Fouling and inactivation of titanium dioxide-based photocatalytic systems

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Abstract

Titanium dioxide is an effective photocatalyst for the breakdown of many environmental contaminants. The complex mixtures that can occur in water matrices can significantly affect the breakdown of the contaminants in water by titanium dioxide (TiO_2). In this paper, we discuss a wide variety of foulants and inhibitors of photocatalytic TiO_2 systems and review different methods that can be effective for their fouling prevention. Approaches to regenerate a fouled or contaminated TiO_2 catalysts are exploredand the effect of substrates on immobilized titanium dioxide is also reviewed.

Keywords: Titanium dioxide; Fouling; Inactivation; photocatlysis; aquatic system

1 INTRODUCTION

Titanium dioxide (TiO_2) is an important photocatalyst for the treatment of water and wastewater. It is used in a range of methods to remove pollutants from water. The ability of TiO_2 to act as a photocatalyst was shown by Fujishima and Honda [1] Formenti, et al. [2], and Djeghri, et al. [3] in the early 1970s. Initial work focused on the electrolysis of water to produce hydrogen (H_{2-}) as well as the breakdown of simple alkanes. Since then, TiO_2 has been shown to be capable of breaking down a wide variety of compounds including various pesticides [4], bisphenol-A [5], pharmaceuticals [6], solvents such as trichloroethylene [7] and many others. This ability to breakdown a wide range of targets has made it an attractive material for the remediation of contaminated water. However, one major issue for all catalysts is that of fouling and poisoning of the material and TiO_2 is no exception. Deactivation can occur in a number of different ways, and different foulants will have different effects on a given target degradation..

the heart of any TiO_2-based photocatalytic system is the generation of electron-hole pairs from incident radiation. The band gap for a given TiO_2 catalyst depends on the production method, doping and crystal phases. For pure anatase TiO_2, the gap is ~3.2 eV and for pure rutile TiO_2, it is ~3.0 eV [8]. These energies correspond to an excitation wavelength in the near UV region of the spectrum ($\lambda < 411$nm for rutile and $\lambda < 385$nm for anatase) [9]. In an isolated system, photogenerated charges will normally quickly relax into trapped states before undergoing recombination after a few microseconds [10] accompanied by the release of heat. In a solution, charge carriers can transfer to species adsorbed on the surface of TiO_2, causing oxidation or reductionleading to the direct breakdown of target compounds. This charge transfer can also produce highly reactive radicals from adsorbed species such as H_2O, OH^- or O_2 as shown in the following reactions:

$$Ti + OH_{ads} + h^+ \leftrightarrow Ti - OH \cdot \quad \textbf{(1)}$$

$$Ti + OH_{2ads} + h^+ \leftrightarrow Ti - OH \cdot + H^+ \tag{2}$$

$$O_{2ads} + e^- \leftrightarrow O_2^- \cdot \tag{3}$$

$$O_2^{-\cdot} + e^- + H^+ \leftrightarrow H_2O_2 \tag{4}$$

$$O_2^{-\cdot} + H^+ \leftrightarrow H_2O \cdot \tag{5}$$

The radical species can then react with target compounds causing their breakdown. The fact that there are two primary pathways for the breakdown in targets (direct hole/electron attack or indirect radical attack) leads to different fouling mechanisms as well as differing effects for the same foulant on different targets.

The position of the bands shifts with pH (though the band gap remains constant) [11]. Therefore, only certain species may be oxidized/reduced by TiO_2 within a certain pH range [12]. The value of the quasi-fermi level has been estimated as:

$$E_f(pH) = E_F(0) - 0.059pH \tag{6}$$

with $E_F(0) = -0.05\ V$ [1] [12, 13] for anatase and 0.15 for rutile [11]. At pH 7, for example, E_f for anatase is approximately -0.46 V.

In this review, we examine the factors that inhibit photocatalyst performance and we examine the mechanisms that underpin these factors. This area is of immense importance as a thorough understanding of the pathways that lead to the inhibition of TiO_2 photocatalyst systems are vital in order to create useful photocatalytic systems. In this work, the literature is reviewed to determine the effect of common inorganic ions and organic compounds on TiO_2. The effect of supports and the stability of immobilised films are also explored. Finally methods for regeneration and prevention are examined.

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[1] All potentials listed in this paper are with reference to the Standard Hydrogen Electrode(SHE)

2 INHIBITORY MECHANISMS

There are a number of mechanisms by which a given species can inhibit the breakdown of target compounds with TiO_2. These are listed with example foulants in Table 1.

The first mechanism is surface blockage. Some compounds can interfere with the breakdown of targets by occupying sites on the surface of TiO_2. The blocked sites allow neither target compounds nor $O_2/H_2O/OH^-$ to adsorb to the surface and react with photogenerated charges. This is a common effect to many species as it requires only that an interfering compound adsorb strongly to the surface. A related mechanism is aggregation of catalyst particles in suspension resulted in a reduced surface area available for reactions. Certain species such as divalent ions can promote this phenomenon by acting as a bridge or adhesive between the particles. [14, 15]. Immobilized film reactors are not susceptible to inactivation due to aggregation as the particles are not in suspension[16].

Interfering compounds may scavenge the photogenerate active species such as holes, OH*-, or O2*-, either removing them or transforming them into less active ones [17]. This can have a significant effect on the overall rate. However, hole/electron scavengers can have an enhancing effect in some cases. For example, if a reaction pathway utilizes holes for the desired chemical transformation then an electron scavenger will decrease the recombination rate of charges by acting as an electron trap. The trapping of charges however can also be a fouling mechanism. The adsorption of some foulants to surfaces can introduce new energy states within the bandgap of TiO_2. These states may act as recombination centres thereby decreasing the number of free carriers available for reactions and reducing the degradation rate.

Some compounds can absorb light in the active region of TiO_2 ($\lambda < 411$nm for rutile and $\lambda < 385$nm for anatase) [9]. If present in the water matrix in sufficient amounts such a compound will reduce the effective illumination of the catalyst, decreasing the charge generation and hence the overall reaction rate. A relatively rare inhibitory mechanism involves compounds that widen the bandgap of TiO_2 [18]. This will reduce the number of useful photons absorbed by the catalyst and thus reduce the charge generation rate and subsequently the overall reaction rate.

The dominant mechanism for a particular combination of target and foulant depends on many parameters. A foulant that primarily blocks adsorption may have little effect on targets that are degraded primarily though indirect radical action. Conversely, a strong radical scavenger may have little effect on a target degraded by direct hole reactions[19]. For example, radical scavenging is a large source of inhibition for compounds such as phenol, which do not adsorb significantly at the TiO_2 surface as reported by Naeem and Feng [20].

3 THE EFFECTS OF SALTS AND IONS

Inorganic ions are commonly found in all natural water systems and they originate from a variety of geological and biological sources. Unlike many organic molecules, they are not subject to breakdown by photocatalysis.

3.1 Ionic strength

High ionic strength can act as either a promoter, foulant, or neither, depending on the target compound(s). The aqueous ionic strength can alter the adsorption properties of targets to the surface of TiO_2. Dionysiou, et al. [21] examined the effect of ionic strength on the breakdown of 4-chlorobenzoic acid and reported a slight decrease in degradation rate with increasing KNO_3 concentrations up to 500 mM, with the primary effect being a reduction in the amount of adsorption. Aguedach et al. [22] reported a large increase in the breakdown of the dye Reactive Black 5 (RB5) at concentrations as low as 10 mM with increasing salt concentration. This was attributed to increased adsorption of RB5 due to compression of the electric double layer and neutralization of positive surface charges. They also found that different ions affect the rate of breakdown with Ca^{2+}>K^{+}>Na^{+}≈Li^{+}.

Anions also affect the reaction rates with hydroxide radicals (Table 2). For example, high levels (>500mM) of chloride ions are reported to greatly increase the rate of breakdown of naphthalene; 2.4 mol/L of chloride gave a rate of more than 4 times that measured in the absence of chloride [23]. It was initially suggested that this was due to an increase in the volatility of naphthalene at higher ionic strength but later experiments showed this not to be the case. Instead, they attributed the increase to the "salting out" of neutral organics in strong salt solutions, leading to an increase in adsorption onto the TiO_2 surface. While high levels of Cl^- were shown to increase the breakdown of naphthalene, they inhibited the removal of hydrophilic breakdown products such as 1,4-naphthoquinone, supporting the salting out theory. A similar phenomenon was reported by Yang, et al. [24] who studied benzene, naphthalene, and Orange II. In contrast to these reports, no effect due to ionic strength was observed for the breakdown of chloroform [25], phenol, cyclohexane, or resorcinol [26]. It is clear that there is no general trend for the effect of ionic strength on the degradation rate and the effect on a given target will be difficult to predict.

3.2 Anions

3.2.1 Chloride and other halogens

Chloride is a commonly found anion in the environment as well as in the laboratory where it is used as a counter ion. Other halogens, particularly iodine and bromine are also common in both natural and artificial waters. Halogens can cause inhibition primarily by surface blockage or scavenging of radicals. Halogens, including chlorine can undergo a variety of reactions that affect the photocatalysis attributed to hydroxyl species [26, 27]:

$$Cl^- + OH \cdot \leftrightarrow ClOH \cdot^- \qquad \textbf{(7)}$$

$$ClOH \cdot^- \rightarrow Cl \cdot H0^- \qquad \textbf{(8)}$$

$$ClOH \cdot^- + H^+ \rightarrow Cl \cdot + H_2 0 \qquad \textbf{(9)}$$

$$Cl \cdot + Cl^- \rightarrow Cl_2^- \cdot \qquad \textbf{(10)}$$

$$Cl_2^- \cdot \rightarrow Cl \cdot + Cl^- \qquad \textbf{(11)}$$

The reactions (7-11) also proceed with other halogens. Hydroxyl radicals can reversibly react with chloride ions to produce a chlorohydroxide radical species (Eq (7)). These can in turn form chloride radicals and hydroxide ions, Eq (8), or react with a proton to produce a chloride radical and water, Eq (9). The reverse reaction of Eq (7) is rapid (on the order of 10^7-10^9 s^{-1} [26]) so this will dominate over Eq (9) unless there is sufficient H^+ present. Thus, the inhibition of photocatalysis by halogens is pH dependent process with the inhibition increasing with the decrease in pH. In the case of chlorine, shifting from pH 1 to 9 causes a drop in the scavenging rate of 4 orders of magnitude [28]. Although both bromine [26] and iodine are stronger scavengers than chlorine, chlorine is more common and thus more of a concern with regard to inhibition of photocatalysis. Other halogens can act as strong hole scavengers. Iodine in particular [29] has been shown to be a powerful hole scavenger and it is commonly used to supress direct hole reactions in order to determine the primary reaction mechanism for a given target [30, 31]. Chen, et al. [30] found that the presence of 10mM of I^- slowed the breakdown of Acid Orange 7 by approximately 75%, due to the scavenging of holes. Further examples can be seen in Table 3.

3.2.2 Phosphate

Phosphate is a highly problematic ion in the context of photocatalytic inhibition, though with a strong dependence on pH. Examples of the effects of phosphate can be seen in Table 4. At high pH, HPO_4^{2-} dominates in solution, at pH near 7, $H_2PO_4^-$, and at low pH, H_3PO_4. Phosphate primarily acts as a inhibitor by surface blockage, which is attributed to the ability of $H_2PO_4^-$ to form a very stable bidentate complex on the surface of TiO_2 [32]. The removal of this surface typically requires rinsing with a basic solution such as 0.1M NaOH or $NaHCO_3$ [17]. Other forms of phosphate also adsorb to the TiO_2 surface although they do so much less strongly than $H_2PO_4^-$, resulting in a pH dependence on the inhibition mechanism.

Phosphate can also act as a promoter for certain targets [33]. Phosphate on the surface of TiO_2 has a negative charge, drawing photogenerated holes to the surface. These holes can react directly with adsorbed substrates or surface hydroxyl groups of phosphate but may also block the adsorption of many species and thus may have an overall negative effect on the reaction rate. However, phosphate can form strong hydrogen bonds with H_2O, anchoring it near the surface allowing for efficient charge transfer to create free OH radicals[34] and H_2O_2[35]. These can react with substances near, but not adsorbed, to the surface increasing their breakdown rate [33-35].

3.2.3 Sulfate

Sulfate ions adsorb strongly to the surface of TiO_2 and act as scavengers of OH radicals causing inhibition. Like phosphate the presence of adsorbed sulphate can increase the amount of H_2O_2 produced for certain targets though the opposite effect is seen for some targets[35]. The mechanism behind this has not been fully explained. Sulphate radicals exhibit a high activity toward many targets, unlike other scavenging-produced radicals [36] and are used in UV/persulfate oxidation systems. This high activity can result in a large increase in the breakdown of susceptible targets [37-39]. Examples of inhibition and promotion due to sulphate are shown in Table 5.

3.2.4 Carbonate

Carbonate is another ion that is extremely common in natural and artificial waters. Aside from artificial sources, natural sources include many mineral and rock formations such as limestone, which are composed mainly of $CaCO_3$.

Of particular concern is that the CO_3^{2-} ion is an efficient scavenger, 46 times faster than HCO_3^-. Carbonate radicals have also been shown to exhibit significant reactivity towards certain compounds, particularly nitrogen-containing organics [40, 41]. This is a likely explanation for the enhanced degradation seen in the presence of some targets such as aniline [42] and dimethoate [43]. Carbonate can also combine with other ions such as calcium to produce precipitates that can reduce the effective illumination in a reactor by absorption and scattering [44]. Table 6 presents data on the effect of carbonate on the breakdown of selected target compounds.

3.2.5 Nitrate

Some researchers have reported a slight depressing effect from nitrate on photocatalytic activity due to a combination of radical scavenging as well as filtering of UV light [45, 46] although others have reported no significant effects [47, 48]. The scavenging ability of nitrate, however, is much less than other common ions and so typically contributes little to the inhibition of processes. Examples of the effect of nitrate can be seen in Table 7. Nitrate can also act as a promoter in theory. It can undergo a photolytic reaction to produce nitrite and an oxygen radical when illuminated in the mid UV light range (absorption maximum at 302 nm) [49]:

$$NO_3^- + \hbar\nu \rightarrow NO_2 + O^- \cdot \qquad \textbf{(12)}$$

However, most of the reported systems do not expose the reactor to significant amounts of light of the necessary wavelength for this reaction to occur (320 nm is a common cut-off wavelength for illumination). Some studies, however, reported an increase in the breakdown of targets that was attributed to this effect [43, 50] despite the low levels of mid UV light producedfrom their systems.

It is clear that many common anions can have large effects on the breakdown of contaminants primarily by surface blockage and radical scavenging. Of particular concern are carbonates, chlorine, and sulphates, which are present in many groundwater systems in relatively high levels. However as is always the case, whether a given foulant is an issue will depend on the degradation mechanism of a given compound.

3.3 Cations

An important issue when analysing data concerning the effect of cations is that many studies report the use of chloride as the corresponding anion [17] due to the typically high solubility it imparts in water. However, the introduction of chloride ions into solution can itself have an inhibitory effect and so some of the reported rate reductions may be due to the effects of chloride rather than solely attributed to a particular cation.

Some metal ions can undergo redox processes with photogenerated electrons/holes:

$$M^{x+} + e^{-} \leftrightarrow M^{x-1+} \quad \textbf{(13)}$$

$$M^{x-1+} + h^{+} \leftrightarrow M^{x+} \quad \textbf{(14)}$$

where M is a metal. Such metals therefore act as inhibitors by scavenging free charges in “short circuit” reactions. The redox potential for the reaction must be more negative than the valence band and more positive than the conduction band of TiO_2 in order for the metal to be oxidized or reduced, respectively. This is the case for Mn^{2+}/Mn^{3+}, Cu^{2+}, Fe^{3+}, Co^{2+} and others as shown in Table 8. This often leads to an initial increase in the degradation rates due to scavenging of electrons which lasts until the metal has been consumed, and so many metals have been reported to act as promoters rather than inhibitors [9, 51]. Metal cations may also lead to a reduction in breakdown rates due to the build-up of species on the surface of the catalyst. Some metals (Fe, Cu) can undergo Fenton-type reactions with H_2O_2 and protons to produce hydroxide radicals [9]:

$$M^{n+} + H_2O_2 + H^+ \rightarrow M^{(n+1)} + HO\bullet + HO^- \quad \textbf{(15)}$$

The reduced metal ions can then be regenerated by reduction with photogenerated electrons as in reaction (13). Furthermore, metals may foul the TiO_2 surface by forming precipitates such as oxides or hydroxides.

3.3.1 Sodium, calcium, potassium

Sodium, calcium and potassium are all common in natural waters and have been shown to have almost no effect on the breakdown rate of various targets [52], particularly when the pH is less than the point of zero charge (PZC). At lower pH, the surface of TiO_2 is positively charged, repelling cations and preventing them from even causing simple site blockage. At pH>PZC of Na^+, Ca^{2+}, and K^+ can have a slight inhibitory effect due to their weak adsorption to the surface. Ca^{2+} and some other divalent ions can also cause aggregation when a particle slurry is used, which will reduce the effective surface area of the catalyst [14, 15, 53]. They have also shown to complex with certain targets to prevent their efficient degradation, including phenol [20]. Divalent ions such as Ca^{2+} and Mg^{2+} have been reported to enhance the breakdown of some anionic compounds at pH>PZC, presumably due to reducing the electrostatic repulsion [54] or bridging structures [53].

3.3.2 Manganese

Manganese has been shown to significantly inhibit photocatalysis on TiO_2 at very low levels. Burns, et al. [17] reported that 37 mM of $MgCl_2$ reduced degradation rates of trichloroethylene (TCE) to 2% of the original rate. They found that the low levels of Mn present after replacing the packed bed reactor and rinsing the remaining components was sufficient to reduce the degradation rate to 11% of its control value. Brezova et al. [52] found a much smaller effect on the degradation of phenol such that 0.28 mM of Mg increased the half-life from 14 to 17 minutes. The redox potential of the Mn^{2+}/M^0 couple is -1.185 V [55] (Figure 1), which is significantly more negative than the conduction band of TiO_2 even at high pH, indicating that Mn^{2+} cannot be directly reduced by TiO_2 [56]. However, Mn^{2+} can be oxidized by TiO_2 to Mn^{3+} by holes. The presence of electron acceptors such as oxygen or oxalate allows for the formation of MnO_2 [57] or Mn^0 [58] on the surface of titanium. Once deposited, these species are stable and difficult to remove. In the absence of these species, Mn^{2+} shows no reduction by or deposition on TiO_2 [56, 59].

As well as Mn ions in solution, MnO_2 is common in many natural water systems due to mineral leaching and can have a large effect on the efficacy of TiO_2. Several studies [18, 60, 61] have reported a large change in the breakdown rate of phenol [18] and methyl orange [60] in the presence of MgO_2 particles (largest dimension ranging from 200-450 nm) at 20 mg/L (0.23 mM). Core-shell type structures were formed as small TiO_2 particles (25-30 nm) deposited on the surface of the larger MnO_2 particles due to electrostatic attraction. Different phases of MnO_2 led to different reductions in photocatalytic activity with δ-MnO_2>α-MnO_2>β-MnO_2. A number of factors contributed to this large effect. MnO_2 absorbs widely in the visible and near UV spectrum and can optically screen the TiO_2 surface thereby reducing the number of photons available to generate charge pairs [60]. The extent of the absorption is dependent on the MnO_2 phase matching the effects on photocatalytic activity with δ-MnO_2>α-MnO_2>β-MnO_2. MnO_2 also introduces a series of bands within the band gap of TiO_2 which leads to an increased recombination rate. Furthermore, the MnO_2 / TiO_2 interface may increase the band gap energy, leading to a blue shift in the absorption edge and effectively reducing the absorption further. Similar effects were reported by Rao and Chaturvedi [62] with P25 immobilized on pebbles made of minerals high in MnO_2.

Manganese has also been reported as a promoter in some studies. Butler and Davis [63] reported a 20% and 35% increase in the breakdown of toluene at pH 3 and 7 with no change at pH 5. Chen et al. [64] reported a significant increase for the breakdown of 2-CP at pH 3. This effect was assigned to the redox couple of Mn^{3+}/Mn^{2+} acting to decrease recombination or through the formation of reactive metallo-organic complexes. At this time, it is not clear what parameters determine whether manganese will act as a foulant or as a promoter but the majority of reports suggest that fouling is the more common effect.

3.3.3 Chromium

Much like Mn, Cr(III) has been shown to greatly reduce photocatalytic activity, even at concentrations as low as 1 μM. Examples of the effect on Cr(III) are shown in Table 9. Except at high pH, the direct reduction of Cr^{3+} does not readily occur on TiO_2. Therefore, unlike Cu or some other metals, Cr does not appear to deposit onto the surface as Cr^0 nor is it converted to Cr^{6+}. Instead it appears to simply displace H^+ on the surface titania, as demonstrated by a drop in pH on the addition of Cr to slurry of TiO_2 [52] or precipitate as $Cr(OH)_3$ [58, 65]. It has been suggested that fouling by Cr is due to a combination of surface blockage and increased recombination [48]. The presence of Cr(VI) can cause an initial increase in the oxidation of organic compounds by acting as an electron scavenger, increasing the charge separation and reducing recombination [66]. However, reduction of Cr(VI) yields Cr(III) by the following reactions:

$$Cr_2O_7^{2-} + 14H^4 + 6e^- \rightarrow 2Cr^{3+} + 7\,H_2O \;\; (\text{E}° = 1.36\text{V}) \qquad \textbf{(16)}$$

$$CrO_4^{2-} + \; 8H^+ + 3e^- \rightarrow \;\; Cr^{3+} + 4H_2O \; (\text{E}° = 1.350\text{V}) \qquad \textbf{(17)}$$

$$CrO_4^{2-} + \; 4H_2O + 3e^- \rightarrow \;\; Cr(OH)_3 + 5OH^- \; (\text{E}° = -0.13\text{V}) \qquad \textbf{(18)}$$

Reaction (16) is predominant at acidic pH, while reaction (17) is predominant at neutral pH, and reaction (18) is under basic conditions [67]. The produced Cr^{3+} can then foul the titanium surface as described above. These reactions also allow for Cr to initially act as a promoter for some reactions by acting as an electron scavenger [66, 68].

3.3.4 Copper

Depending on the target and concentration, copper can act as either a foulant or a promoter. At low concentrations (<50 µM) copper generally acts as a promoter, while at higher levels, it acts as a foulant. Generally, a peak reaction rate occurs at concentrations in the order of 1-10 µM then slowly decreases, eventually reaching a rate less than the original. Table 10 shows examples of the concentration where the peak reaction was observed as well as the concentration at which inhibition began.

Copper can cause inhibition due to a number of mechanisms. As with other metals, Cu can be deposited onto the TiO_2 surface in the form of Cu^0, CuO, or Cu_2O [69-71]. Other precipitates have been reported including copper carbonate and sulphate compounds [63, 72]. Aside from the blocking of active sites, the deposition of copper compounds results in a much more reflective surface resulting in reduced illumination of the surface of TiO_2 [52, 69]. Copper is also known to form metal-ligand complexes with a wide array of compounds. These complexes appear to have different effects on different targets.

A number of mechanisms have been suggested for how Cu^{2+} ions act as a promoter, aside from simple electron trapping and homogenous catalysis. Lam et al. [73, 74] argued that targets form complexes with Cu^{2+} ions followed by the transfer of an electron from the target to copper to form Cu^+, which is later regenerated by photogenerated holes. For the studied targets, the Cu complexes showed higher adsorption onto TiO_2 than uncomplexed Cu which will also lead to higher breakdown rates. Du et al. [51] have argued for the reaction of Cu^{2+} with superoxide radicals. This results in both electron trapping and the formation of H_2O_2, which are responsible for the increase in breakdown rates.

3.3.5 Iron

Like copper, iron is a promoter at lower concentrations (<1 mM) but can act as an inhibitor at higher concentrations (> 10mM) [63]. Unlike copper, where rates quickly peak, iron shows a much larger plateau of peak promotion before rates begins to decrease [48, 52, 75, 76]. In addition to the other promotion mechanisms previously described, certain iron hydroxides can undergo photolysis by light in the 200-300 nm range to produce hydroxide radicals [77-79]. This large peak area means that in most studies iron acts as a promoter rather than an inhibitor in the ranges studied.

3.3.6 Nickel

In general, nickel exhibits similar behaviour to copper but with a pH dependence. Aside from simple direct reduction from Ni^{2+} to Ni^0, at pH>9 nickel is capable of depositing nickel oxides onto the TiO_2 surface based on the following reaction [17, 37, 55]:

$$2Ni^{2+} + 2O_2 + 2H_2O \rightarrow 2NiO_2 + 4H^+ \quad (19)$$

A number of indirect reactions can also occur resulting in the deposition of nickel such as the reduction by carbonate radicals [80, 81]. Similar to copper, nickel is also capable of forming complexes with other molecules and altering reactions [82]. But unlike copper, there appears to be no reports on the acceleration of reactions in the presence of nickel due to complexation.

3.3.7 Others

Brezova et al. [52] reported that the presence of approximately 1 mM of Co^{2+} caused the degradation rate of phenol to drop to 66% of the baseline. Similarly, Kormann et al. [25] reported a drop of 50% for 1 mM of Co^{2+} for the breakdown of chloroform. In both cases the decrease was attributed to the short-circuit reactions, which are possible as the redox potential is -0.28V. Additionally, both of these tests were performed at pH near 7 which is above the PZC of TiO_2 allowing for significant adsorption of the positive cobalt ions.

Although lead is capable of being reduced by TiO_2, the process is slow in the absence of electron donors, likely due to poor adsorption [56, 83-86]. This results in Pb^{2+} having little effect on the degradation of targets by TiO_2. Zn^{2+} has also been examined and has not shown to affect the photodegradation of glyphosate [87], dichlorvos [38], phenol [52], and 2-chlorophenol [88] among others. TiO_2 cannot directly photo reduce Zn^{2+} until pH ~12 as the reduction potential is too high [55], but it can be reduced by indirect methods by radicals such as formate [89]. In contrast to these studies, Kormann et al. [25] reported a 60% decrease in the degradation of chloroform at pH 7. The mechanism by which this inhibition occurred was not adequately explained however but it is may be due to the absorption of the Zn^{2+} to the surface.

4 THE EFFECTS OF ORGANICS

4.1 Alcohols

Low molecular weight alcohols can act as powerful radical scavengers as can been seen by the reaction rates listed in Table 11. Unlike anion radicals, alcohols exhibit almost no reactivity towards targets making their scavenging even more effective. The ability of short chain alcohols to deactivate hydroxide radicals is sufficiently strong that they are used as to help elucidate the degradation mechanism for a given target by all but stopping any hydroxide radical mediated pathways [90, 91]. In contrast to ions, alcohols are susceptible to breakdown by TiO_2 [92].

The degradation rate of carbofuran in the presence of isopropanol (at 100 times the concentration of carbofuran) was reduced by ~50% [90]. A 70% decrease in the breakdown of imazalil was reported [93] for similar ratios of methanol and isopropanol. A range of concentrations were examined and a maximum rate was found for a ratio of ~100:1 (alcohol:target). A reduction of ~80% in the breakdown of bisphenol-A for a ratio of 633 methanol to BPA has been shown [5] and even 1% ethanol reduced the breakdown rate by 40% with similar results seen for methanol, isopropanol and butanol [94]. A close to 90% reduction was reported [95] for the breakdown of clopyralid in a 1% ethanol solution. In contrast, methanol or isopropanol had relatively little effect on the breakdown of Acid Orange 7 [30] and similar results have been shown for flumequine [31].

Alcohols can have a large effect on the breakdown rates for targets where hydroxyl attack is the primary pathway. However, for targets that breakdown by other routes, such as direct hole attack, alcohols show little effect.

4.2 Humic and fulvic acid

The natural organic matter (NOM) in many waters can inhibit the breakdown of targets by three main methods: site blockage, hydroxyl scavenging, and light absorption. Because of these multiple methods, NOM can act as a strong inhibitor for a wide arrange of targets. Humic acid and other dissolved organic matter have been shown to strongly adsorb to the surface of TiO_2, primarily under acidic conditions [96-99] due to charge effects. Adsorption of this matter blocks the adsorption of other species including targets, water, and oxygen preventing the generation of radicals. Dissolved organic matter (DOM) can also act as a scavenger for radicals and holes. This scavenging will result in the DOM being broken down by TiO_2 into smaller molecules, and TiO_2 has been used for this express purpose in some studies [100-102]. As the purpose of most systems is to breakdown anthropogenic compounds, this is seen as inhibition rather than a desired result. Aside from simple site blockage and competitive reactions, humic acid also absorbs UV light, reducing the effective illumination of the catalyst.

The effect of humic substances was examined in the breakdown of 1,2,3-trichlorobenzene and 4-chlorophenol [91]. At 50 mg/L of humic matter, the degradation rate of 123-TCB was reduced by approximately 75% and 4-CP by 50%. 4-CP was also tested in farm runoff water containing an estimated 50 mg/L humic substances and the rate reduced to 25%. This dependence on the composition of the DOM has also been reported in other studies [103]. In the case of quinolone [99], this screening effect was responsible for the majority of the reduction in breakdown. At low concentrations (~6 mg/L), a slight increase in the removal rate was observed, attributed to weak binding of quinoline to humic acid adsorbed on the surface of TiO_2, which increased the rate by increasing the local concentration of quinoline near the site of radical generation. However, this effect is relatively weak and is rapidly surpassed by the UV blocking effect. A 40% reduction was observed in the breakdown of carbamazepine in the presence of 0.5 mg/L NOM and near complete inhibition at 7 mg/L [104] and similar results were observed for iomeprol. Hombikat UV100 (a purpose-designed photocatalytic TiO_2) showed significantly less inhibition from NOM than P25 TiO_2, which was attributed to the larger surface area reducing the impact of competitive adsorption. This finding, coupled with low levels of light absorption indicated that site blockage was the primary inhibition mechanism in this case.

5 SUPPORTS

TiO_2 can be used as either a suspension or as a thin film placed on a support. These films can be made of immobilized particles such as P25 or made from precursors chemicals. In all cases, behind this film is a supporting material typically made of glass, metals, or polymers. While ideally these supports would have no effect on films, it appears from research that the choice of support can affect the performance of a film, primarily by the migration of ions from the support to the film.

5.1 Glass

Some ions, such as Na^+ and Ca^{2+}, are known to migrate from glasses into TiO_2 films during calcination [105-108]. The presence of these ions can lead to films with larger crystallite sizes and delay the formation of the anatase phase until higher calcination temperatures. Both of these factors decrease the efficiency of the resultant catalyst. However, coating the support with a layer of SiO_2 [107] or SiN_x [109] can prevent the migration of these ions into the TiO_2 film.

5.2 Metals

Metals provide stable and strong supports for TiO_2 catalysts. Various scratch and tape testing of TiO_2 films reveal little or no damage on stainless steel [110, 111], silicon [112], or aluminium [113] supports. Some metals cause contamination (resulting in a reduced performance) when used as a substrate for TiO_2 films. Aluminium supports [114] coated with TiO_2 using sol-gel techniques (1 to 7 coating cycles of ~200 nm thickness) showed aluminium migration into all layers, occupying approximately 3 atomic % of the surface for one coating cycle and 0.65% for six coating cycles. In pristine coatings, titanium on the surface was present as Ti^{4+} but after six photocatalytic cycles this decreased to 62% (for one coating cycle films) and 85.7% (for three coating cycle films) but interestingly was maintained at 100% Ti^{4+} for the six coating cycle films. The change was almost entirely to Ti^{3+}, and it was proposed that these sites acted as recombination centres by trapping electrons [115]. Stainless steel has also been shown to release ions into coatings. Fe, Cr, and Mn have been found in sol-gel coatings of TiO_2 [116] and Fe, Cr, and Ni have been reported in atmospheric pressure chemical vapour deposition (CVD) grown films on stainless steel [117]. The effect of these ions on the structure or photocatalytic activity of TiO_2 has not been studied in these situations.

5.3 Other

Naturally occurring rocks have been used as supports for TiO_2 films, but the composition of the rocks can affect the efficiency of the resulting films. Three types of pebbles were examined for the degradation of Reactive Black 5 by immobilized P25 TiO_2: MnO_2 rich, quartz with significant amounts of FeOOH, and quartz/Fe oxide rich [118]. MnO_2-rich pebbles showed significantly less activity than the others, presumably due to the effects of

MnO_2 (as noted above) as well as the dissolution of small amounts of magnesium ions into solution. The Fe rich pebbles were more efficient than the MnO_2 rich pebbles but still much less so than the quartz rich. Films of TiO_2 on ceramics containing Al_2O_3 yielded similar results to those on aluminium alloys [119]. Aluminium ions migrated into the film and replaced some Ti^{4+} sites with Al^{3+}, which acted as recombination sites and decreased the number of free charges in the film.

6 BIOFOULING

Although TiO_2 can inhibit the growth of algae [120-122], TiO_2 films may be susceptible to algal growth over time. P25 on pumice stones formed a film of algae after less than two weeks, which prevented further use [123]. A number of factors may have made these films susceptible to algal growth; they were used outdoors, exposed to sunlight and air which may have influenced the ability of algae to grow on the TiO_2 surface. The films were illuminated from the catalyst side so once a film of a certain thickness had formed it may have blocked further light from reaching the catalyst. No other studies have reported this problem and so the potential impact of algae remains unknown.

7 RELEASE OF CATALYST

In the long term use of immobilized TiO_2 as a photocatalyst, the potential loss of the material from the film should be taken into account. This issue not only affects the lifetime of the catalyst but is also an important factor in determining its environmental safety. Generally, fresh and well prepared films possess strong adhesion. Results from adhesion tests are summarized in Table 12. Some studies have reported delamination or other loss of TiO_2 films prepared from particle slurries [123-125]. Loss of such material was dependant on pH and the ionic strength of the medium [124]. Delamination occurred primarily when the pH was less than 3 or greater than 11 or when the ionic strength was above 0.5 M. It was suggested that the high surface charge (either negative or positive) on the TiO_2 created a repulsive force large enough to cause the release of TiO_2 from the silica support. An alternative explanation was acid or base catalyzed cleavage of Si-0-Ti bonds. The adhesion of immobilized P25 as well as sol-gel derived coatings on glass beads was examined during the oxidation of formic acid [126]. After 50 h of use, the P25 coatings had released 7% of the coating and the sol-gel 33%. Silica grains were also used as supports. These released 21% of the P25 coatings and 52% for sol-gel coatings. Most of the loss appeared to be in the form of small particles rather than large areas of delamination.

A number of other studies using immobilized P25 have not reported any loss or delamination but were within the 'safe' region established by Peill and Hoffmann [113, 127, 128]. In contrast, Rao et al. [123] examined thin film reactors based on P25 on pumice and PC500 on cellulose, operating at near neutral pH. They aged both for up to 4 weeks with a 2.5 mM solution of Acid Orange-7 which was replaced when decoloured. The reaction rates of both were shown to significantly decline with increasing time. Microscopy revealed that in both cases there had been a significant loss of TiO_2 from the surfaces.

A ~40% loss of a plasma CVD coating on glass beads after a single use in a fluidized bed reactor was observed [129] due to uniform erosion (rather than delamination). The release of TiO_2 from Pilkington Activ, which is a CVD deposited film [130], as well as an experimental coating composed of 50% TiO_2 nanoparticles embedded in a siliceous matrix were examined [131]. Water, spiked in some cases with humic acid, NaCl, or both, was recirculated through a glass slide reactor for 4 weeks. The Ti content of the water was then measured to give the cumulative release of TiO_2 over the 4 weeks. TiO_2 was released at cumulative levels of 10 – 100 μg/l for the Pilkington Activ and from 0 − 150 μg/l for the experimental coatings. The amount appeared to depend on the composition of the water; deionized water showed very little release, but with the addition of 10 g/l NaCl, 3 mg/l humic acid, or both, there was a large increase in the amount of titanium in the outflow water. Similarly, a larger amount of Ti was released when the films were exposed to UVA illumination compared with those left in the dark. The levels are somewhat similar to those reported in treated wastewater [132, 133] and an order of magnitude less than those report for the release of Ti from exterior paints [134], likely due to stronger adhesion in photocatalytic coatings [131].

Sol-gel derived films have been fabricated on pre-treated titanium foils [135]. Treatment by either sonication in acetone or boiling in 10% oxalic acid was examined. Films were immersed in deionized water and periodically tested for the breakdown of benzamide under UV light. Acetone treated samples rapidly lost photocatalytic activity, with less than 15% remaining after 60 days of immersion. The loss of activity was explained by the large loss of TiO_2 material found when the foils were examined by electron microscopy. Oxalic acid treated samples showed a much more gradual loss, appearing to stabilize after 200 days with more than 70% activity remaining. A suggested explanation for this was that water was able to penetrate the acetone treated film and react with the titanium support to form a new TiO_2 layer causing the detachment of the coating from the support. The oxalic acid coating was much denser and so water was not able to reach the support resulting in a more stable film.

8 REACTION BY-PRODUCTS

In theory, TiO_2 should completely mineralize many targets but this is not always achieved in practice. Even when the reactions are allowed to precede to full mineralization a number of degradation by-products are temporarily created due to the multiple steps required. Some by-products (including simple ions, liberated anions, or small organics) can act as foulants or inhibitors. For example, methylene blue produces sulphate ions on discoloration and 4-nitrophenol produces nitrate [136]. Some by-products have been shown to adsorb strongly to the TiO_2 surface, preventing the adsorption of other species, and possibly produce screening effects [123, 137]. By-products may be implicated in a change in the colour of the catalyst after use. TiO_2 films on glass exposed to methylene blue in deionized water were fully deactivated after 96 h, which was attributed to the various reaction by-products [138]. During the degradation of trichloroethylene [139], the by-products dichloroacetate, trichloroacetyl chloride and trichloroacetate were formed and were all resistant to further degradation. Other researchers have reported overall efficiency losses were reduced with successive cycles [140] and a significant increase in the breakdown of ibuprofen at later cycles.

It is possible that harmful substances may be generated from certain targets. These can result from the breakdown of larger targets into simpler components or from reactions with other species in the water matrix. For example, the presence of chloride leads to the production of Cl· radicals. While Cl· is much less reactive than OH·, it is still capable of oxidizing targets to produce chlorinated compounds, many of which are harmful and persistent in the environment [141]. In particular, there appears to be the possibility for the formation of significant amounts of trihalomethanes such as chloroform or bromoform, with haloacetic acids being a more minor concern [142-144]. Most of these compounds, however, are susceptible to further photocatalytic breakdown, and their release can be prevented by ensuring a sufficiently long reaction time [144, 145].

9 REGENERATION

The ability to regenerate a fouled catalyst is an important consideration to ensure the economic viability of many processes. A number of techniques have been used successfully for various foulants. These methods and their underlying mechanisms are listed in Table 13. Which method is best depends on the nature of the foulants. Loosely adsorbed foulants such as chloride or nitrate can be washed with clean water [17, 47]. More strongly adsorbed pollutants such as phosphate may require an acidic or basic rinse to remove them. The change in pH either alters the solubility of the foulant or transforms it into a soluble form.

Illumination can also be used to regenerate an aged photocatalyst where the primary fouling species are susceptible to degradation [138, 146]. In this case the catalyst is placed in clean water and illuminated for an appropriate time. For photodeposited copper, oxidation by oxygen has been used to form a dissolved ionic species [72, 147]. For example:

$$2Cu^0 + 2H^+ + O_2 \rightarrow\ Cu^{2+} + 2H_2 0 \qquad (20)$$

As an alternative method or as enhancement to this procedure, an electric current can be applied to accelerate the reaction [69].

Fouled catalysts may be regenerated by heating. This occurs through two primary mechanisms; desorption of the adsorbed species due to the increased energy, and pyrolysis of compounds to form less strongly adsorbed species. For some contaminants, particularly inorganic ions, heating above ~400 °C can result in the contaminant being integrated into the TiO_2 structure. This is a commonly used method for doping and can transform an inhibitor such as Mn^{2+} into a promoter [148].

The regeneration P25 photocatalyst fouled by the degradation of phthalic acid was examined [149] using three methods: a water/methanol rinse, thermal treatment at 350°C, and treatment with H_2O_2. The solvent wash method had little effect in the regeneration of the catalyst. Thermal treatment returned the catalyst to approximately 50% of the base rate while H_2O_2 treatment completely regenerated the catalyst. Treatment with H_2O_2 facilitated the breakdown of recalcitrant carboxylic acids adsorbed on catalyst surface. Carbonaro et al. [6] examined the breakdown of acetaminophen, carbamazepine, iopromide, and sulfamethoxazole in wastewater effluent compared with a buffered electrolyte solution. All four targets showed a significant reduction (between 40% and 80%) in their breakdown rate when the water matrix was switched to the effluent. However, on switching to clean electrolyte the breakdown rates fully recovered for all targets.

10 PREVENTION

There are a number of prevention methods reported to date. Control of the pH is one of the oldest methods. Foulants such as chloride, carbonate and phosphate all show pH dependence in their mechanism. Reducing the pH in groundwater with significant levels of carbonate from 7.2 to ~5 with HCl significantly improved the breakdown rate of TCE by as much as 400% [7]. However, altering the pH may also affect the breakdown of targets and so care should be taken to find the optimum value for a combination of matrix species and targets.

Activated carbon, already widely used in water purification, can be used to remove DOM that would otherwise inhibit the breakdown of the target compounds. Passing wastewater effluent through a GAC filter halved the inhibition for acetaminophen [6] but made little difference for the effects of carbamazepine, iopromide, and sulfamethoxazole.

Metals such as Ag or Pt may be deposited onto the surface of the TiO_2 to prevent fouling. The degradation of Sirius Gelb GC using silver-doped anatase particles was examined [150]. The bare and silver-dope particles were exposed to 250 mg/L of $NaSO_4^-$, $Na_2C_2O_4$, $NaHPO_4^-$, $NaCH_3COO$, $NaSO_3$, NaCl, $NaNO_3$, Na_2CO_3, and sodium citrate. The Ag-TiO_2 material showed lower reduction in the presence of all salts except NaCl and $NaNO_3$. In the case of NaCl, a slight increase in the degradation was seen on bare TiO_2 as opposed to a slight decrease in Ag-TiO_2. Similarly, the deposition of Al(III) onto the surface of P25 greatly reduced the fouling by salicylic acid [151]. This may be attributed to a combination of enhanced breakdown leading to fewer inhibitory species as well as the metal acting as a poor adsorbent site for salicylic acid and its breakdown products.

Some reactor designs are also immune to certain forms of inhibition or fouling. For example, particle aggregation cannot occur in reactors where the TiO_2 has been immobilized onto a support as the particles are not free. An immobilized film illuminated from the rear side of the support is also relatively immune to inhibition due to loss of light absorption as the light does not pass through the solution before illuminating the catalyst.

11 CONCLUSIONS

The compounds present in photocatalytic systems can have a significant effect on the efficiency of the process. Of particular importance is the presence of carbonate ions, as not only are they strong inhibitors for many targets but are also extremely common in both natural and artificial waters. Mn and Cr also appear to be powerful inhibitors though their presence is less common. Even in the absence of inhibitors in the aqueous matrix prior to photocatalysis, various reaction products are capable of fouling the catalyst, in some cases to the extent of almost complete deactivation. Some of these reaction by-products can be toxic somewhat defeating the purpose of the system. While there are methods that can be used to reduce the impact of certain foulants, these methods cannot always be used as they may themselves cause a reduction in the breakdown of target compounds. For example, the effect of carbonate can be reduced by acidification of the water matrix but for some targets this can also cause a decrease in the breakdown rate of targets or increase in the inhibition by another inhibitor present. Further work is needed on methods to prevent fouling that will apply to a wise range of foulants and targets. Some methods have been proposed such as metal coating of the catalyst or pretreatment by activated carbon however more work needs to be done to determine the efficacy of this methods with more foulants and targets. This means that one of the most powerful tools to deal with inhibition is to take its effects into account in the system design and ensure that the reaction time, regeneration cycles, catalyst loading or active surface area are sufficient to achieve the necessary degradation of a given target. Despite these methods fouling remains a serious issue for the efficiency of a reactor and further work is needed to improve the efficiency of TiO2 based photocatalytic reactors.

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Table Captions

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Table 1: Summary of inhibition mechanisms

Mechanism	**Sample inhibitors**	**Occurs at/in**
Surface blockage	$H_2PO_4^-$, Cr^{3+}, Humic acid	Surface
Scavenging	I^-,Cl^-, CO_3^{2-}, Alcohols	Bulk and surface
Complexation with target	DOM, Cu^{2+}, Ca^{2+}	Bulk
Recombination Promoter	Cr, Mn	Surface
Light absorption	DOM, NO_3^-	Bulk
Bandgap shifting	MnO_2	Surface
Particle aggregation	Divalent ions	Surface

Table 2: Reaction rates of various anions with hydroxide radicals

Ion	**Scavenging rate (M s)$^{-1}$**	**Ref.**
CO_3^{2-}	$2.8\text{-}3.9 \times 10^8$	[152, 153]
HCO_3^-	$5.7\text{-}8.5 \times 10^6$	[152, 153]
Cl^-	$1 \times 10^6\text{-}1 \times 10^{10}$	[28, 152]
Br^-	$10^8\text{-}10^{10}$	[28]
NO_3^-	$<1.5 \times 10^5$	[28]
HPO_4^{2-}	$5.9 \times 10^5\text{-}5 \times 10^6$	[28, 153]
$H_2PO_4^-$	$<1.2 \times 10^7$	[28]
PO_4^{3-}	$7 \times 10^6\text{-}1 \times 10^7$	[28, 153]
HSO_4^{2-}	$3.5 \times 10^5\text{-}1.6 \times 10^6$	[28, 154]
HSO_3^-	$4.5 \times 10^9\text{-}9.5 \times 10^9$	[28, 36]
I^-	10^{10}	[152]

1 **Table 3: Effect of Cl^- on the breakdown of various targets**

Concentration (mM)	Target	Catalyst	Relative Rate*	pH	Ref
50	Monocrotophos	Immobilized P25	75%		[39]
50	Aniline	Immobilized P25	50%	4.1	[47]
50	Salicylic acid	Immobilized P25	75%	4.1	[47]
500	Phenol	P25 slurry	30%	5	[20]
5	2-Napthol	P25 slurry	75%	6	[48]
20	Dimethoate	P25 slurry	50%	6	[43]
2400	Naphthalene	P25 slurry	433%	5.7	[23]
0.5	1,2-dichloroethane	P25 slurry	90%	6	[45]
40	Humic acid	P25 slurry	75%	6.8	[100]
1	Uracil	P25 slurry	61%	6	[46]
10	AO7	P25 slurry	75%	5.6	[155]
3	Dichlorvos	Immobilized P25	60%	5	[38]
100	2,3-dichlorophenol	Ti nanotube film	66%	5.3	[156]
1	NH_3/NH_4^+	P25	100	9/10	[157]

2 * Relative to the rate absence of the inhibitory species, i.e., Cl^-.

3

4

Table 4: Effect of phosphate on the breakdown of various targets

Concentration (mM)	**Target**	**Catalyst**	**Relative Rate**	**pH**	**Reference**
0.5	1,2-dichloroethane	P25 Slurry	64%	6	[45]
1	Ethanol	Immoblized P25	56%	4.1	[47]
1	Aniline	Immoblized P25	52%	4.1	[47]
1	Salicylic acid	Immoblized P25	35%	4.1	[47]
10	MX-5B	P25 slurry	183%	2.4	[37]
2	Formic Acid	P25 slurry	38%	3.5	[35]
2	Benzene	P25 slurry	150%	3.5	[35]
100	CBX	P25 slurry	250%	2.4	[37]
2	TCE	Immobilized Pt-anatase	69%	9	[17]
4	Humic acid	P25 slurry	12%	6.8	[50]
10	Methylene blue	P25 slurry	80%		[94]
1	AO7	P25 slurry	75%	5.6	[155]
1	NH_3/NH_4^+	P25	200%	9	[157]

Table 5: Effect of SO_4^{2-} on the breakdown of various targets

Concentration (mM)	Target	Catalyst	Reaction	pH	Reference
1	Aniline	Immobilized P25	78%	4.1	[47]
1	Salicylic acid	Immobilized P25	66%	4.1	[47]
100	MX-5B	P25 slurry	233%	2.4	[37]
100	CBX	P25 slurry	213%	2.4	[37]
5	2-napthol	P25 slurry	<50%		[48]
4.8	TCE	Immobilized Pt-Anatase	82%	6.0-7.0	[17]
0.5	1,2-dichloroethane	P25 slurry	78%	6	[45]
1.8	Sirius Gelb GC	Anatase slurry	105%	3.5	[150]
40	Humic acid	P25 slurry	62%	6.8	[50]
20	Methylene blue	P25 slurry		5.1	[158]
1	Uracil	P25 slurry	46%	6	[46]
10	Acid orange 7	P25 slurry	88%	5.6	[155]
3	Dichlorvos	Immobilized P25	150%	5	[38]
50	Monocrotophos	Immobilized P25	230%		[39]
50	2,3-dichlorophenol	Ti nanotube film	75%	5.3	[156]
1	NH_3/NH_4^+	P25	100	9/10	[157]
2	Formic Acid	P25 slurry	72%	3.5	[35]
2	Benzene	P25 slurry	116%	3.5	[35]

Table 6: Effect of carbonate on the breakdown of various targets

Concentration (mM)	Target	Catalyst	Relative	pH	Ref
110	Aniline	P25 slurry	330%	10.8	[42]
0.5	1,2-dichloroethane	P25 slurry	87%	~6	[45]
30	Naphthalene	P25 slurry	17%	11	[23]
10	Naphthalene	P25 slurry	33%	8.5	[23]
1.5	Dimethoate	P25 slurry	171%	6	[43]
100	Humic acid	P25 slurry	50%	6.8	[159]
1	Uracil	P25 slurry	35%	8	[46]
10	Methylene Blue	P25 slurry	117%	NR	[94]
10	D&C Green 8	P25 slurry	25%	NR	[94]
10	Diatrizoate	P25 slurry	43%	8	[160]
10	Acid Orange 7	P25 slurry	100	5.6	[155]
1	NH_3/NH_4^+	P25	100	9	[157]
1	NH_3/NH_4^+	P25	25%	11	[157]

Table 7: Effect of nitrate on the breakdown of various targets

Concentration (mM)	**Target**	**Catalyst**	**Relative Rate**	**Ref**
10	Dimethoate	P25 slurry	162%	[43]
0.5	1,2-Dichloroethane	P25 slurry	93%	[45]
100	2-napthol	P25 slurry	94%	[48]
40	Humic Acid	P25 slurry	191%	[50]
20	Methylene Blue	P25 slurry	100%	[158]
1	Uracil	P25 slurry	84%	[46]
10 (as $NaNO_3$)	Methylene Blue	P25 slurry	98%	[94]
10 (as HNO_3)	Methylene Blue	P25 slurry	156%	[94]
10	D&C Green 8	P25 slurry	21%	[94]
10	FD&C Red 2	P25 slurry	81%	[94]
10	Acid Orange 7	P25 slurry	90	[155]
100	Ethanol, Aniline, Salicylic Acid	Immobilized P25	100%	[47]
50	Monocrotophos	Immobilized P25	80	[161]
50	2,3-dichlorophenol	Ti nanotube film	85%	[156]

Table 8: Redox potentials of metal ions in solution (adapted from [55])

Redox Pair	Potential (V vs. NHE)
Ca^{2+}/Ca	-2.868
Na^{+}/Na	-2.71
Mn^{2+}/Mn	-1.185
Mn^{3+}/Mn^{2+}	1.5415
Cr^{3+}/Cr	-0.744
Co^{2+}/Co	-0.28
Ni^{2+}/Ni	-0.257
Pb^{2+}/PB	-0.1262
Cu^{2+}/Cu	0.3419
Cu^{2+}/Cu^{+}	0.153
Hg^{2+}/Hg	0.7973
Zn^{2+}/Zn	-0.7618

Table 9: Effect of Cr(III) on the breakdown of various targets

Concentration (μM)	Target	Catalyst	Relative Rate	pH	Reference
200	Dimethoate	P25 slurry	3%	6	[43]
50	2-napthol	P25 slurry	<10%	-	[48]
280	Phenol	P25 slurry	16%	6.75	[52]
0.969	Humic acid	P25 slurry	74%	6.7	[162]

Table 10: Effect of copper on the breakdown of various targets

Target	**Catalyst**	**Relative rate**	**pH**	**Peak promotion (μM)**	**Inhibition start (μM)**	**Ref.**
Methanol	P25 slurry	166%	8.5	2	15	[51]
Phenol	P25 slurry	175%	3.5	1000	7500	[163]
Toluene	P25 slurry	200%	3.5	1	30	[63]
2-napthol	P25 slurry	150%	N.R.	50	200	[48]
Glyphosate	P25 slurry	250	6	10	-	[87]

Table 11: Scavenging rates of various alcohols with hydroxide radicals (Adapted from [152])

Alcohol	**Scavenging rate (M s^{-1})**
Methanol	10^9
Ethanol	1.9×10^9
Isopropanol	1.9×10^9
1-Butanol	1.7×10^8

Table 12: Testing of Adhesion of Catalyst to Support

Catalyst	Support	Method	Result	Ref.
CVD	Glass	Release	Release was seen, amount dependant on conditions. See Text	[131]
SG/P25	Glass	Scratch test	10N Require to cause scratch	[164]
P25	Al Foam	Release	No release	[113]
P25	Steel	Release	No release	[128]
SG	Glass and quartz	Release	No release	[128]
SG	Steel	Tape test (ASTM D3359B-02)	No release	[110]
SG	Si	Tape test	No release	[112]
SG	Soda Lime Glass	Scratch test	Slight damage with fingernail with large pressure	[112]
SG	Borosilicate Glass	Abrasion	No damage with paper with or without solvents	[112]
Ag doped LPD	Quartz	Scratch/tape test/ sonication	No release	[165]
SG	Steel	Pencil scratch test	Scratched by 4B	[111]
SG/P25	Steel	Pencil scratch test	Not damaged by 6H	[111]
SG	Steel	Tape test	No release	[111]
SG/P25	Steel	Tape test	No release	[111]
P25	Quartz	Release	Delamination occurred if pH<3 or	[124]

	optical fibres		>11 or at high ionic strength	
SG/P25	Steel	Tape Test (ASTM D3359B-02)	None for <50 g/l, at 50 slight release (4B) 0B by 100 g/l	[116]
Plasma CVD	Glass beads	Release	No delamination but significant erosion	[129]
P25	Steel mesh	Release	No Release	[127]
P25	Glass beads	Release	7% of coating mass released	[126]
SG	Glass beads	Release	33% of coating mass released	[126]

Table 13: Summary of regeneration methods

Method	Mechanism
Illumination	Photoinduced degradation of foulant
Solvent rinse	Desorption of foulant
Acid/base rinse	Change in solubility of foulant or surface charge of catalyst
Thermal treatment	Desorption or pyrolysis of foulant
Other chemical treatment	Breakdown of target

Figure Caption

Figure 1: Redox potentials of various metal ions [55] and TiO_2 as a function of pH after data in (6).

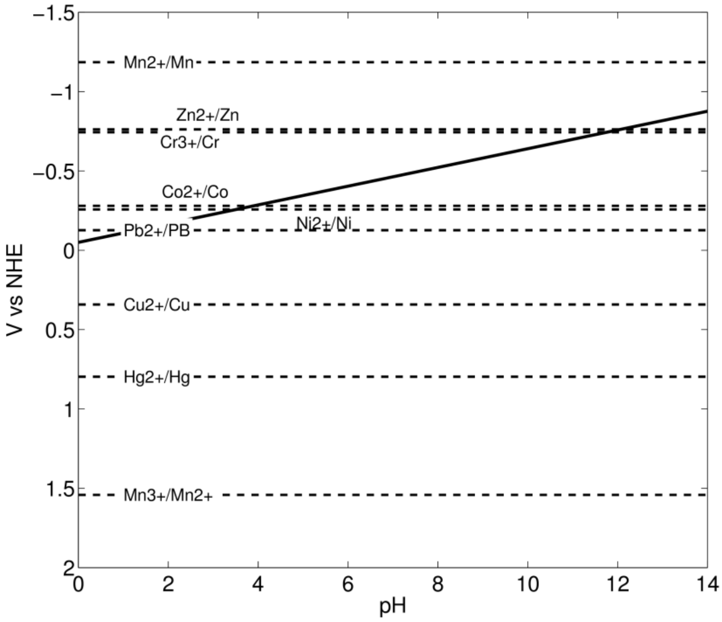

Figure 1: Redox potentials of various metal ions [55] and TiO_2 as a function of pH after data in (6).