

Aqueous Phase Thiosulfate Removal Using Photo catalysis

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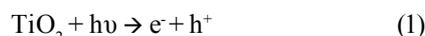
ABSTRACT: Removal of thiosulfate ($S_2O_3^{2-}$, 200 mg/L) from simulated wastewater samples was investigated under varying co-pollutants and pH conditions employing the titanium dioxide (TiO_2) mediated photocatalysis. For thiosulfate only studies higher substrate removal was noted at lower pH with a specific trend of pH 4 > pH 7 > pH 10. Furthermore, near complete thiosulfate removal was also achieved at pH 4. A similar thiosulfate removal trend was also noted for the binary thiosulfate & *p*-cresol and thiosulfate & thiocyanate systems at pH 4, indicating high photocatalysis process efficiency. However, thiosulfate removal from the mixed systems at pH greater than 4 was slower as compared to the respective thiosulfate only systems. Nevertheless for the binary thiosulfate & thiocyanate system, significant thiosulfate removal was noted even at pH 12 when the thiosulfate concentration was reduced to 40 mg/L.

Key words: TiO_2 , *p*-Cresol, Thiocyanate, Advanced Oxidation, pH

INTRODUCTION

The presence of thiosulfate ($S_2O_3^{2-}$) in industrial wastewaters from sources such as petroleum refineries, photo-processing, mining, paper industry, coal processing, etc., remains a matter of concern because thiosulfate can exert a high biochemical oxygen demand. Hence if released without treatment thiosulfate can significantly reduce the dissolved oxygen levels in the receiving water streams thus posing serious ecological and aesthetics challenges. Considering this, the removal of thiosulfate from respective wastewaters is often sought to avoid the related environmental concerns (Schreiber and Pavlostathis, 1998). Furthermore the presence of thiosulfate with co-pollutants cresols and thiocyanate (SCN^-) has also been noted in several industrial effluents, with respective treatment often posing a challenge (Berne and Cordonnier, 1995; Chao *et al.*, 2006). Advanced oxidation processes (AOPs) that have been extensively tested and used for the treatment of several industrial effluents could provide an alternative treatment strategy for the above mentioned mixed waste streams. The titanium dioxide (TiO_2) assisted photocatalytic degradation (PCD) process which is an AOP technology has also been investigated for the removal of aqueous phase pollutants, and its mechanistic details have been described in detail by several researchers (Abdullah *et al.*, 1990; Matthews, 1993; Serpone *et al.*, 1993; Hoffmann *et al.*, 1995). In brief, upon exposure to a near UV radiation (~352 nm) the photocat-

alyst TiO_2 absorbs the light energy and produces an e^-/h^+ pair (electron/hole pair; Equation 1):



The h^+ species that is electron deficient reacts with an adsorbed hydroxyl molecule OH^- on the TiO_2 surface and in turn produces an $\bullet OH$ radical:



The produced $\bullet OH$ radicals are powerful and non-selective oxidants that can typically remove both organic and inorganic pollutants from the concerned wastewaters (Turchi and Ollis, 1990; Serpone *et al.*, 1995; Vohra and Tanaka, 2001). Removal of thiosulfate from the above mentioned industrial wastewater streams are also required to avoid the related environmental concerns. Though use of thiosulfate has been mentioned in several photocatalysis studies under varying subjects including hydrogen production, fixing reagent, hole scavenger, and co-pollutant (Borgarello *et al.*, 1985; Sabaté *et al.*, 1990; Linkous *et al.*, 1995; Huang *et al.*, 1996; Wang *et al.*, 1997; Iliev *et al.*, 2003; Troupis *et al.*, 2003), nevertheless a specific study that compares photocatalysis results from thiosulfate only systems and mixed systems containing thiosulfate, cresols and thiocyanate, has not been completed to the best of our knowledge. Considering this we have investigated the efficiency of PCD process for the removal of thiosulfate both from single systems and binary systems (containing co-pollutants *p*-cresol and

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thiocyanate) under varying pH conditions. Some information that is pertinent to the PCD initiated removal of co-pollutants *p*-cresol and thiocyanate, has also been presented.

MATERIALS & METHODS

All chemicals used for the present study were of high purity reagent grade quality. The major chemicals included titanium dioxide P25 (TiO₂; DEGUSSA), sodium thiosulfate (Na₂S₂O₃·5H₂O; BDH), potassium thiocyanate (KSCN; BDH), *p*-cresol (C₆H₄CH₃OH; FISHER), sodium carbonate (Na₂CO₃; BDH), sodium bicarbonate (NaHCO₃; BDH), pH calibration standards (FISHER), and 1-Butanol (C₄H₁₀O; BDH). The PCD experiments were conducted using a batch type (Pyrex glass) reactor holding 1000 mL of the respective synthetic wastewater sample batch with TiO₂. Fig. 1 provides the reactor details. Batches of synthetic wastewater samples were prepared using high purity water (CORNING Mega Pure™ System) and stock solutions of respective chemicals. For all PCD experiments 1 g TiO₂ was suspended in 1 L synthetic wastewater batch using a magnetic stirrer setup. The initial suspension pH was measured and adjusted to the desired value. For each experiment, two blank samples were collected from the respective wastewater batches, i.e., first one before the addition of TiO₂ and second one after the addition of TiO₂ and initial pH adjustment. These steps accounted for any initial substrate adsorption on to TiO₂ at the given initial pH. The synthetic wastewater batch with TiO₂ was then transferred to the PCD reactor and again subjected to continuous stirring using a magnetic stirrer setup. A 15 W near UV light lamp (F15T8-BLB 15 W, SANKYO DENKI, Japan) that emits rays at wavelength 315–400 nm with peak maximum at ~352 nm was then positioned at the centre of the reactor while it is being separated from the synthetic wastewater batch using a glass sleeve. The UV lamp was then turned on and during the course of photocatalysis several samples were collected through the sampling port (Fig. 1). between reaction time 0 and 360 min. Each collected sample was first filtered through a 0.2 μm cellulose nitrate membrane filter (WHATMAN, Germany) and then analyzed for the target pollutants. The thiosulfate and thiocyanate species were analyzed using an Ion Chromatograph setup (IC 761, METROHM, Switzerland) that was equipped with a conductivity detector. A Metrosep Anion Dual 2 IC column 4.6 mm x 75 mm (6.1006.100, METROHM, Switzerland) was used for the respective analyses. The eluent composition was 3.5 mM Na₂CO₃/1 mM NaHCO₃ and eluent flow rate was 1 ml/min. The IC system was regularly calibrated using appropriate calibration standards prepared using the respective reagent grade chemicals. The *p*-cresol species was analyzed using a

UV-Vis Spectrophotometer setup (UV-1601 PC, SHIMADZU, Japan). The target sample was transferred to the test cuvette and absorption peak at wave length of 270 nm was noted and used for the respective analysis. The total organic carbon was analyzed employing a standard TOC analyzer system (TOC-VCSN, SHIMADZU, Japan) that also incorporates an infrared detector and internal calibration system. The TOC system was calibrated employing the manufacturer-supplied standards. The pH analyses were completed using a pH meter setup (ORION, U.S.A.) that was regularly calibrated using pH calibration standards. The TiO₂ surface speciation modeling was completed using MINTQA2/PRODEFA2 software from U.S. EPA (Allison *et al.*, 1991). The software incorporates the diffuse layer model as used in the present speciation modeling exercise. The other specific details that are required for modeling purpose have been provided under the results and discussion section.

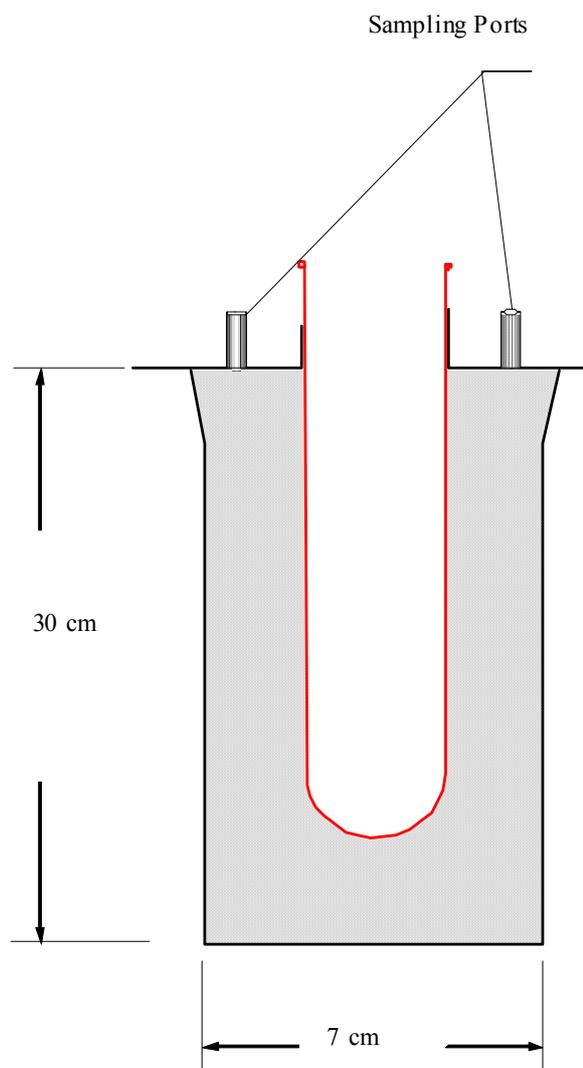


Fig. 1. The reactor layout/details used for the photocatalysis experiments

RESULTS & DISCUSSION

We first conducted thiosulfate only photocatalysis studies at pH 4, 7, and 10. The respective results that are provided in Fig. 2a and Table 1, show higher thiosulfate removal at lower pH with a specific trend of pH 4 > pH 7 > pH 10. For example at pH 4 and pH 10 we observe 98% and 73% thiosulfate removal (at 6 h), respectively. We suggest that degradation of thiosulfate occurs not only in the photocatalyst's near surface region but also transpires in the bulk solution phase. This in conjunction with the pH dependent TiO₂ surface speciation, as indicated by reaction 3 and reaction 4, can possibly explain the pH specific thiosulfate removal trend as noted in Fig. 2a.

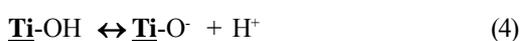


Table 1. Thiosulfate only (200 mg/L) photocatalysis

pH	k (1/min)	R ²	S ₂ O ₃ ²⁻ at 6 h (%)
4	1.12 x 10 ⁻²	0.9933	2
7	0.57 x 10 ⁻²	0.9767	13
10	0.36 x 10 ⁻²	0.9755	27

For Degussa P25 TiO₂ surface acidity constant (Log K_{int}^s) values of -3.9 and -8.7 have been reported for reaction 3 and reaction 4, respectively, along with a surface site density of 2.74x10⁻⁴ moles/g and specific surface area of 55 m²/g (Stone *et al.*, 1993). Using this set of information and employing the MINTEQA2/PRODEFA2 model from U.S. EPA (Allison *et al.*, 1991),

the surface speciation calculations show that the Degussa P25 TiO₂ surface will be positively charged at pH 4, neutral at pH 7, and negatively charged at pH 10 (Fig. 2b). Hence the surface electrostatic conditions at pH 4 and pH 7 should favor adsorption of thiosulfate whereas a negative surface charge at pH 10 is expected to resist thiosulfate adsorption. Indeed the initial thiosulfate adsorption at pH 4 and pH 7 as noted in the present work was approx. 2.2x10⁻⁴ M whereas no notable thiosulfate adsorption resulted at pH 10. We therefore suggest that thiosulfate degradation at pH 10, in spite of its insignificant initial adsorption at that pH, occurs in the bulk solution phase because of reaction with the diffusing •OH radicals. However at pH 4 and pH 7, interaction of thiosulfate both with 1) the near TiO₂ surface •OH radicals (because of an initial substrate adsorption) and, 2) the diffusing •OH radicals (in the bulk solution phase), results in comparatively higher thiosulfate removal. To support this hypothesis that thiosulfate degradation transpires both in the near surface region of TiO₂ and also in the bulk solution phase, two additional PCD experiments were completed at 0.893x10⁻³ M thiosulfate and pH 7; first one with excess 1-butanol (3x10⁻² M) and the second one without it. A comparison between the two experimental findings is given in Fig. 3 and Table 2. Obviously thiosulfate removal 'without 1-butanol' is higher as compared to 'with 1-butanol' study, nevertheless thiosulfate degradation is not completely inhibited in the latter case. However, based on reported •OH aqueous phase reaction rate constant values of 4.2 x 10⁹ M⁻¹s⁻¹ for k[1-butanol + •OH] and 7.0 x 10⁹ M⁻¹s⁻¹ for k[thiosulfate + •OH] from Buxton *et al.* (1988) and us-

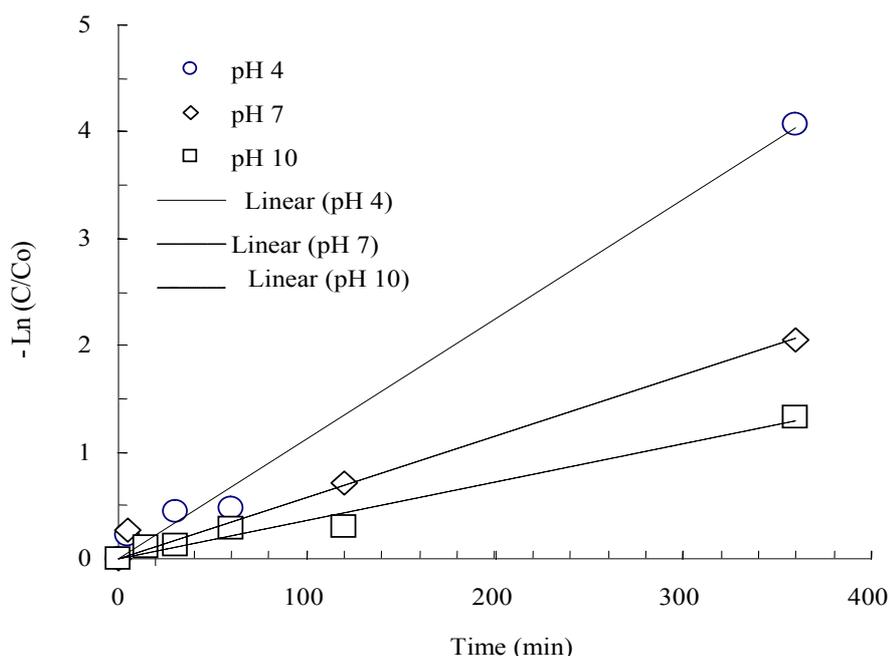


Fig. 2a. Thiosulfate only (200 mg/L) photocatalysis results

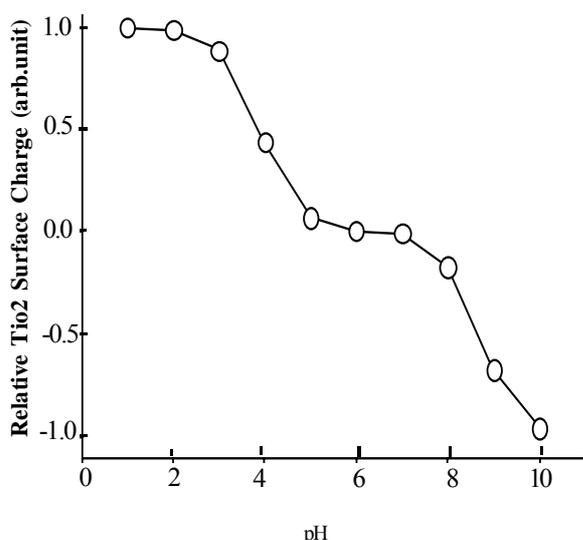


Fig. 2b. Calculated relative TiO₂ surface charge [Using MINTQA2/PRODEFA2 software and considering Ti-OH_2^+ , Ti-OH and Ti-O^- surface species]

ing the respective 1-butanol and thiosulfate concentrations we estimate that approx. 95% of bulk solution phase $\bullet\text{OH}$ radicals should be scavenged by 1-butanol. Hence if thiosulfate degradation were to occur mostly in the bulk solution phase then the presence of 3×10^{-2} M 1-butanol should have significantly reduced former's removal. On the other hand we will expect an insignificant 1-butanol effect on to thiosulfate removal if latter's oxidation were to transpire mostly in the near surface region of TiO₂, which certainly is not the case (Fig. 3 and Table 2). These two observations suggest that degradation of thiosulfate transpires both in the near

surface region of TiO₂ and also in the bulk solution phase. Hence as suggested before, comparatively higher thiosulfate removal at pH 4 and pH 7 possibly results because of simultaneous thiosulfate reaction with $\bullet\text{OH}$ radicals both 1) in the near surface region of TiO₂ and 2) also in the bulk solution phase, whereas comparatively lower thiosulfate removal at pH 10 probably results because of its reaction only with the bulk solution phase $\bullet\text{OH}$ radicals because of an insignificant thiosulfate adsorption at that pH.

We further expanded our study and investigated thiosulfate degradation in the presence of *p*-cresol. As shown in Fig. 4. higher thiosulfate degradation results at pH 4 compared to pH 10, which is similar to Fig. 2a findings. Additionally significant thiosulfate removal does transpire at pH 4 even in the presence of *p*-cresol, indicating high PCD process efficiency. It should however be noted that the overall thiosulfate removal at pH 10 is lower in case of binary system as compared to the respective thiosulfate only system (Table 3 and Table 1, respectively). The possibility of a competitive *p*-cresol degradation causing decreased thiosulfate removal was ruled out because the respective *p*-cresol analysis data had indicated an insignificant removal. An alternative explanation is that at pH 10, presence of an anionic *p*-cresolate species (considering *p*-cresol pK_a of 10.26) and negatively charged TiO₂ surface (considering Fig. 2b data), would render the approach of an already anionic thiosulfate towards the diffuse layer region of TiO₂ even more difficult. This in turn will cause reduced thiosulfate interaction with the $\bullet\text{OH}$ radicals thereby causing the aforementioned comparative decrease in thiosulfate removal at pH 10. As far as the noted insignificant *p*-cresol removal in the pres-

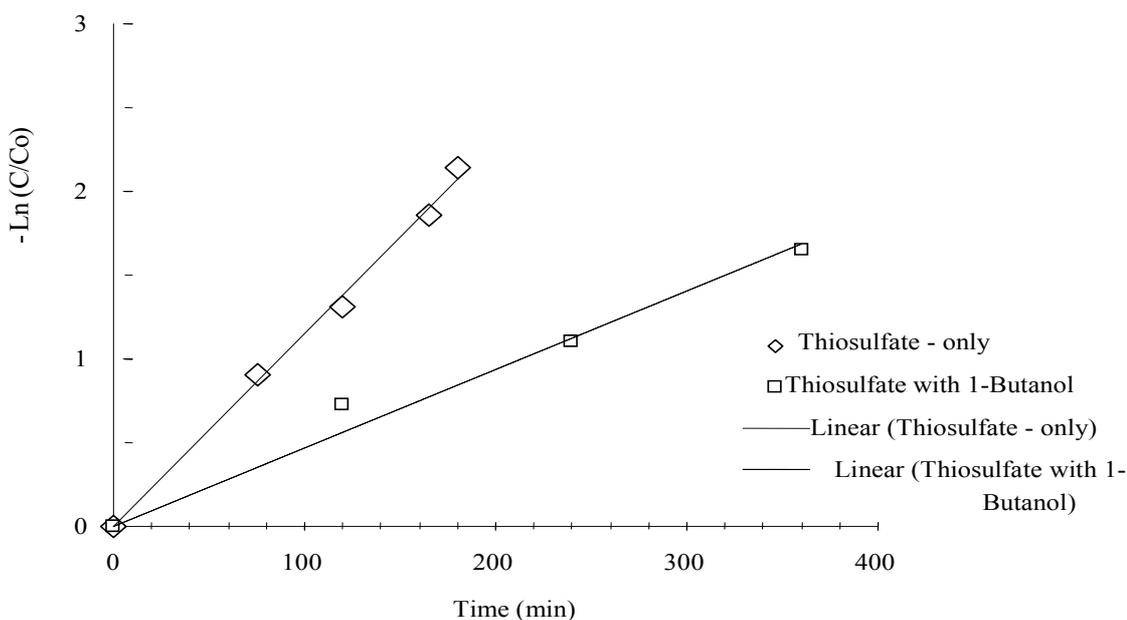


Fig. 3. Thiosulfate (0.893×10^{-3} M/100 mg/L) photocatalysis at pH 7: 1-Butanol (3×10^{-2} M) effect

Table 2 .Thiosulfate (100 mg/L) photocatalysis at pH 7: Effect of 1-Butanol

Condition	k (1/min)	R^2
Without 1-Butanol	1.15×10^{-2}	0.9957
With 3×10^{-2} M 1-Butanol	0.47×10^{-2}	0.9802

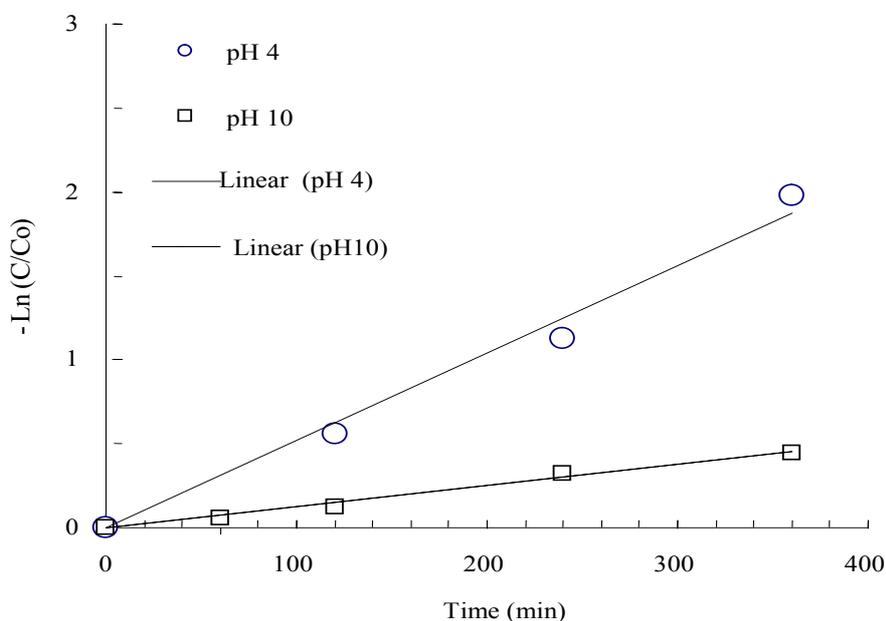


Fig. 4. Thiosulfate (200 mg/L) photocatalysis results in presence of *p*-cresol (20 mg/L)

ence of thiosulfate is concerned it can be explained by a preferential degradation of thiosulfate. [Wang *et al.*, (1997) who studied PCD of phenylmercaptotetrazole also observed reduced removal of the target pollutant in the presence of thiosulfate.] To substantiate this hypothesis, we further investigated the PCD of *p*-cresol only. The pertinent results that are provided in Fig. 5a and Table 4 show 96.5% removal at pH 4, 87.5% removal pH 7, and 64.5% removal at pH 10. Fig. 5b that provides the respective TOC results shows qualitatively similar trends. These observations support the argument that in binary thiosulfate and *p*-cresol systems a preferential PCD of thiosulfate species causes inhibition of *p*-cresol removal. Furthermore significant difference between the pH 4 and pH 10 *p*-cresol removal results (Fig. 5a) can be explained based on the effect of process pH on the overall *p*-cresol adsorption on to TiO_2 . Pulido-Melián *et al.*, (2007) report different adsorption trends for *o*-, *m*-, and *p*-cresol on to TiO_2 with *p*-cresol showing most adsorption. We noted approx. 9% initial *p*-cresol adsorption at pH 4 and insignificant if any at pH 10. Lower *p*-cresol adsorption at higher pH results because of increased electrostatic repulsion between the *p*-cresolate species and negatively charged TiO_2 , which also causes its reduced PCD. It should also be noted that at pH 7 the *p*-cresol remaining at 6 h (Fig. 5a) is lower than the respective TOC value (Fig. 5b), i.e., 12.5% *p*-cresol remaining versus 20% TOC remaining. This trend intensify at pH 10, i.e., 35.5% *p*-cresol remaining versus 53% TOC remain-

ing. This could result because of slower and/or competitive degradation of reaction intermediates, as also noted for *o*-cresol PCD by Arana *et al.*, (2007).

As per our original objective, we also investigated the effect of thiocyanate species on to thiosulfate photocatalysis. The respective results that are provided in Fig. 6 and Table 5 show a significant thiosulfate removal at pH 4 even in the presence of thiocyanate indicating high PCD process efficiency. However, comparing results from Table 1 and Table 5 shows that thiocyanate does lower thiosulfate removal at pH higher than 4. Nevertheless, the respective thiocyanate data showed an insignificant removal. We further explored this point by conducting an experiment at reduced thiosulfate concentration of 40 mg/L and pH 12 (considering it to be a more severe pH case for thiosulfate removal). The respective findings are given in Fig. 7. This time we do note significant removal of both thiosulfate and thiocyanate, however thiocyanate degradation begins only after a near complete thiosulfate removal. For example at 4 h reaction time approx. 98% thiosulfate but only 13% thiocyanate removal is noted. However 74% thiocyanate degradation does transpire at 6 h reaction time. Factors such as differences in the chemical structure and comparative reactivity with the $\bullet OH$ radical species may explain the peculiar behavior noted in Fig. 7. Nevertheless these results do indicate that significant removal of both thiosulfate and thiocyanate species can be achieved employing the PCD process even at pH 12.

Table 3. Thiosulfate (200 mg/L) photocatalysis in presence of *p*-cresol (20 mg/L)

pH	k (1/min)	R^2	$S_2O_3^{2-}$ at 6 h (%)
4	0.52×10^{-2}	0.9852	14
10	0.13×10^{-2}	0.9923	64

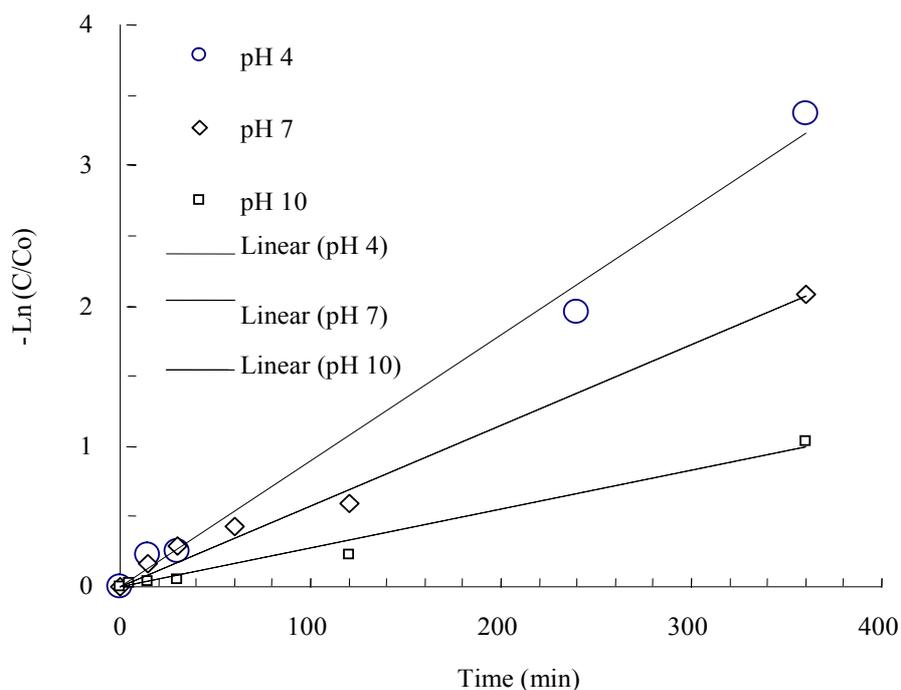


Fig. 5a. *p*-cresol only (20 mg/L) photocatalysis results

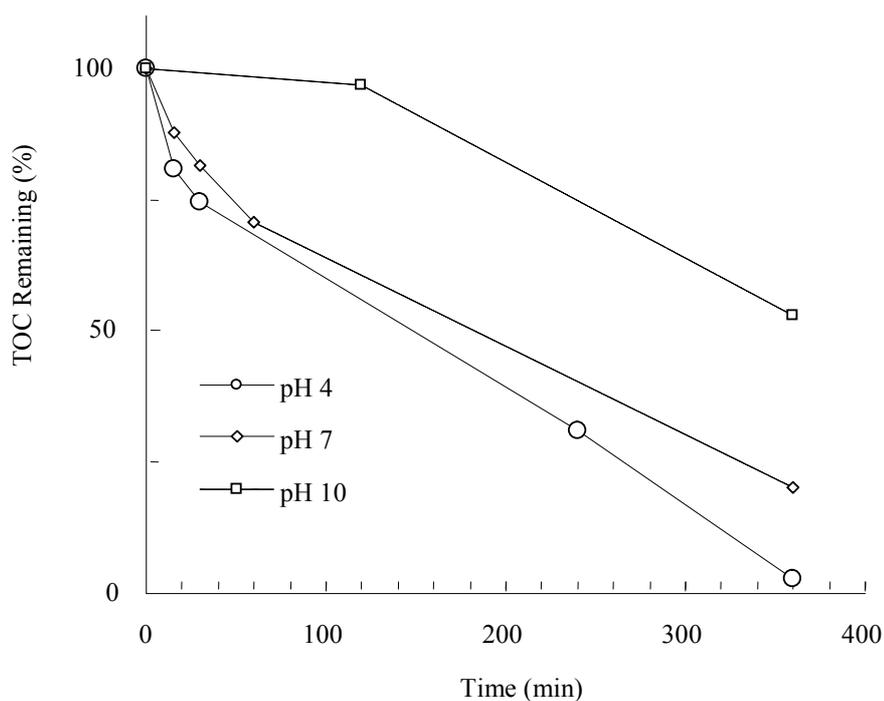


Fig. 5b. TOC results from the *p*-cresol only (20 mg/L) photocatalysis experiments

Table 4. *p*-cresol only (20 mg/L) photocatalysis

pH	<i>k</i> (1/min)	R ²	<i>p</i> -cresol at 6 h (%)
4	0.90 x 10 ⁻²	0.9923	3.5
7	0.58 x 10 ⁻²	0.9878	12.5
10	0.28 x 10 ⁻²	0.9820	35.5

Table 5. Thiosulfate (200 mg/L) photocatalysis in presence of thiocyanate (10 mg/L)

pH	<i>k</i> (1/min)	R ²	S ₂ O ₃ ²⁻ at 6 h (%)
4	1.310 x 10 ⁻²	0.9962	1
7	0.19 x 10 ⁻²	0.9971	52
10	0.20 x 10 ⁻²	0.9972	49
12	0.20 x 10 ⁻²	0.9836	51

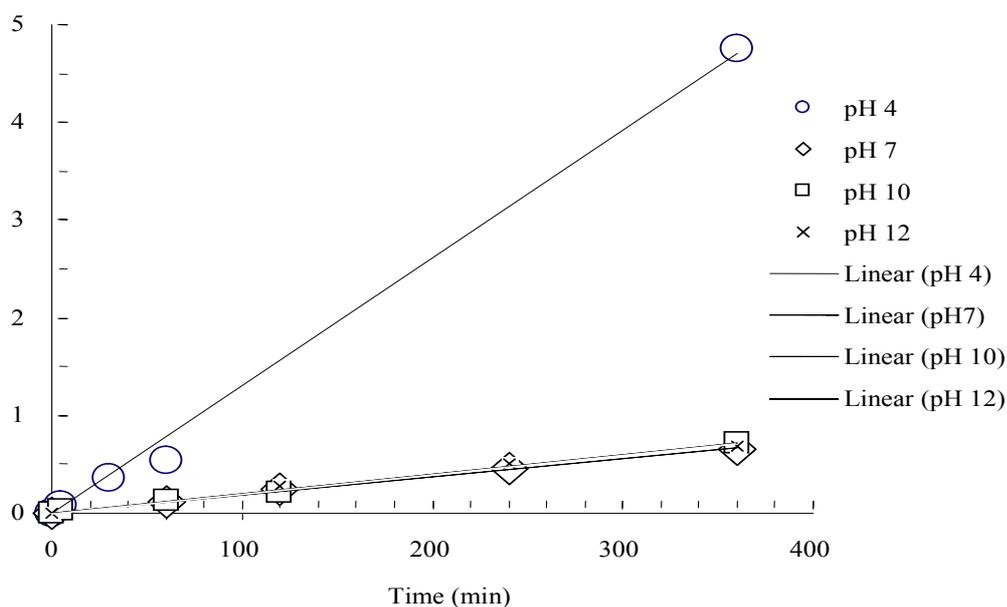


Fig. 6. Thiosulfate (200 mg/L) photocatalysis results in presence of thiocyanate (10 mg/L)

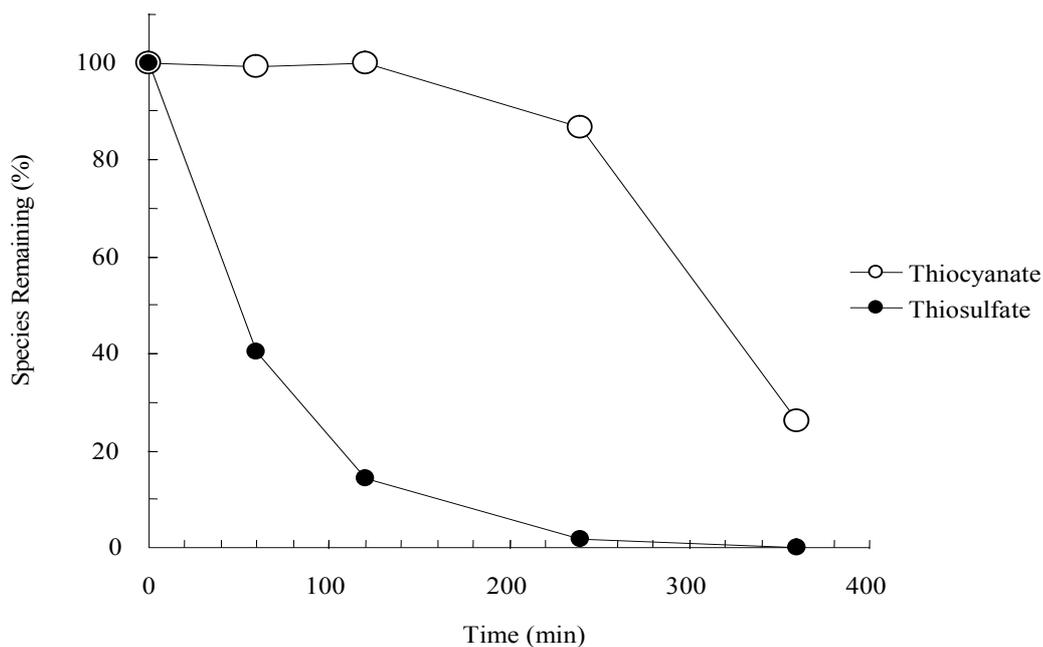


Fig. 7. Thiosulfate (40 mg/L) and thiocyanate (10 mg/L) photocatalysis results at pH 12

CONCLUSION

Removal of thiosulfate (200 mg/L) from simulated wastewater samples was investigated under varying co-pollutants and pH conditions employing the titanium dioxide assisted photocatalytic degradation process. Results from the thiosulfate only systems indicated higher substrate removal at lower pH with near complete thiosulfate removal at pH 4. Findings from the binary thiosulfate & *p*-cresol and thiosulfate & thiocyanate systems at pH 4 showed similar thiosulfate removal trends. However thiosulfate removal from the above mentioned mixed systems at pH values higher than 4, was lower as compared to the respective thiosulfate only systems. Nevertheless for the binary thiosulfate and thiocyanate system, significant thiosulfate removal was noted even at pH 12 when the initial thiosulfate concentration was reduced to 40 mg/L.

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