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Effects of Ag and Pt on photocatalytic degradation of endocrine disrupting chemicals in water

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Abstract

The effects of silver and platinum metals on the photocatalytic degradation of endocrine disrupting chemicals (EDCs) in water over TiO_2 (Degussa P25) were investigated. The natural oestrogens 17β-oestradiol and oestriol were studied as well as the synthetic oestrogen 17α-ethynyloestradiol and the xenoestrogens bisphenol A, resorcinol and 2,4-dichlorophenol. Ag/TiO_2 and Pt/TiO_2 catalysts were prepared by photodeposition. Photocatalytic reactions were carried out in an immobilised TiO_2 system and a TiO_2 slurry system. It was found that the addition of silver or platinum had no effect on the photocatalytic degradation or mineralisation of all the endocrine disrupting chemicals at concentrations found in water. This was attributed to the high concentration of holes and hydroxyl radicals in the system compared to the low amount of organic matters to be degraded. It is therefore not viable to add expensive metals to photocatalytic systems for the removal of low concentrations of organic pollutants in water. At high concentration of EDC, a significant increase in the reaction rate was observed for bisphenol A and resorcinol over Pt/TiO_2. However, there was a decrease in reaction rate for bisphenol A over Ag/TiO_2 and no significant effect with resorcinol, indicating that the reactions are metal specific, substrate specific and may depend on the substrates molecular structure. The catalytic properties as well as the photocatalytic properties of the catalyst should also be considered. It was concluded that there is no universal explanation to explain the effects of metals on photocatalysis of organics in water and that there are many factors which should be considered.

Keywords: Titanium dioxide photocatalysis; Endocrine disrupting chemicals; 17β-Oestradiol; Oestriol; 17α-Ethynyloestradiol; Bisphenol A; 2,4-Dichlorophenol; Resorcinol; Ag/TiO_2; Pt/TiO_2

1. Introduction

The last few decades has seen an increased interest and concern in endocrine disrupting chemicals (EDCs) in the aquatic environment. These are chemicals which have the ability to interfere with natural hormonal mechanisms and have been shown to display binding to oestrogen receptors and, in some instances, mediate responses, which are characteristic of oestrogens [1–4]. The range of substances that have been reported to cause endocrine-disrupting effects is diverse, and continues to expand as the number of studies increases. Compounds of concern include the natural oestrogens, synthetic oestrogens and a wide range of compounds which have the ability to mimic oestrogens (xenoestrogens). This work deals with the natural oestrogens, 17β-oestradiol (17β-E2) and oestriol (E3), the synthetic oestrogen, 17α-ethynyloestradiol (17α-EE2), and the xenoestrogens, bisphenol A (BPA), resorcinol (ReOH) and 2,4-dichlorophenol (2,4-DCP).

Current water treatment methods are ineffective in removing these compounds from our water supplies. Titanium dioxide photocatalysis is a promising alternative technology for the removal of organic pollutants in water, particularly at low concentrations. In titanium dioxide photocatalysis for water purification the pollutants are usually organic compounds and, therefore the overall process can be summarised by the following reaction [5]:

$$\text{Organic pollutant} + O_2 \xrightarrow[h\nu,\ \lambda\leq 400\,\text{nm}]{TiO_2} CO_2 + H_2O \qquad (1)$$

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The main advantage of photocatalysis for the degradation of EDCs in water is that these compounds are found at very low levels (ng/l levels) in the environment [6,7], and the technology is effective to mineralise low concentrations of pollutants to CO_2.

The initial process for heterogeneous photocatalysis of organic and inorganic compounds by semiconductors is the generation of electron–hole pairs in the semiconductor particles [8]. When a photon of light, of sufficient energy ($E \geq E_{bg}$) strikes a TiO_2 particle, the energy of the photon is absorbed and used to promote an electron (e^-) from the valence band to the conduction band. This movement of an electron leaves a hole (h^+) in the valence band. These species (h^+ and e^-) produced by the absorption of light, can either recombine or they migrate to the surface of the TiO_2 particle where they can react with other species at the interface. The holes can directly oxidise organic species adsorbed onto the TiO_2 particle or can give rise to hydroxyl radicals ($OH^\bullet$) by reacting with water or OH^-. These highly reactive hydroxyl radicals then attack organic compounds present at or near the surface [5]. It is necessary that the electrons promoted to the conduction band be removed rapidly from the TiO_2 to prevent recombination with the holes and allow the mechanism to continue. Usually the electrons are passed on to molecular oxygen at the interface [8].

Deposition of metals onto titanium dioxide has been widely used as a technique to improve its photocatalytic activity. Metals such as Cu, Fe, Ag, Cr, Pd, Pt, Rh, Ir, Os and Au have been used to tackle the electron–hole recombination problem [9,10]. This serves the purpose of mediating the electrons away from the TiO_2 surface, hence preventing them from recombining with holes. The work presented investigates the effect of silver and platinum on the photocatalytic degradation of several EDCs. A substantial amount of work has been reported on the effects of silver and platinum on the photocatalytic degradation of organic substrates with contrasting findings. A summary of the literature on the effects of Ag/TiO_2 and Pt/TiO_2 in the photocatalytic oxidation of organics is shown in Tables 1 and 2 along with the experimental conditions.

As can be seen from the two tables, contradictory results have been reported. For example, Dobosz and Sobczynski [22] found 3.6 times enhancement when Ag/TiO_2 was used to mineralise phenol compared to bare TiO_2, while a slight detrimental effect was observed by Vamathevan et al. [27]. However, this may be due to different photocatalysts being used (Aldrich and Degussa P25). Similarly, Pt/TiO_2 was shown to slightly increase the degradation of 4-chlorophenol by Moonsiri et al. [29], in the absence of oxygen but decrease in the presence of oxygen while Hufschmidt et al. [32] have shown that Pt/TiO_2 gave a detrimental effect (21–38%) and Lindner et al. [36] found that Pt/TiO_2 did not give any significant effects.

The positive effect of metal particles on the photoactive surface has been explained by several reasons. The most common postulation is that metal deposits on the photocatalyst surface behave as electron sinks, providing sites for the accumulation of electrons. This improves the separation of electrons and holes as well as the separation of reduction (metal deposits) and oxidation (TiO_2) sites on the surface of the photocatalyst [35,37]. If this postulation is correct, the mineralisation of all organic matters will be enhanced in the

Table 1
Summary of the literature on the effects of silver on the photocatalytic degradation of organics

Compound	Effect	Conditions				Reference
		TiO_2	Ag loading (at.%)	Substrate (mg/l)	pH	
Chloroform	Enhanced 1.25 times	Aldrich	0.75	200	3	[11]
Urea	Enhanced 5.2 times	Aldrich	0.75	100	3	[11]
1,4-Dichlorobenzene	Enhanced by 35%	Degussa P25	1.5			[12]
Methyl orange	Enhanced	Merck			8.75	[13]
Malic acid	Enhanced by 12%	Quartz supported TiO_2	6	50		[14]
Methyl violet dye	Enhanced 2 times	Aldrich	0.75	20	7	[15]
2-Propanol	Enhancement	Rutile	0.5	30000		[16]
E. coli	Enhancement	Aldrich	0.75		7	[17]
Sucrose	Enhanced 4 times	Degussa P25	2	100	3.5	[18]
Oxalic acid	Enhanced 5 times	Degussa P25, 1 g/l	2×10^{-4} M Ag	450	3 ± 0.3	[19]
Methylene blue	Enhanced 2.2 times	Rutile TiO_2				[20,21]
Phenol	Enhanced 3.6 times	Aldrich	0.4	16.7		[22]
Methyl orange	Enhanced 2 times	Degussa P25, thin films	10^{-3} M Ag	6.12	9.2	[23]
Rhodamine B	Enhanced by 30%	Degussa P25	2	4.79		[24]
2-Chlorophenol	Enhanced 1.5 times	Degussa P25	4.5×10^{-4}	111	4.5	[25]
Sirius Gelb GC (Azo dye)	Enhanced 2.5 times	Aldrich	0.75	20	3.5	[26]
2-Propanol	Retarded	Anatase	0.5	30000		[16]
Salicyclic acid	No effect	Degussa P25	2	100	3.5	[18]
Phenol	No effect (2 at.%), Retarded (20 at.%)	Degussa P25	2, 20	100	3.5	[27]
Resorcinol	No effect	Degussa P25	0.1–20	9.7	3 ± 0.5	[28]
4-Chlorophenol	Enhanced	Degussa P25 (sol/gel)	0.5	64.3	5.5	[29]

Table 2
Summary of the literature on the effects of platinum on the photocatalytic degradation of organics

Compound	Effect	Conditions				Reference
		TiO_2 (g/l), Degussa P25	Pt loading (at.%)	Substrate (mg/l)	pH	
Cr(VI)	No effect	5.0	0.08–0.2	20.8	3.0	[30]
EDTA, sodium salt	Enhanced by 13–16%	5.0	0.08–0.2	870	3.0	[30]
Bisphenol A	Enhanced 3–6 times	0.1	0.08–0.4	20.0	3.0 and 10	[31]
4-Chlorophenol	Retarded	1.0	0.2-0.4	129	3.0 and 9	[32]
Dichloroacetic acid	Enhanced 2.2–3.5 times	1.0	0.2–0.4	645	3.0 and 9.0	[32]
Methanol	Enhanced 2.4–7.8 times	–	0.4	660	10.9	[33]
		–	0.4	134	5.1	
Ethanol	Enhanced 2.4–4.2 times	–	0.4	667	10.9	[33]
		–	0.4	340	5.1	
Chloroform	Retarded 40%	–	0.4	154	5.4	[33]
Trichloroethylene	Retarded 92%	–	0.4	39.0	5.3	[33]
Ethylamine	Retarded slightly	0.02	1	22.5	10.0	[34]
Diethylamine	Retarded slightly	0.02	1	36.6	10.0	[34]
Ethanolamine	Retarded slightly	0.02	1	30.5	10.0	[34]
Diethanolamine	Retarded slightly	0.02	1	52.5	10.0	[34]
Triethanolamine	Retarded slightly	0.02	1	74.6	10.0	[34]
Formic acid	Enhanced faradaic efficiency by 30%	Thin film	0.4	460	3.2	[35]
4-Chlorophenol	Retarded (O_2) enhanced (no O_2)	Sol/gel	1	64.3	5.5	[29]
Dichloroacetic acid	Enhanced 2–3 times photonic efficiency	5.0	0.4	128.9	3.0	[36]
4-Chlorophenol	No effect	5.0	0.4	128.6	3.0	[36]

presence of metals, which is not the case. Some also suggest that organic compounds are degraded at an elevated rate on metal/TiO_2 particles due to the higher extent of organic adsorption on the particle surface [38,39]. However, Vamathevan [40] has shown that the presence of Ag enhances the adsorption of phenol, but does not enhance the mineralisation of this organic.

Several theories have been presented in the literature to explain the detrimental effects of metal surface modification on titanium dioxide photocatalysis. Metal deposits may occupy the active sites on the TiO_2 surface for the desired photocatalytic reactions causing the photocatalyst to lose its activity [37]. This can also cause a light shielding effect, which normally happens at higher loadings. It has also been suggested that due to electron transfer from the TiO_2 support to the metal, the photoadsorption of oxygen as the O_2^- species on titanium dioxide is inhibited [41]. Also, the rate-determining step in photooxidation reactions may be the half-reaction occurring on the anodic area of the catalyst rather than reduction of oxygen molecules. Therefore, reaction steps such as the adsorption of the organic substrate onto the photocatalyst and the transfer of electrons from the substrate to the photocatalyst surface may be rate limiting. In this situation, the accumulation of electron on metal deposits results in the attraction of photogenerated holes to the metal sites. This encourages charge-carrier recombination and the metal deposits behave as recombination centres [33,41].

It has been shown previously that photocatalysis is effective for the degradation of the natural oestrogens (17β-E2, E1 and E3), the synthetic oestrogen (17α-EE2) [42–44] and some xenoestrogens (BPA, ReOH) in water [28,31,45]. However, the effects of noble metals on the photocatalytic degradation and mineralisation of endocrine disrupting chemicals in water has not been widely studied. This paper presents the results of a study on the effects of surface metallisation (silver and platinum) on the photocatalytic degradation of endocrine disrupting chemicals in water—the natural oestrogens 17β-oestradiol (17β-E2) and oestriol (E3), the synthetic oestrogen 17α-ethynyloestradiol (17α-EE2) and the xenoestrogens bisphenol A (BPA), resorcinol (ReOH) and 2,4-dichlorophenol (2,4-DCP). Two reactor systems were used—an immobilised TiO_2 reactor for experiments with the natural and synthetic oestrogens and a suspension TiO_2 reactor for experiments with the xenoestrogens. An immobilised system was used for the natural and synthetic oestrogens so that the samples did not need to be filtered as there was a problem of adsorption of oestrogens on the filters. The suspension reactor is obviously more efficient than the immobilised system due to higher mass transfer and the higher surface area available for reaction but the immobilised system is more practical and economical as there is no need for filtration.

2. Experimental details

2.1. Chemicals

The following chemicals were used: 17β-oestradiol, oestriol, oestrone and 17α-ethynyloestradiol (>98%, Sigma–Aldrich), acetonitrile (>99.8%, HPLC grade, Sigma–Aldrich) bisphenol A (99.5%, Sigma–Aldrich), resorcinol (Ajax Chemicals), 2,4-dichlorophenol (99%, Sigma–Aldrich), perchloric acid (70%, Ajax Chemicals), titanium dioxide (Degussa P25), 20% hydrofluoric acid

(40 wt.% analytical grade, Aldrich Chemicals), silver nitrate (99.9%, Ajax Chemicals), hexachloroplatinic acid (>99%, Ajax Fine Chemicals), formic acid (96%, Sigma–Aldrich), methanol (Ajax Chemicals).

2.2. Experiments with 17β-E2, E3 and 17α-EE2

2.2.1. Photocatalytic reactor set-up and analytical method

The photocatalytic experiments were carried out in a glass borosilicate spiral reactor (volume = 85 ml) with TiO_2 immobilised onto the inside wall of the reactor. A black light blue fluorescent lamp (NEC, 15 W, maximum emission at ~350 nm, emission range 300–400 nm) was fitted through the centre of the coil. The glass coil reactor was connected to a peristaltic pump (Masterflex® Quick-Load, Cole-Palmer Instrument Co.) by Masterflex flexible tubing to enable solution circulation through the reactor at a flow rate of 60 ml/min and to an online fluorescence spectrometer (Perkin-Elmer LS-45 with FLWinLab software) which monitored the degradation of the oestrogens at $\lambda_{ex} = 230$ and $\lambda_{em} = 310$ nm.

2.2.2. Immobilisation of TiO2

The TiO_2 was immobilised by first filling the reactor with 20% hydrofluoric acid for 1 h to etch the inside surface of the reactor. A 1% wt./vol. TiO_2 solution (sonicated in an ultrasonic bath for 20 min) was then pumped through and allowed to stand for approximately 1 h and dried in the oven at 60 °C. This process is repeated 3–4 times. A thin film of TiO_2 was formed on the inside wall of the reactor. This process was repeated twice prior to photodeposition of the two metals—Ag and Pt—on the same reactor system. These are referred to as system 1 (pre-deposition of Ag) and system 2 (pre-deposition of Pt) in the results and discussion.

2.2.3. Preparation of Ag/TiO2 and Pt/TiO2

The immobilisation of silver and platinum metal onto the TiO_2 particles was carried out by photodeposition. Based on previous findings [18,27] a 2 at.% metal loading was used. Silver nitrate was used as the source of silver ions and hexachloroplatinic acid was used as the platinum precursor. Eighty microlitres of the $AgNO_3$ or H_2PtCl_6 of the desired concentration to give 2 at.% Ag^+ or Pt^{4+} in solution was added with 85 ml of 100 μg/l formic acid into the glass coil reactor with the immobilised TiO_2 and circulated in the dark for 15 min to allow the system to equilibrate. The UV lamp was then turned on and the solution was circulated for 2 h to allow photooxidation of the formic acid and photoreduction of the metal ions to occur.

2.2.4. Photocatalytic reactions

A standard solution of 3 μM of oestrogen (0.82 mg/l 17β-E2, 0.86 mg/l E3 and 0.89 mg/l 17α-EE2) was made up in MilliQ water from stock solutions in acetonitrile. One hundred and twenty millilitres of 3 μM oestrogen was pumped through the reactor set-up at a flow rate of 60 ml/min for approximately 5 min to allow the solution to equilibrate before the experiment was started. The UV lamp was then turned on and the 'timedrive' method (FLWinLab software) which measured fluorescence intensity over time was started where measurements were taken every second. This procedure was carried out for each oestrogen in duplicate on bare TiO_2, Ag/TiO_2 and Pt/TiO_2.

2.3. Experiments with BPA, ReOH and 2,4-DCP

2.3.1. Preparation of Ag/TiO2 and Pt/TiO2

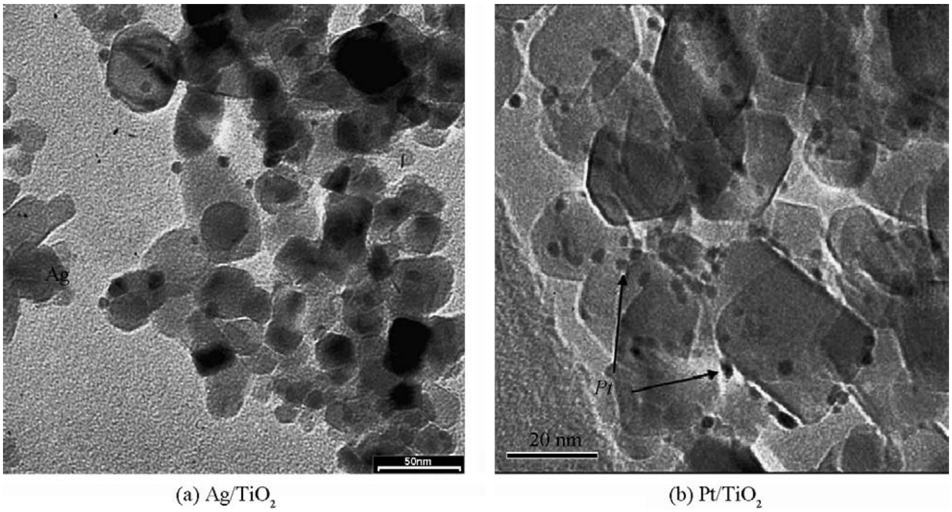
Both Ag/TiO_2 and Pt/TiO_2 particles were prepared by the photodeposition method in the presence of a sacrificial organic hole scavenger as described in earlier publications [27,31]. A brief description of the method is as follows. A pre-determined amount of TiO_2 was suspended in water, transferred into the photoreactor, and irradiated under UV for 30 min to mineralise any adsorbed organic impurities. Aliquots of either silver nitrate or hexachloroplatinic acid and a sacrificial organic were added to the suspension and irradiated under UV for 60 min (to give a loading of 2 at.%). After UV irradiation, the particles were recovered by centrifugation and washed repeatedly with water to remove adsorbed chemicals. Finally the particles were dried and stored under vacuum in a desiccator. The Ag/TiO_2 and Pt/TiO_2 particles were characterised using a Philips CM200 Transmission Electron Microscope.

2.3.2. Photocatalytic reactions

The photocatalytic degradation of ReOH, BPA and 2,4-DCP by titanium dioxide and metallised titanium dioxide were conducted using a spiral, slurry-type photoreactor. The detailed description of the apparatus used in this work can be found in an earlier publication [27]. 50 ml of TiO_2 suspension (1 g/l) was first introduced into the photoreactor and the pH of the suspension was adjusted to a value of 3 by the addition of perchloric acid. The suspension was then irradiated with UV for 30 min to mineralise any adsorbed organic impurities. A pre-determined volume of the organic chemical was then injected to the suspension followed by a 30 min mixing period to allow dark adsorption of organic molecules onto the photocatalyst surface. The amount of organic compound injected in each degradation experiment was equivalent to 50 or 2000 μg carbon depending on the experiment to be carried out which is equivalent to 1 and 40 mg/l of carbon, respectively. Finally the suspension was irradiated with UV and the rate of carbon dioxide generation was monitored by an online conductivity meter.

3. Results and discussion

The TEM images of the Ag/TiO_2 and Pt/TiO_2 particles prepared by photodeposition are shown in Fig. 1. The TEMs show that Ag particles are 5–50 nm in size and Pt particles are 2–10 nm in size.



(a) Ag/TiO_2 (b) Pt/TiO_2

Fig. 1. TEMs of Ag/TiO_2 and Pt/TiO_2 particles prepared by photodeposition.

For the natural (17β-E2 and E3) and synthetic (17α-EE2) oestrogens, previous work has shown that the photocatalytic degradation reactions follow first order reaction kinetics [42–44]. The results were therefore plotted as ln of concentration over initial concentration ($\ln C/C_0$) against time for each oestrogen to determine the first order rate constant. Fig. 2 shows a histogram of the rate constants for photocatalysis of the natural and synthetic oestrogens over bare TiO_2 (system 1, pre-photodeposition of Ag) and Ag/TiO_2. It can be seen clearly that all three oestrogens degrade at similar rates on bare TiO_2 and on Ag/TiO_2. Fig. 3 shows the results for photocatalysis of the natural and synthetic oestrogens over bare TiO_2 (system 2, pre-photodeposition of Pt) and Pt/TiO_2.

A similar trend was observed for the natural and synthetic oestrogens over Pt/TiO_2 as shown in Fig. 3. There is no significant effect of adding Ag or Pt for photocatalysis of the natural or synthetic oestrogens in water. On comparison of system 1 (pre-deposition of Ag) and system 2 (pre-deposition of Pt) for photocatalysis over bare TiO_2, it can be seen that there is a slight difference in rates, particularly for E3. However, these are still within experimental errors. Significant errors arise due to variation in the immobilisation of TiO_2. Even though the same method of immobilisation was used for each system, there may be variation in the actual amount of catalyst deposited on the surface of the reactor resulting in different rates.

The results obtained for rate for 50% mineralisation of 50 μg of carbon of the xenoestrogens BPA, ReOH and 2,4-DCP (1 mg/l of carbon which corresponds to 1.27 mg/l BPA, 1.53 mg/l ReOH and 2.26 mg/l of 2,4-DCP) on bare TiO_2, Ag/TiO_2 and Pt/TiO_2 are shown as a histogram in Fig. 4. It can be seen clearly that there is no significant effect on the addition of silver and platinum metals on the photocatalytic activity of TiO_2 under these conditions.

Figs. 2–4 indicate that there is no significant effect of adding metals (silver and platinum) on the photocatalytic activity of TiO_2 (Degussa P25) for the degradation of low concentrations of the EDCs in water. At low concentration of organic, as used in this study (0.8–2.3 mg/l), the amount of highly reactive holes and hydroxyl radicals generated in the photocatalytic process are considerably higher in concentration in comparison. These oxidising species are therefore in excess and thus able to degrade the organic present in the

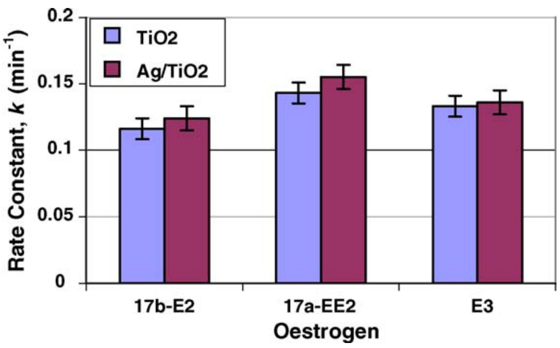


Fig. 2. Rate constants for the photocatalytic degradation of 3 μM (∼0.8 mg/l) of 17β-oestradiol (17β-E2), oestriol (E3) and 17α-ethynyloestradiol (17α-EE2) over bare TiO_2 and Ag/TiO_2.

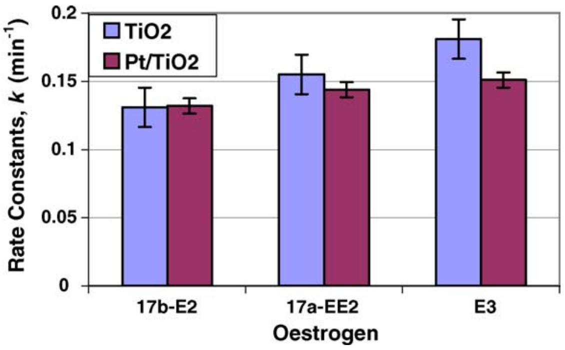


Fig. 3. Rate constants for the photocatalytic degradation of 3 μM (∼0.8 mg/l) of 17β-oestradiol (17β-E2), oestriol (E3) and 17α-ethynyloestradiol (17α-EE2) over bare TiO_2 and Pt/TiO_2.

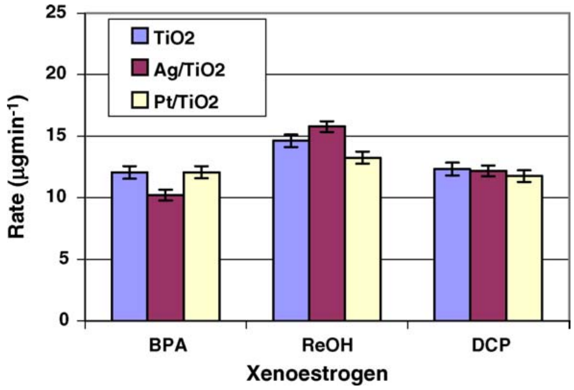


Fig. 4. Rate for 50% mineralisation for photocatalysis of 50 µg (1 mg/l) of carbon of bisphenol A (BPA), resorcinol (ReOH) and 2,4-dichlorophenol (DCP) over bare TiO_2, Ag/TiO_2 and Pt/TiO_2.

water efficiently. The effect due to the addition of a metal to the system therefore becomes insignificant at these low concentrations of organic since diffusion would be the rate limiting factor.

This theory was investigated further by studying the effects of Ag and Pt at higher concentrations of pollutant (2000 µg or 40 mg/l of carbon corresponding to 51 mg/l BPA and 61 mg/l ReOH). Fig. 5 shows the results obtained in the form of a histogram showing the rate for 50% mineralisation of 2000 µg of carbon of BPA and ReOH over bare TiO_2, Ag/TiO_2 and Pt/TiO_2.

It can be seen clearly that the addition of Pt significantly increases the mineralisation rate of 2000 µg of carbon of BPA compared to bare TiO_2 indicating that the addition of platinum enhances the photocatalytic reaction. The rate for 50% mineralisation is increased by over 70% on the addition of Pt compared to bare TiO_2. However, a different trend is seen for Ag where a slight decrease of 21% in the rate is observed compared with bare TiO_2. The rate for 50% mineralisation for Pt/TiO_2 is more than double that of Ag/TiO_2. The results for resorcinol (see Fig. 5) also show a significant enhancement on the addition of Pt. The rate of mineralisation was increased by almost 70% on the addition of Pt compared to bare TiO_2, agreeing with the result for BPA. However, there is only a slight decrease (1.45%) or almost no effect on the addition of Ag compared to bare TiO_2, agreeing with previous work by Lam et al. [28]. Significant enhancement (70%) was only observed at high concentrations of BPA and ReOH on the addition of 2 at.% Pt, confirming our postulation that an effect with metals is only seen at higher concentrations of organic. On the addition of silver, there was a slight decrease in the rate for BPA and little or no effect for ReOH, indicating that the reactions are metal and substrate specific. Chiang et al. [31] reported that the photocatalytic degradation of 20 mg/l of BPA was enhanced when platinum was added to the system. At pH 3 and 1.0 wt.% Pt, platinisation increased the photocatalytic activity by 3.2 times for TiO_2 (Degussa P25). Enhancement was also observed when Hombikat UV 100 TiO_2 and Millennium PC50 TiO_2 were used as the photocatalyst. However, no significant enhancement was observed when the photocatalytic oxidation reactions were carried out at pH 10. The lack of enhancement at pH 10 was attributed to the different intermediate products generated (therefore different reaction pathways) compared to that at the lower pH.

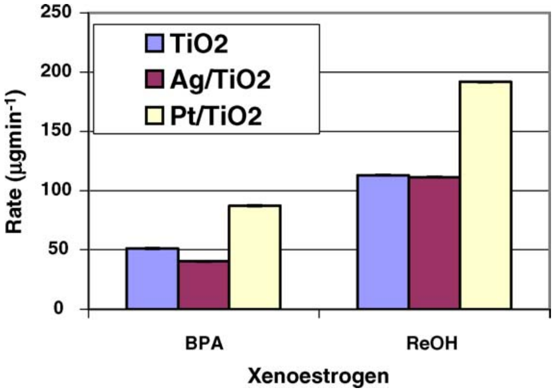


Fig. 5. Rate for 50% mineralisation for photocatalysis of 2000 µg (40 mg/l) of carbon over bare TiO_2, Ag/TiO_2 and Pt/TiO_2.

The presence of silver did not enhance the photocatalytic oxidation of the natural and synthetic oestrogens, BPA, ReOH or 2,4-DCP when they are present at low concentrations. At high concentrations, a slight decrease in rate is observed for BPA with little or no effect for ReOH. Our previous studies shows that Ag metal only enhances certain organic matters. Vamathevan et al. [27] observed no enhancement in photocatalytic oxidation of phenol in the presence of Ag, in contrast to the findings of others who have reported an enhancement in the rates of phenol oxidation [46,47]. Sclafani et al. [47] reported that the rates of phenol oxidation were enhanced by approximately 2 times and Dobosz et al. reported the reaction was enhanced by 3.6 times [22]. There was also no effect of adding silver to the photooxidation of salicyclic acid at either high or low concentrations. The only organic substrate that experienced an enhancement due to the presence of Ag in work by Vamathevan et al. [18,27] was sucrose. Interestingly, it was found that increasing dissolved O_2 in the sucrose system reduced the enhancement effect of the noble metal. This strongly suggests that the enhancement factor is substrate specific and should not be taken as universal.

The enhanced activity due to the presence of metals such as Ag, Pt, Au, etc., is normally attributed to an increase in the separation of the electron–hole pairs in the semiconductor, causing a higher production rate of oxidising species, holes and hydroxyl radicals [32]. The enhanced charge separation by itself could not explain the great enhancement observed for some organic matters but not others. There should not be a universal explanation for the effect of metals on the photocatalytic degradation of organic pollutants, since metals on TiO_2 surface can have no effect or even a detrimental effect. Metals can act as recombination centres or can occupy active sites on the TiO_2 surface to give a detrimental effect and in some cases these negative effects can balance out the positive charge separation effects resulting in insignificant enhancement.

The effect of metals on the photocatalytic breakdown of organics is obviously more complex than previously reported. The reactions may also be metal specific. In this study, at higher concentrations of BPA we observed an enhancing effect with Pt and a retarding effect with Ag. It has been reported that, of all the metals studied, Pt is the most effective with respect to transferring photogenerated electrons to reducible species at the surface of the catalyst [48]. One explanation may be that in this case Pt/TiO_2 is more efficient than Ag/TiO_2 in breaking down the intermediate products formed or different reaction pathways are occurring. Chiang et al. [31] observed different intermediate products at different pHs for the photocatalytic mineralisation of BPA over Pt/TiO_2. Chen et al. [33] found that for the photocatalytic oxidation of ethanol over TiO_2 and Pt/TiO_2 the rate of reactions were enhanced with Pt due to the higher amount of acetaldehyde formed (which is more easily oxidised) as opposed to acetic acid with bare TiO_2. Moonsiri et al. [29] found that Ag did not have any effect on the degradation rate of 4-chlorophenol but adding 0.5 mol% Ag to TiO_2 enhanced the degradation rates of the intermediate products.

Another explanation could be due to the different catalysing effects of the nano Ag and Pt particles. Pt particles are known to be a good dehydrogenating catalyst, while Ag is an oxidation catalyst [49,50]. Sano et al. [51] studied acetaldehyde degradation by Pt/TiO_2 and reported that the Pt on TiO_2 may provide two types of enhancement effects; one is for photocatalytic activity attributable to an increase in charge separation efficiency, and the other is for thermocatalytic activity attributable to surface of nanoparticle metals. Only the deposition of metal Pt on TiO_2 increased the acetaldehyde degradation activity. However, the deposition of other metals (Ag, Pd) decreased the activity. ESR measurements suggested that the difference in activity of metal-deposited TiO_2 was due to the amounts of ${O_2}^-$ formed by UV absorption. A part of acetaldehyde was degraded thermocatalytically by Pt on TiO_2 without CO_2 formation at 70–190 °C, and UV irradiation is necessary for mineralising acetaldehyde completely. The mineralisation of acetaldehyde was considered to be enhanced by the partial oxidation of acetaldehyde by Pt thermocatalyst and the oxidation of intermediates into CO_2 by TiO_2 photocatalyst at temperatures above 70 °C. Sclafani et al. [16] found that a small amount of silver caused the photocatalytic degradation of 2-propanol, although the rate was much lower than that with platinum which possesses dehydrogenating properties. More recently Sclafini and Herrmann [37] reported that a deposit of noble metals such as Pt, Pd, Rh and Ni has been found beneficial only for reactions involving hydrogen either as a reactant or as a reaction product. Chen et al. [33] found that the photocatalytic oxidation of methanol and ethanol was enhanced by Pt but results in lower activity in the case of chloroform and trichloroethylene. The enhancement is obviously substrate specific as well as metal specific. The catalytic properties of Pt/TiO_2 and Ag/TiO_2 also seem to be substrate specific and dependent upon its molecular structure. This hypotheses is currently being investigated further and our initial studies have shown that Ag metal enhanced the mineralisation of organic compounds with more C–O bonds compared to C–H bonds [52]. More recently Lee and Choi [53] have found that platinum effects in photocatalysis are highly substrate specific and depend on the Pt–substrate interaction as well as the properties of platinum deposits.

To sum up, there is a diverse range of endocrine disrupting chemicals present in the aquatic environment. The effect of metal dopants on the photocatalytic degradation of these different chemicals varies depending on the rate limiting factor. Endocrine disrupting chemicals are present in the environment at low ng/l levels [6,7], therefore surface reactions become less important and the addition of metals onto the TiO_2 surface becomes irrelevant to the photocatalytic reaction rate. For industrial/real applications for the treatment of low concentrations of organics by photocatalysis, it is therefore impractical to add expensive metals to enhance the photocatalytic process.

4. Conclusion

The migration of photoexcited electrons to metal deposits has been widely accepted and used to explain the phenomenon in metallised TiO_2 under UV illumination. Due to the ohmic contact between the metal and the semiconductor, the photoexcited electrons migrate to the metal centre on the surface and become trapped there. However, from the results obtained in this study and from examining others work, it can be concluded that there is no universal explanation for the effects of metals on the photocatalytic degradation of organics in water. There are obviously many other factors to consider when studying the effects of metals on the photocatalytic activity of TiO_2. These include TiO_2 type, substrate type, substrate concentration, molecular structure of substrate and intermediate products, pH, O_2 concentration, metal type, metal loading, intermediate products formed and other reaction mechanisms which may be taking place. The catalytic properties as well as the photocatalytic properties of the catalyst should also be taken into consideration. In this study the low concentrations of EDCs studied seems to be the main factor to explain the photocatalytic activity over TiO_2, Ag/TiO_2 and Pt/TiO_2. At low concentrations of organic, the reactions at the surface of the catalyst are less important and mass transfer is rate limiting. The fact that metals are present in the system is irrelevant as any enhancement on the surface will not affect the overall reaction rate. At higher concentrations of pollutant a significant increase in rate is observed over Pt/TiO_2 for both bisphenol A and resorcinol compared to a decrease in rate over Ag/TiO_2 for bisphenol A and little or no effect for resorcinol. The reactions are therefore metal specific, substrate specific and may depend on the molecular structure of the substrate and intermediate products formed. This is currently being investigated further by studying the effects of Pt and Ag on the photomineralisation rates of several organics with varying molecular structures. In conclusion, in a real situation where EDCs are found at very low concentrations, it is not viable to add expensive metals to photocatalytic systems for the removal of low levels of organic pollutants in water.

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