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Effects of organic hole scavengers on the photocatalytic reduction of selenium anions

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Abstract

The photocatalytic reduction of selenium anions, selenate (Se(VI)) and selenite (Se(IV)) to elemental selenium (Se) over UV-illuminated TiO_2 was performed using formic acid, acetic acid, methanol, ethanol, sucrose and salicylic acid as the organic hole scavengers. Photoreduction was only observed in the presence of formic acid, methanol or ethanol. The fastest rate of Se ions photoreduction was observed in the presence of formic acid followed by methanol and ethanol. This was attributed to the ability of formate ions to adsorb onto TiO_2 in the presence of Se ions, its fast mineralisation rate and its ability to form reducing radicals quickly. For the methanol and ethanol systems, these two organic compounds could not compete with Se ions for the TiO_2 surface and were not easily mineralised. The photocatalytic reduction of Se ions observed in the presence of these two organic compounds was attributed to their ability to form reducing radicals. When formic acid was used, optimum pH values at pH 3.5 and 4.0 was encountered for the Se(VI) and Se(IV) photoreduction, respectively. When methanol and ethanol were used as the hole scavenger in the pH range of 2.2–4.0, the greatest extent of Se ions photoreduction was encountered at pH 2.2. This suggests the different role of formic acid and methanol/ethanol in the photoreduction of Se ions.

Keywords: Selenite; Selenate; Titanium dioxide; Photoreduction; Organic hole scavengers

1. Introduction

A variety of organic and inorganic substrates have been shown to be successfully photooxidised and photoreduced in UV-illuminated TiO_2 suspension [1–9]. Photocatalytic reactions are initiated by the photogenerated holes (h^+) and electrons (e^-) when the TiO_2 photocatalyst is illuminated. The holes react with the adsorbed water (H_2O_{ads}) or hydroxyl groups (OH^-_{ads}) on the photocatalyst surface, forming the hydroxyl radicals ($OH^\bullet$), which are generally accepted to be responsible for initiating the oxidation pathway. On the other hand, the electrons are responsible for initiating photoreduction reactions.

The photoreaction rates are dependent on many factors, such as substrate adsorption, the reactivity of the intermediates, illumination intensity and catalyst dosage, just to name a few. The rapid recombination rate of the photogenerated electrons and holes greatly affects the photoreaction rate. Some techniques used to overcome the rapid recombination rate include the deposition of metal on the TiO_2 surface [10–12] and the addition of a hole or electron scavenger to the reaction system [13,14]. Both techniques serve to mediate the photogenerated charge carriers away from the TiO_2 surface. This prolongs their lifetime, giving them sufficient time to initiate reduction and oxidation reactions, respectively.

During photocatalytic reduction processes, the presence of a hole scavenger, usually an organic compound, is necessary. Oxygen is normally not desired in the photoreduction process as it competes with the substrate for the photogenerated electrons. For efficient photoreduction, it is desired that the oxidation of the organic substrate is relatively straightforward so that the reduction process will not be retarded.

A widely investigated inorganic ion in photocatalytic reduction studies is the carcinogenic chromate anions [5,15,16]. Other inorganic compounds which have also been studied include Hg(II) [17], Cd(II) [18] and Ag(I) [19]. The reduction of organic compounds, such as benzoquinone [20], 4-nitrophenol [8] and hydrazine [21], has also been investigated.

Prairie et al. [22] have investigated the effects of various organic additives on the photoreduction of chromate. The organics investigated were EDTA, citric acid, salicylic

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acid, acetic acid, ethanol and methanol He found the type of organic is important in determining the rate of chromate reduction, with EDTA and citric acid resulting in the fastest reduction rates. They suggested chelating and adsorption may contribute to the observed results. They have also suggested that conduction band reduction reactions were faster for organics that were more easily oxidised.

The photoreduction of other compounds using different organics have also been investigated. The photocatalytic reduction rates of nitro-aromatic compounds [8] and Cd^{2+} [18] were found to follow the order of formate > methanol > ethanol > *n*-propanol. The trend was explained in terms of the different rate of reducing radicals' formation when these compounds were reacted with hydroxyl radicals. The reactions involved the abstraction of a hydrogen atom from the α-position carbon to the hydroxyl group of the organic compounds [23]. The process, using formate and alcohols as examples, occurs as described in reactions (1a) and (1b), respectively:

$$HCOO^- + OH^\bullet \rightarrow {}^\bullet COO^- + H_2O \tag{1a}$$

$$R\text{–}CH_2\text{–}OH + OH^\bullet \rightarrow R\text{–}{}^\bullet CH\text{–}OH + H_2O \tag{1b}$$

The relative yields of hydrogen abstraction have been reported to be in the order of formate > methanol > ethanol > *n*-propanol, with primary alcohols having greater relative yields than the secondary alcohols [24]. Attempts have also been made to correlate solvent properties (such as viscosity, solvent polarity and polarisability) of the alcohols to the photocatalytic reduction rate [8]. The solvent properties were shown to affect the electron transfer kinetics [25].

This study focuses on the role of different organic compounds on the photoreduction of selenate and selenite (Se(VI) and Se(IV)). The presence of excess Se ions in the natural system poses great risk to the ecosystem. Birth defects were observed in birds and mammals having significant Se level in the blood [26]. The current Se limit for drinking water is 10 ppb [27]. Se(IV) is deemed less hazardous than Se(VI) due to its strong adsorption onto soil and sand particles, lowering its chance of ending up in the waterways [28].

To the best of our knowledge, all previous investigation on Se ions photoreduction utilised formic acid as the organic hole scavenger [29,30]. This could be due to the reason that formic acid has a simple one-carbon molecular structure. Hence, its oxidation to carbon dioxide is straightforward and involves minimal intermediate products [31]. Also, formic acid is capable of forming reducing radicals, which could help in the reduction [23] reaction. The current work aims to investigate the role of various organic hole scavengers on the photoreduction on Se anions. The organic compounds investigated in this study are sucrose, acetic acid, salicylic acid, formic acid, methanol and ethanol.

2. Equipment and procedure

2.1. Catalyst and reagent

Degussa P25 titanium dioxide was selected as the photocatalyst. Its polycrystalline structure is composed of approximately 70% anatase and 30% rutile. It has a specific surface area of $49\,m^2/g$ and is approximately 25 nm as primary particles and 400 nm to 3 μm as aggregates in size. Sodium selenite pentahydrate ($Na_2SeO_3{\cdot}H_2O$) was used to prepare the Se(IV) solutions while sodium selenate (Na_2SeO_4) was used as the Se(VI) source. The organic compounds used were formic acid, acetic acid, salicylic acid, methanol, ethanol, and sucrose. 5×10^{-4} M copper(II) sulfate and 0.1 M sodium hydroxide solutions were used as two scrubbers in series to trap the hydrogen selenide gas from the system, which was only generated when all the Se ions were exhausted from the solution [30]. In the $CuSO_4$ scrubber, the H_2Se gas would be removed from the system by reacting with Cu^{2+} to form copper selenide precipitate. The NaOH scrubber would provide an alkaline condition to dissolve any remaining H_2Se that might have escaped the $CuSO_4$ scrubber. The chemicals were used without further purifications. Deionised pure water was used for the preparation of all solutions. The pH of the solution was adjusted between pH 2.0–5.0 using sodium hydroxide and perchloric acid as the perchlorate ions were found to have minimal adsorption onto the TiO_2 particles [32].

2.2. Photoreactor and experimental procedure

Two different reactors were used in the current study: one was for the Se ions photoreduction study and the other one was to study the organic mineralisation. The schematic of the experimental setup for the Se ions photoreduction experiments has been illustrated elsewhere [30]. The glass reactor is cylindrical in shape with 1.2 l capacity. A side quartz-window enables UV illumination from a 200 W mercury lamp (Oriel 66001-373) into the reactor. The lamp mainly provides irradiation of wavelength below 380 nm. The photon flux into the reactor was determined to be 3.08 μmol photon/sec by chemical actinometry [33–35]. The reactor was placed on top of a magnetic stirrer for agitation, while the purging of nitrogen gas introduced from the top of the reactor maintained an anoxic environment while providing additional agitation. The required concentrations of the Se ions and organics were made up to 1 l test solution. This was followed by the addition TiO_2 powder (1.1 g TiO_2/l) and pH adjustment. The suspension was allowed to mix for 30 min prior to illumination to allow sufficient time for Se ions adsorption onto TiO_2. After illumination, samples were taken from the suspension at regular time intervals and immediately filtered through a 0.22 μm Millipore filter. The filtrate and residue were analysed as required.

A spiral reactor capable of measuring CO_2 generation in situ was used to study the mineralisation of the organic compounds under an anoxic environment. The reactor consisted of a glass coil (borosilicate tubing, 5.0 mm inside diameter, 6.0 mm outside diameter) of 300 ml. A blue–black light fluorescent lamp (NEC, 15 W, maximum emission at ∼350 nm, emission range 300–400 nm) fitted through the centre of the glass coil was used for the illumination of TiO_2 suspensions. The suspension of TiO_2 (2.0 g TiO_2/l, 150 ml) was adjusted to pH 3.0 prior to the reaction using perchloric acid. Nitrogen was then purged through the system for 1 h, followed by the introduction of the organic compound into the suspension. The photocatalyst suspension containing the organic was circulated through the reactor for 10 min to allow for uniform mixing, after which the lamp was switched on. The amount of carbon dioxide generated during the reaction was detected by an online conductivity meter (Alpha 800). Conductivity readings were converted to the mass of carbon dioxide generated (in terms of mass of carbon) by means of a calibration curve. Each experiment was duplicated to ensure the reproducibility of the results. A more thorough explanation of the experimental procedure has been given in another publication [1].

2.3. Analysis

The total Se concentration (Se(IV) or Se(VI)) in the filtrate was determined by Varian induced coupled plasma-atomic emission spectroscopy (ICP-AES). Total organic concentration was determined by analysing the total organic carbon (TOC) in the solution using Anatoc II TOC analyser.

3. Results and discussion

Previous investigations by the same authors [30,36] found that the photocatalytic reduction of Se(VI) and Se(IV) to elemental Se only occurred in the presence of formic acid and was significantly enhanced in the absence of oxygen. The photoreduction was evident by the colour change of the white suspension to an orange–pink colour. The orange–pink colour particles were identified to be elemental Se by Energy Dispersive X-ray analyser (EDX) in-built in a Transmission Electron Microscope (TEM). In the absence of formic acid, no Se ions photoreduction was observed and the removal of the Se anions was solely attributed to adsorption. Se(IV) removal by adsorption and photoreduction was found to be higher than that of Se(VI).

The photoreduction and dark adsorption of Se ions in the presence of the various organic additives were performed in an anoxic environment and the experimental results are summarised in Table 1. The photocatalytic reduction experiments involving Se(IV) are discussed first. It can be seen in Table 1 that after 120 min of irradiation, when formic acid was used as the organic additive, the greatest amount of Se(IV) was removed from the system (Set 1). The second highest amount of Se(IV) removed was observed with experiments using methanol (Set 2) and the least with ethanol (Set 3). The colour change from white to orange pink of the system was also observed for these three experiment sets, indicating the reduction of Se(IV) ions to elemental Se. However, in the cases of acetic acid (Set 4), salicylic acid (Set 5) and sucrose (Set 6), and also the experimental set with no organic additive (Set 7), no colour change and no further reduction of Se(IV) ions from the solution was observed during and after illumination. Hence, it can be deduced that the Se(IV) removal in Sets 4–7 was solely attributed to adsorption. In addition, as it can be seen in Table 1, it was found that the amount of organics mineralised was related to the amount of Se ions reduced; a greater reduction of Se ions corresponded to a greater extent of organic mineralisation, showing the synergism of the photocatalytic redox reactions. Negligible amount of organic mineralised was observed for Sets 4–7. This prompted the suggestion that the mere presence of an organic compound was not sufficient for effective photocatalytic reduction of Se ions.

Table 1
Results of the adsorption and photocatalytic reduction of Se anions in the presence of various organic additives

Set	Organic additives	Adsorption experiments				Photocatalytic reactions (120 min)			
		Se anions adsorbed (mg/g TiO_2)		Organic adsorbed (mg C/g TiO_2) in presence of Se anions		Se ions concentration remaining in solution (ppm)		TOC remaining in solution (ppmC)	
		Se(IV)	Se(VI)	Se(IV)	Se(VI)	Se(IV)	Se(VI)	Se(IV)	Se(VI)
1	Formic acid	6.87	3.63	0.73	2.31	1.98	2.76	287	291
2	Methanol	7.71	4.52	ng	ng	7.72	10.28	291	296
3	Ethanol	7.78	4.45	ng	ng	9.02	12.45	292	298
4	Acetic acid	7.69	4.36	ng	ng	12.26	15.03	298	301
5	Salicylic acid	7.85	4.47	ng	ng	12.23	15.78	303	301
6	Sucrose	7.79	4.56	ng	ng	12.42	15.45	305	303
7	Nil	7.84	5.52	Nil	Nil	12.44	15.02	302	302
Error (%)		±2.0		±5.0		±2.0		±5.0	

Experimental conditions: 20 ppm initial Se anions concentration, 300 ppmC initial organic concentration, pH 3.0, 1 l test solution, 1.1 g TiO_2/l, N_2 purging, 293 K. ng: negligible.

Table 2
The comparison between the individual adsorption of the organic additives and the simultaneous adsorption of Se(IV) ions and the organic additives

Organic additives	Adsorption of the organic additives (mg C/g TiO_2)	Adsorption of the organic additive in the presence of Se(IV) (mg C/g TiO_2)
Sucrose	0.74	–
Acetic acid	1.38	–
Salicylic acid	1.12	–
Formic acid	2.84	0.73
Methanol	0.56	–
Ethanol	0.68	–

Experimental conditions: 20 ppm initial Se(IV) concentration, 300 ppmC initial organic concentration, pH 3.0, 1 l test solution, 1.1 g TiO_2/l, N_2 purging, 293 K.

The fastest Se(IV) photoreduction rate when formic acid was used could be attributed to a number of factors. Unlike the other studied organic compounds, formate ions could compete with Se(IV) ions for the TiO_2 surface. The amount of Se(IV) adsorbed was 6.87 mg/g TiO_2 and that of formic acid was 0.73 mg C/g TiO_2 (see Table 1). When the other organics compounds were used (Sets 2–6), their extent of adsorption was found to be negligible and the adsorption of Se(IV) in the presence of those organic compounds was similar to that in the absence of the organic compounds, at an average value of 7.75 mg/g TiO_2. Table 2 presents the results of the amount of organic adsorbed onto TiO_2 in the absence and presence of Se(IV). The adsorption results in the absence of Se(IV) showed that all of the studied organic compounds adsorbed significantly onto TiO_2 surface, with formic acid adsorbed the most followed by acetic acid and salicylic acid, and a similar amount of methanol, ethanol and sucrose. However, only formic acid was adsorbed significantly in the presence of Se(IV). This could be rationalised by the fact that formic acid was a small molecule and could be ionised into the negatively charged formate ions ($pK_a = 3.77$) at pH 3.0, hence, its ability to be adsorbed onto the positively charged TiO_2 surface [30]. The other organic compounds were either less likely to form negatively charged ions at the studied pH or/and too big to compete with Se(IV) and Se(VI) for the TiO_2 surface [37]. This indicates the importance of organic adsorption on the TiO_2 surface to ensure its effectiveness as a hole scavenger for photocatalytic reduction of selenite.

From the results in Table 1, even though the methanol and ethanol did not show significant adsorption on the TiO_2 surface, Se(IV) photoreduction was still observed to occur. Prairie et al. [22] have suggested that the rate of photoreduction was faster when a more easily photooxidised hole scavenger was used. Hence, a possibly higher rate of mineralisation of the organic compounds, for example methanol and ethanol, in an anoxic environment might explain the effectiveness of them as the hole scavenger in the photoreduction of Se(IV), even without themselves being adsorbed. The rate of photomineralisation of the six selected organic compounds in an anoxic environment and in the absence of Se(IV) ions was studied. The results are summarised in Fig. 1. It can be seen that formic acid could be mineralised in the presence of nitrogen and showed the fastest mineralisation rate, of which complete mineralisation of 15 mg carbon was achieved in about 40 min. Acetic acid was also found to have high mineralisation but slower than that of formic acid. Methanol, ethanol, sucrose and salicylic acid showed little mineralisation.

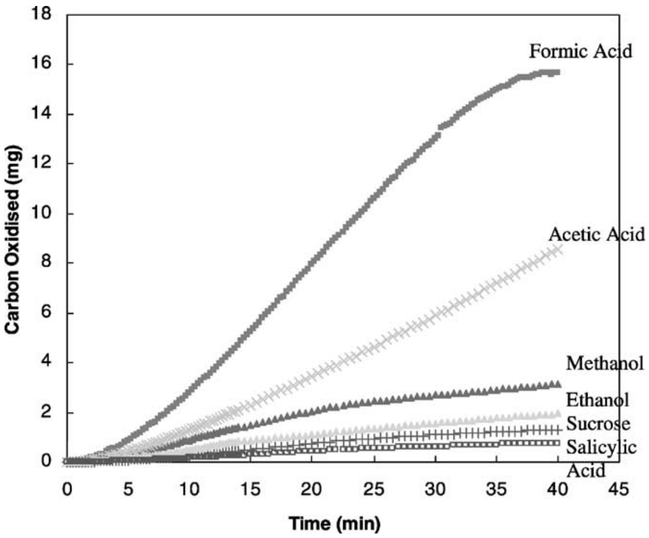


Fig. 1. The extent of mineralisation of various organic compounds in the presence of nitrogen. Experimental conditions: 15 mg carbon of organic used, 0.15 l test solution, 2.0 g TiO_2/l, N_2 purging, pH 3.0.

The reason for the greater mineralisation of formic and acetic acids in an anoxic environment was attributed to their abilities to react with the TiO_2 lattice oxygen [38,39]. In comparison with the mineralisation of formic acid, the lower mineralisation of acetic acid was due to the formation of intermediate compounds (such as methane and ethane) instead of just carbon dioxide and water (as in the case of formic acid). Other studies involving the photooxidation of alcohol, using propanol as an example, found that the presence of gaseous oxygen was crucial for its mineralisation [40]. Penpolcharoen et al. [41] suggested that the low sucrose mineralisation in anoxic environment was due to the formation of intermediates that could block the active surface sites. These intermediates might require oxygen to be further degraded [41]. The importance of oxygen for the mineralisation for methanol, ethanol, sucrose and salicylic acid might explain their limited mineralisation in an anoxic environment.

The photomineralisation result (in the absence of Se ions) shows another positive characteristic of formate ions as an effective hole scavenger. In addition to its ability to compete with Se ions to adsorb on TiO_2 surface, formate ions can be easily mineralised in an anoxic environment. However, for the case of acetic acid, despite its high photocatalytic mineralisation in anoxic environment, the photoreduction of Se(IV) or Se(VI) ions was not observed in its presence. As shown previously in Tables 1 and 2, acetic acid adsorption was negligible in the presence of Se ions. This indicates that to be an effective hole scavenger, the organic compound has to be able to adsorb on the TiO_2 surface as well as can be mineralised easily in that environment.

The insignificance adsorption (dark adsorption) of methanol and ethanol in the presence of Se ions and their limited amount mineralised in anoxic environment suggested that these organic compounds would have another role in assisting the photocatalytic reduction of Se ions. It is therefore suggested that the ability of these organic compounds to form reducing radicals by reacting with hydroxyl radicals could play an important role in the photoreduction of Se ions. The formation of reducing radicals from formate and alcohols by the reactions with hydroxyl radicals has been well discussed in literature [24,42] and has been shown to contribute to the photoreduction of Cd ions [18]. Formate ions could form reducing radicals more effectively than the alcohols [24]. The redox potentials of the radicals formed from formate, methanol and ethanol with respect to the Se ions are depicted in Fig. 2. These reducing radicals have potentials greater than that of the Se(IV)/Se(0) and Se(VI)/Se(0) redox couples and hence thermodynamically are capable of reducing the Se ions.

It is interesting to see that even though acetic acid had a greater extent of mineralisation than methanol or ethanol under N_2 environment and in the absence of Se(VI) and Se(IV) (refer to Fig. 1), no Se ions reduction was observed when it was used as the hole scavenger. This could be attributed to the fact that acetate ions could not compete with Se(VI) and Se(IV) for adsorption on TiO_2 surface and also that it is not capable of forming reducing radicals due to the absence of hydrogen at the α-carbon position. Similarly, sucrose and salicylic acid do not adsorb onto TiO_2 and cannot form reducing radicals. From Table 1, the increase in the rate of Se ions reduction in the presence of the different organics follows the order of formate > methanol > ethanol. This is in agreement with another study [18] involving the use of these three organic compounds as the hole scavengers. They explained their observation by relating the photocatalytic activity to an increase in the extent of hydrogen abstraction to form reducing radicals from formic acid, ethanol and methanol.

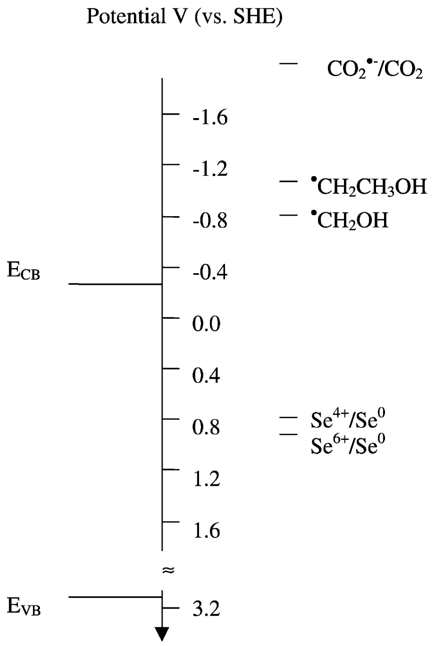


Fig. 2. Relative position of the conduction band and valance band edges for TiO_2 in a pH 3 aqueous medium and selected redox levels [18,43].

The photoreduction and adsorption of Se(VI) were found to follow similar trends to those of Se(IV), although less Se(VI) ions were removed from solution compared to the Se(IV) system for the same organic additive. This can be explained by the greater adsorption of Se(IV) ions due to the difference in the ionic structure of the two ions [36]. The extent of Se(VI) photoreduction was found to be higher in the presence of formate compared to methanol and ethanol. It was found that formate ions could competitively adsorb onto the TiO_2 surface while the other organic additives could not significantly adsorb in the presence of selenate and selenite ions.

To summarise the above findings, it can be deduced that the factors for efficient Se ions photoreduction were adsorption of the organic compounds, ease of mineralisation of the organics and/or the organics' ability to form reducing radicals. Formic acid was found to be the best organic additive in achieving efficient Se ions reduction. This could be attributed to its ability to simultaneously adsorb with Se(VI) and Se(IV) on the TiO_2 surface in the form of formate ion, and its ease of mineralisation, rendering it an effective hole scavenger. In addition, it is also suggested that formate could efficiently form highly reducing radicals by scavenging the hydroxyl radicals formed (a hole scavenging process). For the case of methanol and ethanol, even though they were not significantly adsorbed (Table 2), their abilities to form reducing radicals with hydroxyl radicals resulted in some Se ions photoreduction with efficiencies lower than that of formic acid.

Further studies were carried out for the above systems using formic acid, methanol and ethanol in the photoreduction of Se ions. These involved varying the organic concentrations as well as the reaction system pH. The results are presented in Figs. 3 and 4, respectively. From Fig. 3, as was observed earlier, the extent of Se(IV) photoreduction in 120 min, with respect to the types and at different concentrations of organic additives used, was again in the increasing order of formic acid > methanol > ethanol. From Fig. 3, it can also be observed that increasing the organic concentration resulted in an increase in the amount of Se(IV) reduced. The latter observation could be attributed to the increase in mass transfer of the organic compounds to the TiO_2 surface at higher organic concentration, hence, resulting in an enhanced hole scavenging and possibly an enhanced formation of the reducing radicals.

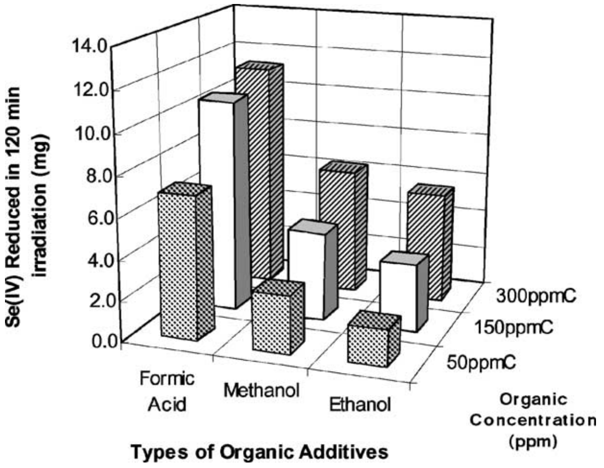


Fig. 3. Photocatalytic reduction of Se(IV) in various concentration of formic acid, methanol and ethanol at pH 3.0 in 120 min. Experimental conditions: 20 ppm initial Se(IV) concentration, 1 l test solution, 1.1 g TiO_2/l, N_2 purging, 293 K.

Fig. 4 shows the experimental results for Se(IV) and formate ions adsorptions and the extent of Se(IV) photoreduced at four pH values ranging from pH 2.2–5.0. The adsorption results will be discussed first. The Se(IV) adsorption decreased with increasing pH while the opposite trend was observed for formate adsorption. The lower Se(IV) adsorption found at higher pH could be explained in terms of the increase in the negativity of TiO_2 surface charge and the greater formate ionisation. An increase in the TiO_2 surface negativity caused a decrease in Se(IV) adsorption. A greater formate ionisation at the higher pH resulted in greater formate ion adsorption, hence contributing to the overall decrease of Se(IV) adsorption due to the competitive adsorption of Se(IV) and formate ions [30]. Similar observations were encountered for Se(VI) ions.

An optimum pH value corresponding to the highest extent of Se(IV) photoreduction was encountered at pH 4.0 even though the amount of Se(IV) adsorbed was not as high as those at the lower pH values. This shows that an optimum ratio of Se(IV) and formate ions on the TiO_2 surface is essential to achieve a maximum photocatalytic reduction of Se(IV), confirming the fact that the most efficient electron–hole scavenging condition would result in efficient Se(IV) photoreduction. This phenomenon was also encountered in our previous investigation involving Se(VI) photoreduction. The detailed discussion on the need of an optimum ratio for Se(VI) photocatalytic reduction was presented elsewhere [30].

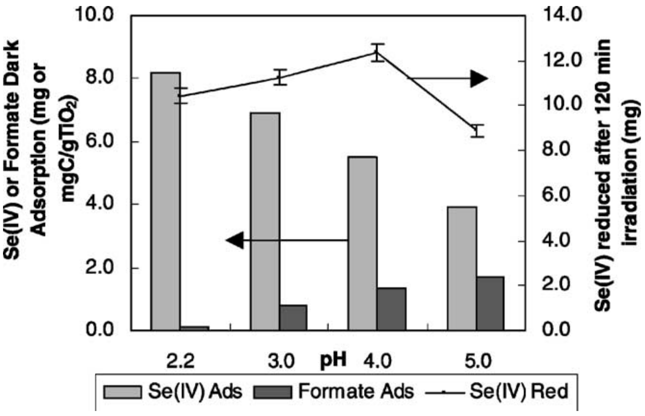
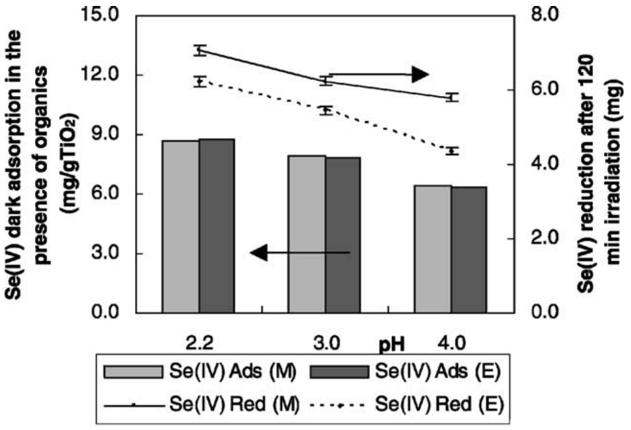
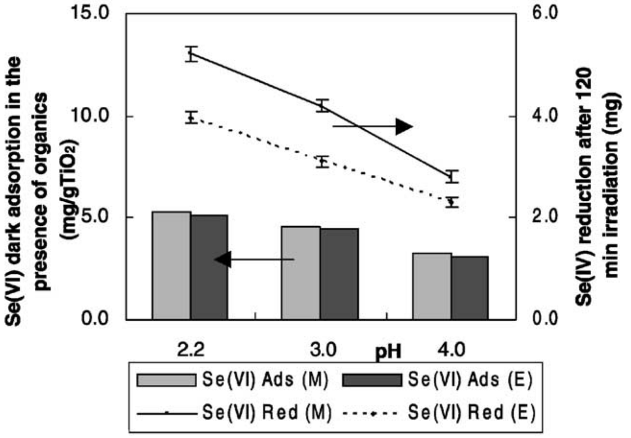


Fig. 4. Se(IV) photoreduction at various pH and 300 ppmC formic acid. 20 ppm initial Se concentrations, 1.1 g/l TiO_2, 293 K, 1 l test solution, N_2 purging.



(a) Se(IV) experiments.



(b) Se(VI) experiments.

Fig. 5. Comparison of Se ions dark adsorption and reduction at various pH and 300 ppmC methanol and ethanol; 20 ppm initial Se(IV) concentrations, 1.1 g/l TiO_2, 293 K, 1 l test solution, N_2 purging.

The effect of pH on the extent of Se ions photoreduction in the presence of methanol and ethanol was also carried out. Fig. 5a and b show the results for adsorption and photoreduction of Se(IV) and Se(VI) ions respectively in the presence of methanol and ethanol in the pH range of 2.2–4.0. The adsorption of Se ions in the presence of methanol and ethanol was found to decrease with increasing pH owing to an increase in the net surface negative charge of TiO_2. It can also be seen that, for the same pH value, the amount of Se(IV) adsorbed was similar in the presence of methanol and ethanol (Fig. 5a). This observation also applied to the Se(VI) ions (Fig. 5b) and suggested that both methanol and ethanol did not affect the Se ions adsorption. It has also been found that in the presence of Se ions, negligible methanol and ethanol was adsorbed in the investigated pH range.

Upon UV illumination, the extent of Se ions photoreduction in the presence of methanol was greater than that of ethanol at the range of pH values investigated. This can be explained in terms of the faster rate of hydrogen abstraction to from reducing radicals for methanol compared to ethanol as discussed earlier. The extent of Se(IV) photoreduction was also faster than that of Se(VI). It was also found that the highest amount of Se ions reduced after 120 min illumination occurred at the lowest pH investigated (a value of 2.2), while the least Se ions reduced was encountered at pH 5.0. These corresponded to the highest and the least amount of Se ions adsorbed respectively. This further suggests that the role of formic acid in the Se ions photoreduction is different from that of methanol and ethanol. In order to maximise its ability as an effective hole scavenger, the amount of formic acid present on the TiO_2 surface had to be optimised. Since methanol and ethanol could not adsorb on the TiO_2 surface in the presence of Se ions, the role of these organic compounds in the photoreduction of Se ions was mainly through their ability to form reducing radicals. Hence, a pH condition that promotes good Se adsorption would result in efficient Se ions reduction.

4. Conclusions

The photocatalytic reduction of Se(VI) and Se(IV) to elemental Se was performed using sucrose, acetic acid, salicylic acid, formic acid, methanol and ethanol. Photoreduction was only observed in the presence of formic acid, methanol or ethanol and the rate of Se ions photoreduction was found to be in the order formic acid > methanol > ethanol. The reason for formic acid being the most efficient hole scavenger is postulated to be due to its ability to compete with Se ions for TiO_2 surface, its fast mineralisation rate and its ability to form reducing radicals quickly. Even though methanol and ethanol did not adsorb significantly in the presence of Se ions and were not easily mineralised, their presence enabled the reduction of Se ions due to their ability to form reducing radicals. Increasing the concentration of the organic additives resulted in greater extent of Se(IV) reduction for all the three organic compounds used. When formic acid was used, optimum pH values at pH 3.5 and 4.0 were encountered for the Se(VI) and Se(IV) photoreduction, respectively. This was explained in terms of the role of formate ions as the hole scavenger, which required optimum amounts of Se and formate ions to be on the surface in order to maximise electrons and holes transfer. When methanol and ethanol were used as the hole scavenger in the pH range of 2.2 to 4.0, the greatest extent of Se ions photoreduction was encountered at pH 2.2 which corresponded to the highest amount of Se ions adsorbed. This shows that methanol and ethanol have a different role compared to formic acid in the photoreduction of Se ions.

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