan). The QCM sensor was a platinum electrode deposited on both sides of the circular quartz plate (diameter 13 mm). The frequency of the QCM balance was monitored continuously with a frequency counter. In summary, the QCM system was comprised of a thin quartz crystal wafer, an oscillating circuit, a frequency counter, and a personal computer (Fujitsu, FM-V6866 SL7) as schematically illustrated in Fig. 1.

The quartz crystal was sandwiched between two metal electrodes used to establish an electric field across the crystal.



**Fig. 1** Experimental setup of the quartz crystal microbalance (QCM) system.

Where an alternating electric field and appropriate electronics are used, the crystal can be made to oscillate at its resonant frequency. The measured frequency depends on the combined thickness of the quartz wafer, of the metal electrodes, and the material deposited on the surface of the quartz crystal microbalance. In essence, the QCM device relies on the piezoelectric properties of quartz. Mass changes occurring on the QCM surface result in frequency changes according to the well-established Sauerbrey eqn. (5) for thin, uniform, and purely elastic added layers.<sup>5</sup> The frequency of the QCM sensor in an aqueous solution can be correlated to whatever interfacial reaction(s) takes place that involve mass changes. Accordingly, for the AT-cut shear mode QCM balance the measured frequency shift  $\Delta F$  (in Hz) is given by

$$\Delta F = -\frac{2F_0^2}{A\sqrt{\rho_q/\mu_q}}\Delta m \quad (5)$$

From the values provided below, the mass change  $\Delta m$  (in ng) is then given by

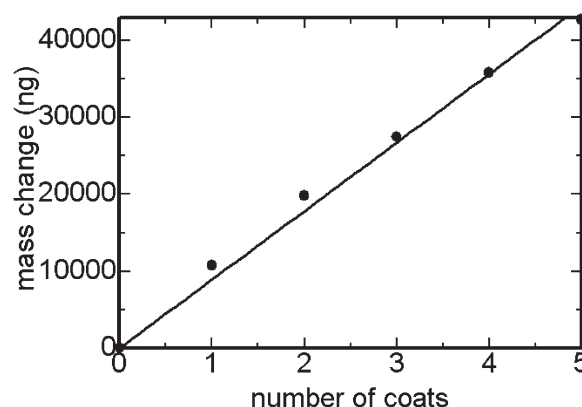
$$\Delta m = -16.28 \Delta F \quad (6)$$

where  $F_0$  is the fundamental frequency of the QCM device (6 MHz),  $A$  is the electrode area ( $1.3273 \text{ cm}^2$ ),  $\rho_q$  is the density of quartz ( $2.648 \text{ g cm}^{-3}$ ), and  $\mu_q$  is the shear modulus of quartz ( $2.947 \times 10^{11} \text{ dynes cm}^{-2}$ ).

### $\text{TiO}_2$ -coating preparations

$\text{TiO}_2$  coating of the QCM sensor was achieved by a method in which titanium(IV) tetraisopropoxide was dissolved in pure ethanol to yield the titania sol on hydrolysis in aqueous nitric acid media. The optimal ratio of the sol–gel reagents was  $\{\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4\} : \text{C}_2\text{H}_5\text{OH} : \text{H}_2\text{O} : \text{HNO}_3 = 1 : 100 : 10 : 0.04$ .<sup>6</sup> The QCM sensor was dip-coated (speed,  $0.01 \text{ mm s}^{-1}$ ) into this sol after prior cleaning in acetone, after which it was allowed to gel on drying at  $60^\circ\text{C}$ . The  $\text{TiO}_2$  nanoparticulate film was subsequently fixed onto the QCM by sintering at  $250^\circ\text{C}$  for 20 min at a rate of 2 degrees per minute, and then cooled to ambient temperature. The procedure was repeated five times and, as illustrated in Fig. 2, the quantity of  $\text{TiO}_2$  sol–gel particles deposited scaled linearly with the number of coatings. The relevant mass changes occurring on the QCM surface were determined by the QCM technique (see Fig. 2).

Adsorption of phenol and catechol on the  $\text{TiO}_2$ -coated QCM sensor was examined in 300 mL volume of ion-exchanged deionized water at  $25^\circ\text{C}$ . The measured temperature was thermostatically controlled (Iuchi, LTB-125) precisely



**Fig. 2** Dependence of the quantity of titanium dioxide sol–gel particles that coated the QCM sensor after each dip-coating.

since the temperature-dependent QCM frequency increases at *ca.* 20 Hz per degree. The crystalline structure of TiO<sub>2</sub> particles coated on the QCM by the sol-gel method was determined with a Rigaku RV 200 X-ray diffractometer (XRD; Cu K $\alpha$  radiation; 40 kV and 30 mA;  $2\theta$  from 20 to 60 degrees; scan speed 4.0 degrees per minute; scan step 0.02 degree). The surface morphology of the TiO<sub>2</sub> film on the QCM sensor was examined by scanning electron microscopy (SEM) using a Hitachi 2-4700 II SEM microscope (see Fig. 3).

The TiO<sub>2</sub>-coated QCM sensor was immersed in the ion-exchanged water (300 mL) and the aqueous solution of substrates was injected under stirring. The pHs of 5, 7, and 9 were adjusted either with H<sub>2</sub>SO<sub>4</sub> or with NaOH solutions.

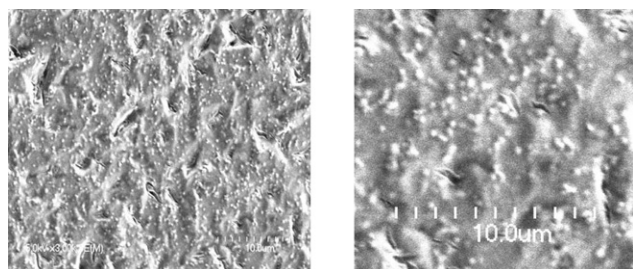
### Analytical procedures

The photocatalytic activity of TiO<sub>2</sub> deposited on a glass plate (area, 1.5 cm  $\times$  2 cm) was evaluated for each sample solution (0.01 mM; 30 mL) in a 50 mL Pyrex vessel. Irradiation was accomplished using a Toshiba 45 Watt SHLS-100 2A mercury lamp positioned in front of the TiO<sub>2</sub>-coated plate. The solutions were magnetically stirred continuously during irradiation. Loss of the phenyl moiety in phenol and catechol was assayed spectrofluorimetrically with a Jasco FP-770 spectrofluorimeter. The relevant excitation and emission wavelengths were, respectively, 270 nm and 589 nm for phenol, and 276 nm and 613 nm for catechol.

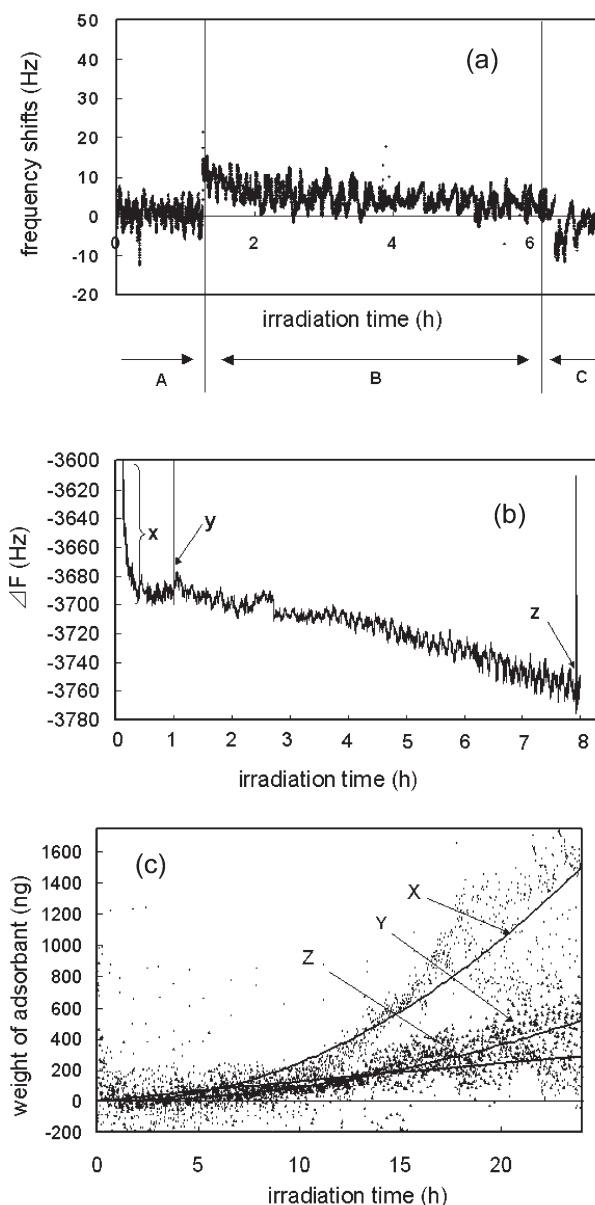
### Results and discussion

The nature of the surface of the TiO<sub>2</sub>-coated QCM sensor from sol-gel dip-coating three times is shown in the SEM micrograph of Fig. 3. The islands-like deposition of TiO<sub>2</sub> is appropriate to assess the sensitivity of the QCM for adsorption/desorption events. If the photocatalyst had covered the entire surface of the QCM sensor, no changes in the frequency would have been possible with the obvious consequence of not being able to observe adsorption/desorption behavior during the photo-catalyzed degradation of the organic substrates because a rigidly covered surface attenuates the regular oscillations of the sensor. The average size of the TiO<sub>2</sub> particles deposited was about 0.2 to 0.5  $\mu$ m. After calcinating at 350  $^{\circ}$ C, this TiO<sub>2</sub>-coated QCM sensor was used for all further experiments involving the photodegradation of phenol and catechol.

The crystalline nature of the TiO<sub>2</sub> film, even after calcinations at 250  $^{\circ}$ C, was identified to be anatase by XRD methods. It should be noted that dip-coating the glass plate or the QCM sensor only three times revealed relatively small XRD peaks at the  $2\theta$  expected for anatase. However, increasing the number of coatings to five showed significantly greater anatase peaks. As well, the peaks for Pt and quartz (Si) for the QCM sensor were also clearly visible. The temporal fluctuation of the frequency in a TiO<sub>2</sub>-free QCM sensor under UV illumination in aqueous media is shown in Fig. 4a. The device stabilized



**Fig. 3** Scanning electron micrographs of the TiO<sub>2</sub> particles deposited on the surface of the QCM sensor after three dip-coatings in the TiO<sub>2</sub> sol-gel.



**Fig. 4** (a) Frequency shifts occurring during the adsorption/desorption of water molecules on a TiO<sub>2</sub>-free QCM. (A is under dark conditions before illumination. B is under light-irradiation conditions by the Hg light source. C is under dark conditions after illumination). (b) Frequency changes occurring on adsorption/desorption of water molecules on a TiO<sub>2</sub>-coated QCM sensor. (Region X designates the adsorption of H<sub>2</sub>O molecules when the sensor was immersed into the aqueous media; Y shows the point when illumination was initiated by the Hg lamp; Z denotes the point when illumination was terminated). (c) pH dependence of the quantity of water adsorbed/desorbed as a function of UV irradiation time. (X is pH = 7, Y is pH = 5, and Z is pH = 9).

( $\Delta F = 0 \pm 5$  Hz) in the dark within *ca.* 20 to 30 min, after which it was UV-light irradiated. The frequency shift rose initially to 10–15 Hz temporarily, subsequent to which it stabilized after *ca.* 3 hours to a  $\Delta F = 3 \pm 5$  Hz. When the Hg lamp was switched off, the frequency returned to the same value as before the irradiation, namely  $\Delta F \sim 0$  Hz. This phenomenon is related to the initial voltage of the Hg light source. All the experimental results of photoirradiation have been normalized to it. A similar experiment was carried out with a TiO<sub>2</sub>-coated QCM sensor. The amount of adsorbed H<sub>2</sub>O molecules was greater than observed for the TiO<sub>2</sub>-free sensor before UV illumination. In other words, H<sub>2</sub>O molecules stepped up to the QCM surface owing to the presence of the TiO<sub>2</sub> adsorbent. Upon turning on the UV illumination, the behavior of

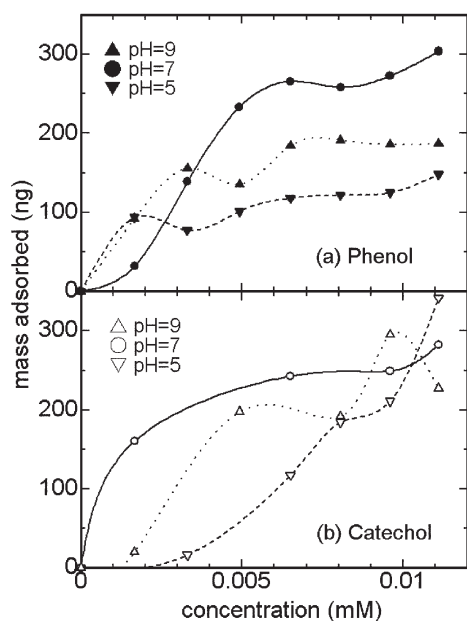
oscillation exhibited the same initial tendency as seen for the  $\text{TiO}_2$ -free sensor. However, in this case the frequency decreased significantly (region X) under UV irradiation relative to the  $\text{TiO}_2$ -free QCM sensor, as witnessed in Fig. 4b. This Figure also shows a significant frequency shift (0 Hz to  $-3690$  Hz) on addition of water in the dark (allowing 20 min to stabilize), after which photoinduced chemisorption of water occurred with irradiation time (point Y). Evidently, adsorption of water on the  $\text{TiO}_2$  film surface was enhanced under irradiation for about 7–8 hours (at point Z, irradiation was stopped).

Frequency measurements at different pHs were also performed for a  $\text{TiO}_2$ -coated QCM sensor under UV illumination. They are reported in Fig. 4c as the quantity of water chemisorbed *versus* illumination time up to 24 hours. In the first 8 hours of irradiation, the quantity of water adsorbed on the QCM followed the order  $\text{pH } 7 > \text{pH } 9 > \text{pH } 5$ , subsequent to which  $\text{H}_2\text{O}$  molecular assemblies or aggregates collected on the  $\text{TiO}_2$  surface in the order  $\text{pH } 7 > \text{pH } 5 > \text{pH } 9$ . Note that the same behavior, as illustrated in Fig. 4c, was exhibited irrespective of the mass of  $\text{TiO}_2$  deposited on the QCM sensor. The pH value with only water present in the QCM device shifted to the acidic side for pHs 7 and 9 after 24 h of irradiation, implying formation of protons generated by the oxidation of  $\text{H}_2\text{O}$  molecules (see reaction 2 and Table 1).

Fig. 5 displays the extent to which phenol and catechol were adsorbed on the  $\text{TiO}_2$ -coated sensor as a function of initial concentrations at pHs 5, 7, and 9. The data were obtained in the dark after the device had stabilized for about 20 min. For phenol, adsorption increased with concentration to reach near saturation at all three pHs at *ca.* 0.007 mM in the order  $\text{pH } 7 > \text{pH } 9 > \text{pH } 5$ . By comparison, catechol adsorption behaved somewhat similarly. All subsequent experiments on the photodegradation of these two substrates were carried out at a concentration of 0.010 mM.

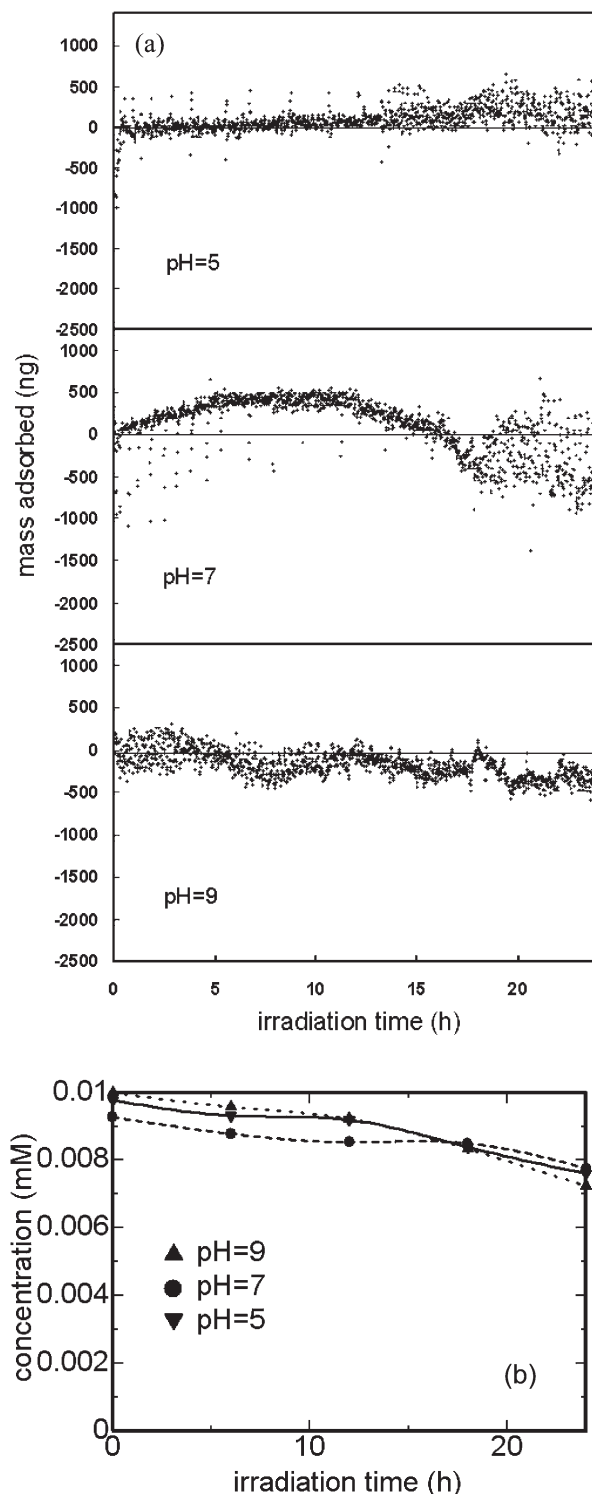
**Table 1** Change of pH in water after UV irradiation

Irradiation time	0 h	24 h
pH = 5	5.00	5.63
pH = 7	6.50	5.72
pH = 9	9.00	7.29



**Fig. 5** Quantity of phenol (a) and catechol (b) initially adsorbed on the  $\text{TiO}_2$ -coated QCM sensor in the dark as a function of initial concentration of substrate at pH = 5, 7, and 9. The frequency in water before addition of the organic substrates ranged from  $-3100$  Hz to  $-3170$  Hz.

The mass changes occurring for phenol on the QCM microbalance with irradiation time for up to 24 hours are illustrated in Fig. 6a, whereas Fig. 6b depicts the extent to which phenol degraded for the same irradiation period at the three pHs examined, namely pH 5, 7, and 9. It is clear that at pH 5 there is no change in mass for *ca.* 10 hours of irradiation, subsequent to which the mass on the QCM sensor increased to about 200 ng, consistent with increased adsorption of phenol (mostly) and some quantity of intermediate species produced from the



**Fig. 6** (a) Mass changes taking place on the  $\text{TiO}_2$ -coated QCM surface during the photodegradation of phenol at pH = 5, 7, and 9. (b) Plots showing the degradation dynamics of phenol with irradiation time at the same three pHs of 5, 7, and 9. The concentrations were obtained from spectrofluorimetric analyses.



photocatalyzed degradative process. Photodegradation was rather slow as evidenced from spectrofluorimetric results (Fig. 6b). Approximately 25% of the phenol degraded after 24 hours of UV illumination. By contrast, at pH 9 there was gradual loss of mass at the sensor reaching *ca.* 450 ng after 24 hours of irradiation. The quantity of phenol that degraded under these conditions after this time period was *ca.* 28%. The behavior at pH 7 was rather intriguing. Initially we observed immediate increased adsorption to *ca.* 500 ng after about 8 hours of irradiation for catechol and/or intermediate species, a process which presumably takes place through a photoinduced adsorption process. Following this, a total mass loss of *ca.* 300 to 400 ng occurred through a photoinduced desorption process on further irradiation to 24 hours. Note that the overall quantity of phenol degraded was only *ca.* 22% after this time.

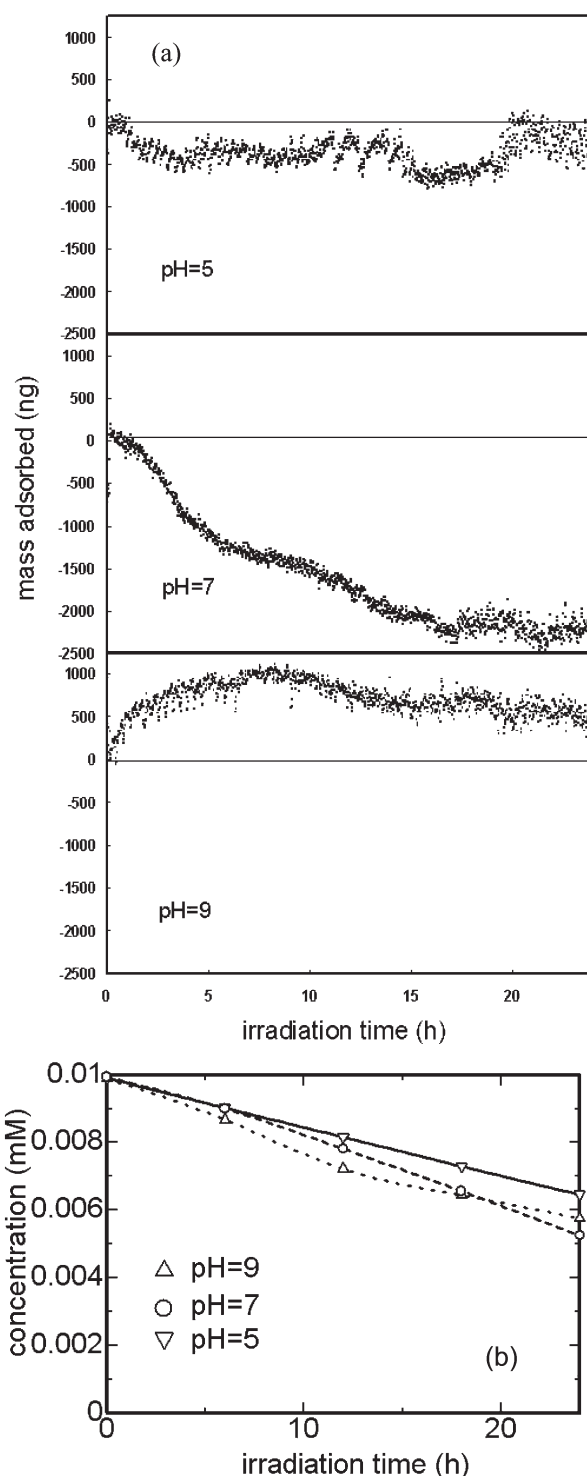
The behavior of catechol was completely and diametrically opposite to that of phenol at all three pHs examined. Past experience in our laboratories indicates that phenol is only slightly adsorbed (less than *ca.* 5%) under dark equilibration conditions, whereas catechol is extensively adsorbed (close to *ca.* 50%) in the dark on the TiO<sub>2</sub> particle surface forming, as indicated earlier, surface complexes with surface titanium(IV) species.<sup>4,7</sup> The variations in the behavior of catechol are depicted in Fig. 7a, whereas Fig. 7b illustrates the extent to which catechol degraded after a 24 hour irradiation period. At pH 5, there is an initial rather rapid loss of mass (*ca.* 500 ng; Fig. 7a) reaching some stationary state after *ca.* 2–3 hours of irradiation maintained for up to *ca.* 20 hours of UV irradiation, after which some re-adsorption occurred (probably intermediate species). To the extent that the amount of catechol degraded after this time was somewhat small (less than *ca.* 5%; after 24 hours it was about 35% Fig. 7b), this loss of mass on the QCM sensor must originate mostly with the photodesorption of catechol initially adsorbed in the dark. By contrast, at pH 9, we observed a rapid increase of mass (*ca.* 1000 ng after 8 hours) on the sensor, which we attribute to further adsorption of catechol through a photoinduced process. Further irradiation for 24 hours caused some mass loss (approximately 500 ng), albeit rather slowly. Fluorimetric results indicate that *ca.* 42% of catechol had photodegraded after this time. Again the behavior observed on the QCM microbalance at pH 7 was somewhat peculiar, and more dramatically so for catechol compared to phenol. In neutral aqueous media, the catechol initially adsorbed on the sensor in the dark equilibration stage tended to photodesorb rapidly, almost exponentially with irradiation time reaching a stationary state around 17 hours of UV illumination (mass loss of *ca.* 2200 ng of catechol and/or intermediates). Fig. 7b shows that nearly half of the initially available catechol had degraded after 24 hours of UV irradiation.

### Concluding remarks

This article has examined the use of a quartz crystal microbalance to monitor the changes in mass taking place on the surface of a TiO<sub>2</sub>-coated device. Although the changes remain mostly silent as to the nature of the species that photoadsorb and photodesorb during the photodegradative process(es), nonetheless significant changes are observed with irradiation of the TiO<sub>2</sub> coating. The most dramatic changes occurred at pH 7 for both phenol and catechol.

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**Fig. 7** (a) Mass changes taking place on the TiO<sub>2</sub>-coated QCM surface during the photodegradation of catechol at pH = 5, 7, and 9. (b) Plots showing the degradation dynamics of catechol with irradiation time at the same three pHs of 5, 7, and 9. The concentrations were obtained from spectrofluorimetric analyses.

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