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An Adsorption Water Purifier with *in Situ* Photocatalytic Regeneration

Simple devices are described for the purification of water combining adsorption of organic impurities with *in situ* photocatalytic oxidation regeneration of the adsorbent/photocatalyst. The adsorbent was silica gel and the photocatalyst was Degussa P25 TiO_2 in one purifier and colloidal TiO_2 on silica gel in the other. The adsorbent/photocatalysts were arranged in the annuli of hollow cylinders, with tubular fluorescent lamps occupying the central cavity. Apart from the central illumination the purifiers were analogous to chromatographic columns. The arrangement permitted more uniform distribution of light to the photocatalyst, better access of water to the photoactivated catalyst, improved contact time between impurities in the water and the photoactivated surface, and continuous regeneration of the adsorbing surface, by destructive photocatalytic oxidation. A single pass at 20 ml min^{-1} under 20-W illumination reduced the phenol concentration from 940 μg $liter^{-1}$, in the influent, to 940 ng $liter^{-1}$ in the effluent stream, i.e., a 99.9% removal of phenol.

INTRODUCTION

Activated charcoal has long been used to remove impurities from liquids and gases, and activated charcoal filters are extensively used as domestic water purifiers. Because of the large surface areas readily obtainable and strong adsorption for many molecules, small units have a sufficient capacity to significantly decrease impurity levels in hundreds of liters of water. All adsorption sites eventually become saturated, however, and when this happens the charcoal must be regenerated or renewed. The latter is the normal alternative for domestic units. There is a need for adsorbent purifiers that can be readily regenerated.

It has been reported that titanium dioxide illuminated with near-ultraviolet light photocatalyzes the oxidation of organic impurities in aqueous aerated solutions to carbon dioxide (*1–4*). Some of these impurities are quite resistant to biological oxidation and have been described as intractable (*5*). The titanium dioxide photocatalyst has adsorbent properties, and since the oxidation reactions occur at the surface of the catalyst the adsorption characteristics are particularly important in the removal of low concentrations of impurities (*6*). This led to the attempt to exploit adsorption properties by combining known adsorbents with photocatalysts.

The attachment of a photocatalyst such as TiO_2 to a transparent adsorbent offers a number of possible benefits:

(i) the photocatalyst can be diluted with the adsorbent substrate, allowing a greater volume to be penetrated by the photoactive light and hence a larger surface of the photoactivated catalyst to be exposed to the solution;

(ii) a substrate that is a strong adsorbent for molecules weakly adsorbed by TiO_2 may be selected, thus increasing their surface contact time;

(iii) the adsorbent may be continuously regenerated *in situ* by photocatalytic oxidation of adsorbed impurities when the light is switched on; and

(iv) photocatalytic oxidation removes organic impurities by converting them to

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TABLE 1

Analytical Wavelengths for Solutes Studied

Compound	λ_{ex} (nm)	λ_{em} (nm)
Salicylic acid	294	412
Phenol	267	300
2-Chlorophenol	264	298
4-Chlorophenol	278	313
2-Naphthol	272	356
Fluorescein	486	570
Catechol	274	316

harmless inorganic products. It is thus a destructive purification process in contrast to simple adsorption processes in which possibly harmful impurities are transferred from the liquid to the solid phase thereby becoming a solid waste disposal problem.

To try to apply these concepts, simple water purifiers were built using silica gel as the adsorbent and titanium dioxide as the photocatalyst. A description of these devices and the results obtained follow.

EXPERIMENTAL

All chemicals were of laboratory reagent grade, or better, and obtained from reputable suppliers.

Degussa P25 titanium dioxide, which has a BET surface area of 50 ± 15 m^2 g^{-1} and which is predominantly anatase, was attached to Merck silica gel (35–70 mesh ASTM) by rotary evaporation of an aqueous slurry under vacuum at 90°C. The TiO_2 loading was 0.15 g/60 g silica gel. The TiO_2-coated silica gel was poured into the annulus between a Philips TLK 40 W/05 tubular low-pressure mercury vapour fluorescent lamp, 57 cm long by 38 mm o.d., and a borosilicate glass jacket, 42.5 mm i.d. The ends of the jacket were sealed with silicone rubber sealant and water flowed through the annulus by means of inlet and outlet ports at each end. The ends were packed with glass wool to retain the photocatalyst. This was designated reactor 1.

A solution of colloidal TiO_2 (1.26 g in 750 ml 0.03 *M* HCl) was prepared from titanium tetraisopropoxide by a method described elsewhere (*7*) and left in contact with 70 g Merck silica gel for several days. The slurry was rotary evaporated to dryness under vacuum at 90°C and then baked in a vacuum oven at 100°C for several hours. The dry powder was poured into the annulus between a 20-W NEC T10 blacklight fluorescent tube (32.5 mm o.d. by 59 cm long) and a surrounding borosilicate glass tube, 38 mm i.d. This was designated reactor 2. The end sealing was the same as that for reactor 1.

Different loadings of Degussa P25 TiO_2 on silica gel were also prepared by rotary vacuum evaporation at 90°C and used (separately) instead of the photocatalyst of reactor 2.

Solutions were prepared using water from a Millipore Waters Milli Q system. Water was pumped through the photoreactor at controlled flow rates by a peristaltic pump. The concentration of organic solutes was measured with a Perkin–Elmer LS-5 luminescence spectrometer, calibrated with solutions of known concentrations of the compounds.

The analytical wavelengths for the various compounds are given in Table 1.

The 40-W lamp used in reactor 1 had a rated useful life of 2000 h. According to the manufacturer it emitted radiation between 300 and 460 nm with a maximum at 365 nm. The 20-W lamp used in reactor 2 had a rated useful life of 7500 h. It had a much narrower band emission than the 40-W lamp, with little output in the visible and maximum emission at 350 nm. According to the manufacturer, the radiative output was 4.0 W.

RESULTS AND DISCUSSION

Salicylic acid moved rapidly through the column of reactor 1 and after approximately 8 min the concentration in the effluent was the same as that in the influent. This column therefore had a limited adsorption capacity for salicylic acid. How-

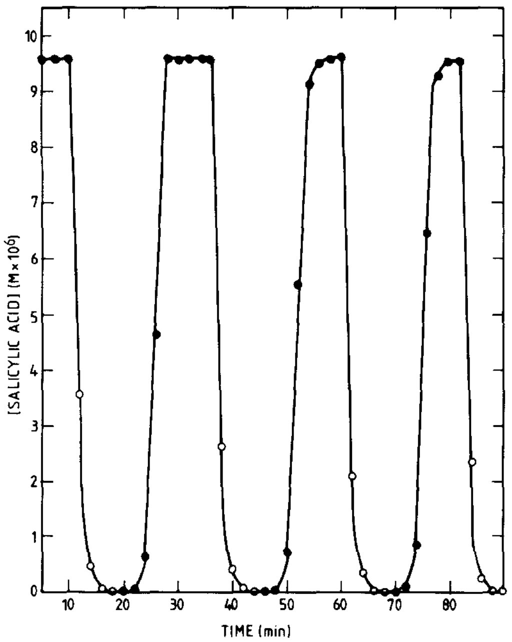

FIG. 1. Effect of on–off illumination on salicylic acid (10 μM) destruction in reactor 1. Adsorbent/photocatalyst 0.15 g P25 TiO_2/60 g silica gel. (●) Light off. (○) Light on. Flow rate 10 ml min^{-1}.

ever, when the light was switched on, as indicated by the open circles in Fig. 1, there was a dramatic decrease in salicylic acid concentration in the effluent, reflecting rapid photocatalytic oxidation. The behaviour was easily reproduced by switching the light off (solid circles) and on again.

The luminescence spectrometer easily detected a 10 nM concentration of salicylic acid which approximated the concentration in the effluent stream after 8 min of illumination. The decrease in salicylic acid concentration was therefore approximately 1000-fold for an influent concentration of 1380 μg $liter^{-1}$.

When the concentration of a solute is increased in the influent stream the rate of solute removal is increased, provided the concentration-dependent region of the Langmuir adsorption isotherm is involved (*8*). However, the photocatalytic oxidation reactions may not occur fast enough to decrease the solute concentration to very low levels; this is shown by the results for the salicylic acid influent concentration of 50 μM in Fig. 2. On the other hand, doubling the phenol concentration in the influent stream from 8.5 to 17 μM made no significant difference to the concentration of phenol in the effluent stream.

The adsorption capacity of the column depends on the nature of the solute being adsorbed. The results in Fig. 3 show that fluorescein is poorly adsorbed, traversing the column in 4 min, whereas 2-chlorophenol and 2-naphthol require 12 to 20 min for the effluent concentration to approach the influent concentration. Catechol is strongly adsorbed requiring approximately 30 min. The failure of 2-naphthol and catechol to achieve clear plateaux is probably caused by the oxidized impurities in these solutions. Since the flow rates were the same it is obvious that much greater amounts of the

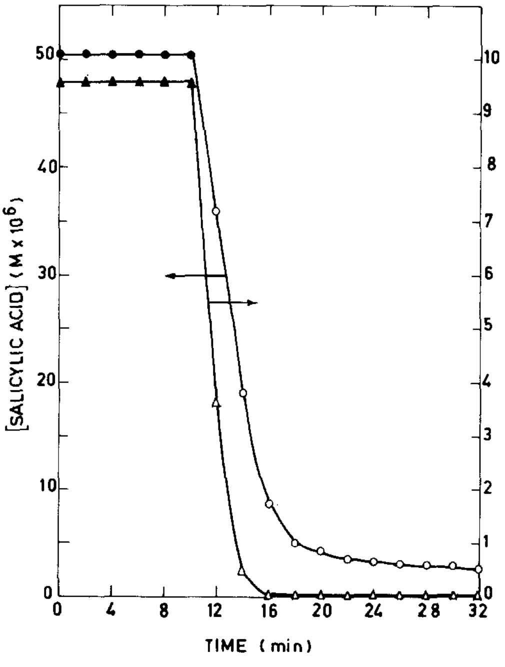

FIG. 2. Effect of salicylic acid concentration on destruction in reactor 1. Adsorbent/photocatalyst 0.15 g P25 TiO_2/60 g silica gel. Flow rate 10 ml min^{-1}; 40-W lamp. (●) Influent concentration 50 μM, no light. (○) Light on. (▲) Influent concentration 10 μM, no light. (△) Light on.

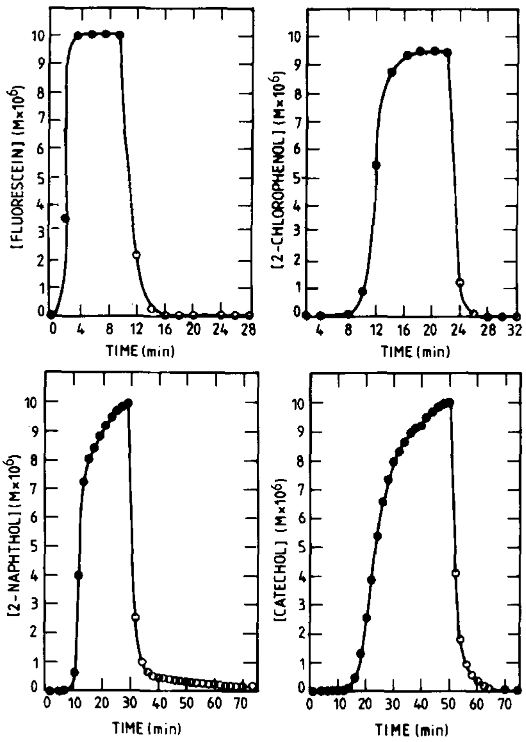

FIG. 3. Adsorption/photocatalytic oxidation profiles for other solutes in reactor 1. Adsorbent/photocatalyst 0.15 g P25 TiO_2/60 g silica gel. Flow rate 10 ml min^{-1}; 40-W lamp. (●) No light. (○) Light on.

slower-appearing solutes are adsorbed on the column. When the light was switched on, a rapid decrease in the solute concentration in the effluent was observed, with low concentrations being rapidly achieved (see Table 2).

Reactor 2 was considerably more efficient than reactor 1. The apparent first-order rate constants (*9*, *10*) for the disappearance of salicylic acid and phenol in continuous recirculation mode were 0.188 ± 0.002 and 0.141 ± 0.002 min^{-1}, respectively, at a flow rate of 120 ml min^{-1} and temperature range of 20 to 25°C. At a flow rate of 240 ml min^{-1}, the apparent first-order rate constant for phenol was 0.299 ± 0.010 min^{-1}. The relationship between flow rate and the Langmuir adsorption isotherm has been discussed elsewhere (*11*).

Reactor 2 also gave a better performance than reactor 1 in single-pass mode. The natural logarithm of the phenol concentration in the effluent is plotted against time in Fig. 4 for varying flow rates with or without illumination. Without illumination and at a flow rate of 20 ml min^{-1}, phenol appears in the effluent after 6 min and reaches the same concentration as that in the influent after 12 min. The light was switched on at 16 min and the concentration in the effluent decreased to 0.1% of the influent concentration at 26 min. At 30 min the flow rate was increased to 30 ml min^{-1} and the concentration increased to 0.3% of the influent concentration at 40 min. At 42 min the flow rate was increased to 40 ml min^{-1} and a further increase in the influent concentration to 2.5% occurred at 50 min. The light was switched off at 58 min and the concentration in the effluent increased to that in the influent at 64 min. When the flow rate

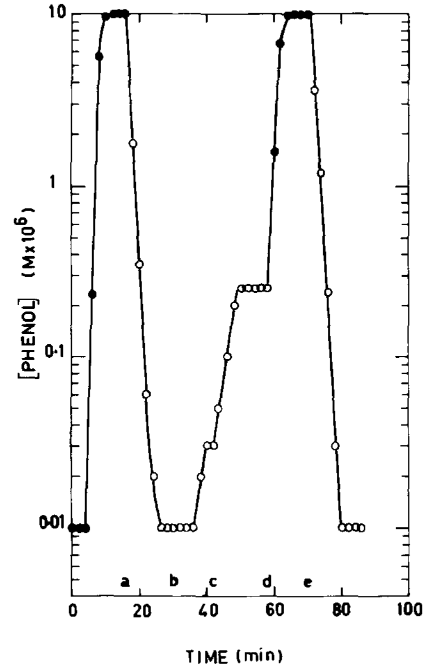

FIG. 4. Destruction of phenol (10 μM) in reactor 2 in single-pass open-system mode. Effect of illumination and flow rate. Adsorbent/photocatalyst 1.25 g colloidal TiO_2/70 g silica gel; 20-W lamp. (●) No light. (○) Light on. (a) 20 ml min^{-1}, light on. (b) 30 ml min^{-1}. (c) 40 ml min^{-1}. (d) Light off, 40 ml min^{-1}. (e) Light on, 20 ml min^{-1}.

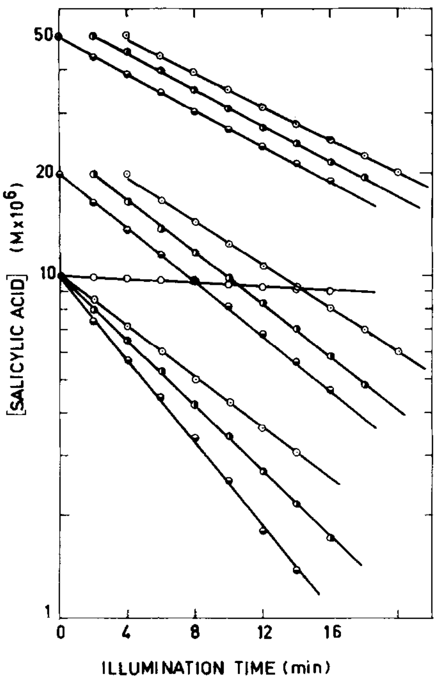

FIG. 5. Effect of TiO_2 loading on the rate of destruction of salicylic acid solutions at differing initial concentrations (500 ml of each at 120 ml min^{-1}); 20-W NEC lamp. (○) Silica gel with no TiO_2. (⊙) 0.050 g P25 TiO_2/80 g silica gel. (◑) 0.100 g P25 TiO_2/80 g silica gel. (◒) 0.150 g P25 TiO_2/80 g silica gel. At the two higher initial concentrations the data points have been shifted progressively to the right to facilitate plotting.

was decreased to 20 ml min^{-1} and the light switched on at 70 min, the concentration in the effluent again decreased to 0.1% of the influent concentration. It can be seen that although the amount of phenol destroyed per unit time increases with flow rate, the ability of the column to maintain very low concentrations in the effluent stream is exceeded. Maximum efficiency is therefore obtained by recycling the solution through the reactor at high flow rates.

The effect of the loading of Degussa P25 TiO_2 on the silica gel support on the rate of destruction of salicylic acid is shown in Fig. 5. The apparent first-order destruction rate constants from the slopes of the lines were plotted against the TiO_2 loading on silica gel in Fig. 6. It is seen that the destruction of salicylic acid at concentrations of initially 50 μM proceeds at approximately the same rate irrespective of the TiO_2 loading. When the initial concentration is 20 μM there is a slight increase in the rate and when it is initially 10 μM a significant increase in the rate occurs. This result shows that for the removal of low concentrations of solutes, higher TiO_2 loadings are beneficial.

The question Why is an increase in the TiO_2 loading not helpful when the initial solute concentration is high? arises. As the TiO_2 loading is increased the amount of solute adsorbed on the surface increases and, other things being equal, this favours an increase in the photocatalytic oxidation rate. But as the TiO_2 loading is increased the penetration of photoactivating light into the silica gel diminishes and the volume of photoactivated TiO_2/silica gel shrinks. There is therefore a balance between increasing adsorption at high TiO_2 loadings favouring increased rate and an opposing effect decreasing the rate due to the shrinkage in the photoactivated volume.

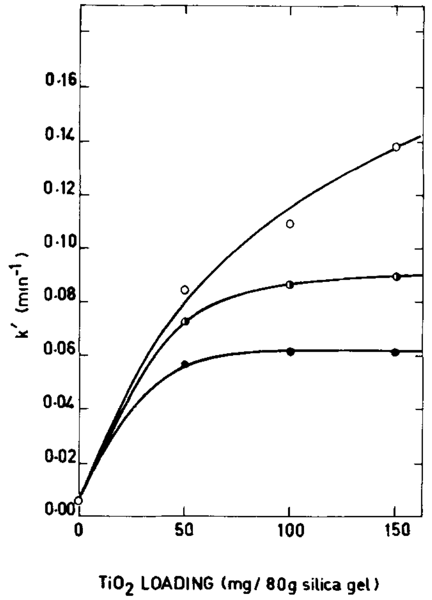

FIG. 6. Apparent first-order rate constant for salicylic acid versus TiO_2 loading on silica gel support. Results from Fig. 5. (○) Initial concentration of salicylic acid 10 μM. (◑) Initial concentration of salicylic acid 20 μM. (●) Initial concentration of salicylic acid 50 μM.

TABLE 2

Removal of Various Organic Compounds from Water Using Reactor 1 in Single-Pass Mode

Solute	Inlet concentration		Outlet concentration	
	(μM)	(μg liter^{-1})	(μM)	(μg liter^{-1})
Phenol	10	940	<0.01	<0.94
Phenol	20	1860	<0.01	<0.94
Salicylic acid	10	1380	<0.01	<1.38
Salicylic acid	50	6900	2.6	359
Fluorescein	10	3320	<0.01	<3.32
2-Chlorophenol	10	1286	0.02	2.6
4-Chlorophenol	10	1286	0.08	10.3
2-Naphthol	10	1442	0.01	1.4
Catechol	10	1100	0.04	4.4

Note. Photocatalyst 0.15 g Degussa P25 TiO_2 on 60 g Merck silica gel; 40-W lamp; 10 ml min^{-1} flow rate.

It is clear that this balance is affected by differing initial concentrations of solute. The rates of photocatalytic oxidation of many solutes over TiO_2 have been shown to depend on concentration in the same fashion as a Langmuir adsorption isotherm (*1, 4, 6, 8, 11, 12*). That is, there is a low-concentration regime in which the rate increases approximately linearly with concentration and a high-concentration regime in which the rate is independent of concentration because all reactive surface sites are occupied by adsorbed solute species. In the case of salicylic acid, the concentration-independent region is being approached at 50 μM (*8*). It therefore seems likely that the effect of initial solute concentration in Fig. 6 reflects a change in the balance of opposing effects with change in the degree of adsorption becoming more significant at low concentrations.

Reactors 1 and 2 have trivial adsorption capacity in relation to activated charcoal; nevertheless, they do demonstrate the concept of removal by adsorption combined with *in situ* regeneration by photocatalytic oxidation. Even these simple prototypes have the potential to remain effective for much longer than nonregenerable adsorption filters. Another reactor using a 20-W tube but with photocatalysts similar to those of reactor 1 has shown consistently better than 99.0% removal of 10 μM salicylic acid at a flow rate of 10 ml min^{-1} over 100 days of operation, with no evidence of decrease in photocatalytic activity (*13*).

Methods for the removal of heavy metals and noble metals from dilute aqueous solutions by photocatalytic deposition onto TiO_2 suspensions have been recently described (*14–16*). There seems little doubt that the combination of the photocatalyst with a suitable adsorbent as the photocatalyst support would make the process more amenable to continuous operation with the possibility of improved photocatalytic efficiency.

CONCLUSIONS

Two reactors based on the concept of combined adsorption and photocatalytic oxidation were made and used to purify water. The adsorbent/photocatalyst was titanium dioxide supported on silica gel. Degussa P25 TiO_2 and colloidal TiO_2 were each used. The best performance was obtained with the latter. Illumination sources were 40- and 20-W near-UV fluorescent tubes. In closed-system continuous-recirculation mode at a flow rate of 120 ml

min^{-1}, 500 ml of 10 μM salicylic acid solution was destroyed, with an apparent first-order rate constant of 0.188 ± 0.002 min^{-1} ($t_{0.5}$ = 3.68 min) using the 20-W lamp and supported colloidal TiO_2 photocatalyst. Under the same conditions, the apparent first-order rate constant for phenol was 0.141 ± 0.002 min^{-1} ($t_{0.5}$ = 4.91 min). In open-system single-pass mode, using the 20-W lamp reactor and supported colloidal TiO_2 photocatalyst, 99.9% destruction of a 940 μg $liter^{-1}$ phenol influent stream was achieved at a flow rate of 20 ml min^{-1}.

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