

Decontamination of hexavalent chromium and tri-ethyl phosphate stimulants through photocatalytic oxidation

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ABSTRACT: In this paper, the photocatalytic decontamination of hexavalent chromium and tri-ethyl phosphate, two important wastewater contaminants, are studied by the ultraviolet / nano-titanium dioxide process. The pH value and synergic effect between the oxidation of tri-ethyl phosphate and the reduction of hexavalent chromium were investigated in different concentrations of tri-ethyl phosphate and hexavalent chromium. Furthermore, the effects of ultraviolet and nano-titanium dioxide were investigated in a solution which contained tri-ethyl phosphate and hexavalent chromium. Results of adsorptions showed that hexavalent chromium was adsorbed better in acidic pH while the better adsorption for tri-ethyl phosphate was occurred in alkalinity pH. The reduction rate of hexavalent chromium was higher in acidic solutions while it was obtained at natural pH for tri-ethyl phosphate. In co-adsorption of hexavalent chromium and tri-ethyl phosphate pollutants, tri-ethyl phosphate slightly increased adsorption of hexavalent chromium, but hexavalent chromium had no influence on the adsorption of tri-ethyl phosphate on nano-titanium dioxide particles. In contrast, tri-ethyl phosphate has an improving effect on the reduction reaction rate of hexavalent chromium which increases with the interaction of the concentration of tri-ethyl phosphate in mixture. The same is true for the oxidation rate of tri-ethyl phosphate.

Keywords: Adsorption; Kinetic reaction rate; Synergetic effect; Ultraviolet / Nano-Titanium dioxide process; Wastewater treatment

INTRODUCTION

Nowadays, an important environmental constrain is the effort to improve water quality and remove pollution from wastewater. This can be done through different physical, chemical and biological treatment processes. These processes are also being used for oxidizing, removing and mineralizing various surfaces and ground waters (Joseph *et al.*, 2009; Ambashta *et al.*, 2010; Sun *et al.*, 2011). A novel method that has become popular in recent decades is the Advanced oxidation processes (AOPs) which are very potent in oxidization, decolorization, mineralization, reducing heavy metals and degrading organic pollutants (Atafar *et al.*, 2010; Gharbani *et al.*, 2010; Nouri *et al.*, 2011). Due to the high oxidation rate of the chemical reactions caused by AOPs, the behavior of the chemicals is significantly

affected after the treatment (Andreozzi *et al.*, 1999; Bang *et al.*, 2005; Gerven *et al.*, 2007; Thiruvengkatachari *et al.*, 2008).

Organophosphate is a very complicated contaminant in wastewater which contains insecticides, pesticides and detergents. These types of pollutants are found in industrial, agricultural and also domestic wastewater. Organophosphate degrades to several intermediate materials; phosphate appears as a solution when it is completely degraded. The Tri-ethyl phosphate (TEP) is an organophosphate which is used as an industrial catalyst, a polymer resin modifier, a plasticizer, an intermediate for pesticides and other chemicals, a stabilizer for peroxides, a strength agent for rubber and plastic including vinyl polymers and unsaturated polyesters, etc (Percherancier *et al.*, 1995; Malato *et al.*, 2000; Kozlova *et al.*, 2004). TEP can be hydrolyzed and

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degraded to mono and diethyl phosphate which are more toxic than TEP.

Heavy metals are also a significant environmental contaminant worldwide such as hexavalent chromium Cr(VI). Cr(VI) and trivalent chromium Cr(III) are two oxidation states of chromium, Cr(VI) is usually highly soluble and highly toxic and is a suspected carcinogen and mutagen (Wuana *et al.*, 2010). In contrast, Cr(III) is relatively insoluble in an aqueous systems and exhibits no toxicity (Ku *et al.*, 2001; Jiang *et al.*, 2006; Xu *et al.*, 2006). The wastewater of pesticide manufacture, including animal poisons, insecticides, fungicides and herbicides, commercially manufacturing, blending, mixing or formulating pesticides usually contain both Chromium and TEP (Chirwa *et al.*, 2000; Kozlova *et al.*, 2004).

Researchers have studied the photocatalytic oxidation of some organophosphorus pesticides (acrinathrin, methamidophos, malathion, diazion, carbetamide, and insecticide fenitrothion) (Kerzhentsev, *et al.*, 1996; Doong and Chang, 1997; Kozlova *et al.*, 2004). The main intermediates in the degradation of pesticides in wastewater have been studied by Percherancier *et al.* (1995). They reported that hydroxylated products and its derivatives as well as products of cyclized through the side chain can be made. The intermediate material in the decomposition of some organophosphate was investigated by Kozlova *et al.* (2004). The previous works show that final products of organophosphate degradation are phosphate, carbon dioxide and water. Moreover, several reports have been presented for the reduction of Cr(VI); the effects of important parameters such as pH values (Chirwa *et al.*, 2000), titanium dioxide (TiO₂) dosage (Khalil *et al.*, 1998), light intensities, dissolved oxygen levels and other operating conditions were investigated (Chenthamarakshan *et al.*, 2000; Colon *et al.*, 2001; Uyguner and Bekbolet, 2004; Wang *et al.*, 2008). There is not any report on type of kinetic reaction rate and effect of different parameters on the TEP photocatalytic reaction rate. Also, there are TEP and Cr(VI) metals in some wastewater streams; therefore studying their adsorption, photocatalytic oxidation and synergic rate are something important and interesting which is yet to be done.

In this work, adsorption of Cr(VI) and TEP over the TiO₂, the simultaneous decontamination of Cr(VI) and TEP by the UV/TiO₂ photocatalytic process and the possibility of synergic effect were investigated.

Furthermore, effects of pH, UV radiation, TiO₂ dosage and operation condition parameters on the TEP and Cr(VI) oxidation reaction rates were studied. At the end, the kinetic reaction rate for the TEP and Cr(VI) as a function of pH and initial concentration was obtained. This research has been done at Amirkabir University, Tehran on 2010.

MATERIALS AND METHODS

Materials and analysis

TEP with over 99.5 % purity and potassium chromate (K₂CrO₄) were obtained from Merck Co. (Germany). Titanium dioxide nano particle (P-25, ca. 80 % anatase and 20 % rutile) with an average particle size of 20 nm was supplied by Degussa, Germany.

The concentration of Cr(VI) was analyzed colorimetrically at a wavelength of 540 nm UV/visible spectrophotometer (Cecil, CE 2501 model 2000, Instruments, UK) following the standard method with 1,5-diphenylcarbazide (Kim *et al.*, 2001). The phosphate concentration was measured by a UV / visible spectrophotometer at a wavelength of 640 nm. The gas chromatograph (GC) equipped with a flame-ionization detector equipped and a WCOT fused silica column (50 m × 250 μm × 0.4 μm) to measure the TEP concentration.

The specific surface area (BET method), specific pore volume and average pore diameter (BJH method) of the TiO₂ nano particle determined by N₂ adsorption-desorption isotherms using a SORPTOMATIC 1990 Series instrument at -196 °C. The X-ray diffraction (XRD) pattern was obtained using a Philips X'Pert diffractometer (X'pert diffractometer using CuK α radiation).

Adsorption measurements

The adsorption value measurements were carried out in a 200 ml glass bottle with 40 mg TiO₂ into 100 ml aqueous solution containing Cr(VI) (40 mg/L) and TEP (30 mg/L). The suspensions were continuously stirred under darkness for 4 h at a constant temperature of 25 °C under five different pH levels which were adjusted to desired values from 2 to 12 using a dilute solution of HCl (0.01N) and NaOH (0.01N). After absorption equilibrium, all samples were centrifuged, and then filtered through 0.2 μm Millipore syringe filters in order to remove the TiO₂ particles. The remaining Cr(VI) and TEP were analyzed to obtain the percent of adsorption via calculation of the mass

balance:

$$\% \text{ adsorption percent} = \frac{C_i - C_o}{C_i} \times 100 \quad (1)$$

Where C_i and C_o are the concentrations of TEP and Cr (VI) [mg/L] in the initial and final liquid, respectively.

Study of photoreaction process

The oxidation of TEP and Cr(VI) were carried out in a batch reactor shown in Fig. 1. The reaction mixture inside the glass bottle was maintained in suspension by shake. Six 15W UV-C lamps were used as a light source and the reactor temperature was stable by means of cooled water at $25.0 \pm 0.1^\circ\text{C}$. The concentration of TiO_2 in the suspension was 0.4 g/L containing Cr(VI) and TEP. The concentration of Cr(VI) and TEP was changed from 25 to 55 mg/L and from 10 to 50 mg/L, respectively.

RESULTS AND DISCUSSION

Structure and surface characterization of TiO_2

The volume and surface area of the TiO_2 nano particle, as determined by N_2 -porosimetry were $0.15 \text{ cm}^3/\text{g}$ and $50.1 \text{ m}^2/\text{g}$, respectively. The surface characteristics and pore size value for the photocatalyst is shown in Table 1. The X-ray diffraction (XRD) pattern of the nano- TiO_2 are shown in Fig. 2 which exhibited strong diffraction peaks at 27° , 36° and 55° (Tompsett *et al.*, 1995; Zhang *et al.*, 2000). Ordinary peaks were exhibited at 25° and 48° indicating that TiO_2 was in the rutile and the anatase phase, respectively. The crystallite size of the prepared particles obtained from the XRD line broadening using Scherrer's equation is 20 nm. The nitrogen adsorption-desorption isotherm and the pore size distribution plot can be seen in Fig. 3 which had characteristics of a type II isotherm.

Adsorption on TiO_2 surface

Adsorption of Cr(VI) on TiO_2

The adsorption amounts of Cr(VI) by TiO_2 particles at different pH values are shown in table 2. The equilibrium adsorption capacity of Cr(VI) on TiO_2 particles were 12.82 %, 7.65 %, and 0.18 % at pH levels of 2, 7, and 12, respectively. These results show that adsorption amounts of Cr(VI) through TiO_2 particles at low pH level was much more than neutral pH. The results have shown good agreement with previous works (Khalil *et al.*, 1998; Chirwa *et al.*, 2000; Colon *et al.*, 2001; Uyguner and Bekbolet, 2004; Wang *et al.*, 2008). The photocatalytic oxidation reaction depends on the amount of adsorption on the surface catalyst, therefore, at lower pH levels the reaction rate were highest.

Table 1: Surface characterization of TiO_2

| Name | $S_{\text{BET}} (\text{m}^2/\text{g})$ | $S_t (\text{m}^2/\text{g})$ | $V_p (\text{cm}^3/\text{g})$ | $D_p (^\circ\text{A})$ |
|----------------------------|--|-----------------------------|------------------------------|------------------------|
| TiO_2 Degussa P25 | 50.1 | 47 | 0.15 | 315 |

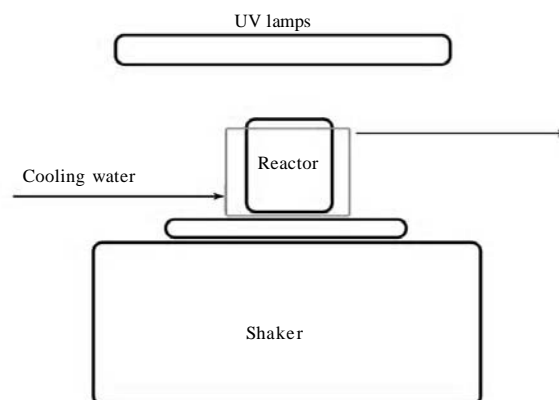


Fig. 1: Schematic diagram of the photocatalysis system

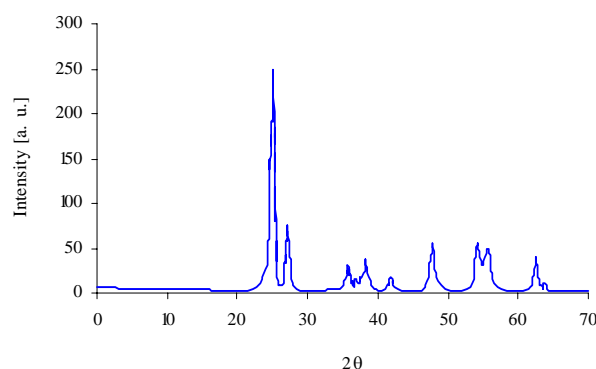
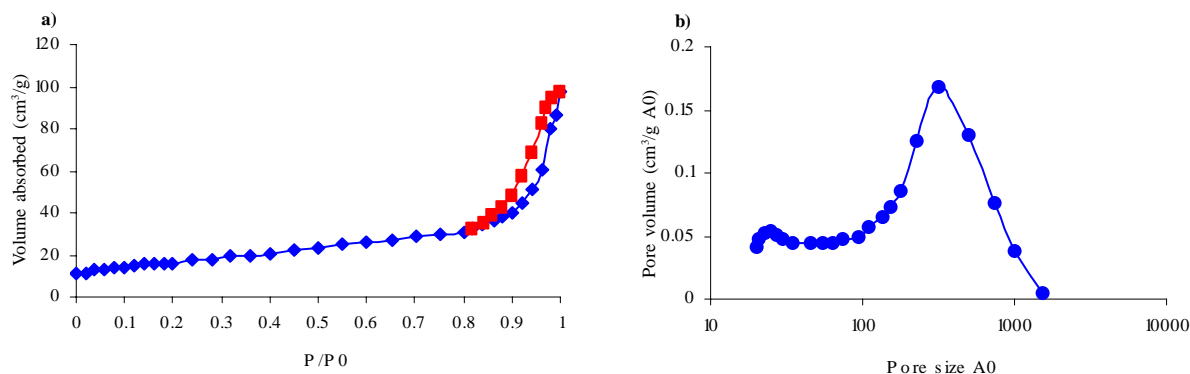


Fig. 2: XRD pattern of TiO_2

Adsorption of TEP on TiO_2

The effect of the pH values on adsorption behavior of TEP on TiO_2 particles was also investigated. TEP adsorption percentage at different pH levels, which was calculated by Eq. 1, is shown in Table 2. At pH value of 12, the adsorption of TEP on TiO_2 particles was highest; therefore, maximum adsorption amounts of TEP on TiO_2 particles will be occurred at alkaline media. At pH value of 2, TEP will be protonized to carry the positive charge while the surface of TiO_2 is electropositive. Therefore at low pH vales the adsorption of TEP on TiO_2 particles does not favor. When pH goes to higher values, TEP comes to a neutral state and adsorption of TEP on TiO_2 surfaces increased.

Fig. 3: a) N_2 adsorption-desorption isotherm of TiO_2 b) Pore size distribution of TiO_2 Table 2: Adsorption of Cr(VI) and TEP on TiO_2 surface ($TiO_2=0.4$ g/L, Cr(VI)=40 mg/L, TEP=30 mg/L)

| pH value | 2 | 4 | 7 | 10 | 12 |
|----------|-----------------|----------------|----------------|----------------|-----------------|
| Cr(VI) | 12.82 ± 0.4 | 7.65 ± 0.3 | 5.57 ± 0.3 | 1.34 ± 0.1 | 0.18 ± 0.03 |
| TEP | 14.01 ± 0.5 | 22.3 ± 0.7 | 24.7 ± 0.7 | 27.2 ± 0.7 | 34.02 ± 0.7 |

Table 3: Co-adsorption of Cr(VI) and TEP on TiO_2 surface ($TiO_2=0.4$ g/L, Cr(VI)=40 mg/L, TEP=30 mg/L)

| pH value | 2 | 4 | 7 |
|----------|-----------------|-----------------|-----------------|
| Cr(VI) | 15.8 ± 0.4 | 8.7 ± 0.3 | 5.63 ± 0.3 |
| TEP | 14.21 ± 0.7 | 22.63 ± 0.7 | 24.47 ± 0.7 |

Adsorption of TEP and Cr(VI) mixture on TiO_2

Adsorption of TEP and Cr(VI) mixture on TiO_2 were also investigated. As shown in table 3, at the presence of organic molecules (TEP), Cr(VI) adsorption efficiency decreased because of the competitive adsorption on the active sites of the catalyst while pH goes to higher values. In contrast at lower pH values, a significant enhancement were observed to adsorption of Cr(VI) on TiO_2 surface. The results indicated that TEP had little influence on the adsorption of Cr(VI) on TiO_2 particles while Cr(VI) had no influence on the adsorption of TEP on TiO_2 particles in acidic media.

Photocatalytic reactions

Photocatalytic reduction of Cr(VI) by UV/ TiO_2

The kinetic reaction were carried out in solutions at different Cr(VI) concentrations and pH levels to investigate the photocatalytic reduction of Cr(VI) by the UV/ TiO_2 process. The reduced kinetic reaction of Cr(VI) at different initial concentration in solution, which suggests a first-order reaction, under constant pH value

are shown in Fig. 4a. Several experimental results reported by previous researchers indicate that the apparent global rate of photocatalytic reduction reactions seem to follow the first-order kinetics. In addition, the Langmuir-Hinshelwood reaction rate was reported by Ku and Jung (2001) which had not been seen in this research.

The experimental results in Fig. 4b showed a significant enhancement on the photocatalytic reduction rate of Cr(VI) while pH values decreased. However, the photocatalytic reduction of Cr(VI) was not detected when the pH value reached 10 and 12. The value of k_{red} can be calculated from the slop of plotting $\ln[Cr(VI) / Cr(VI)_0]$ versus time. The rate constants k_{red} of Cr(VI) were 0.81, 0.51 and 0.38 h/r at different pH values of 2 to 7, respectively. These results can be correlated by Eq. 2.

$$\frac{dc}{dt} = -k_{red} C \quad (2)$$

$$\text{Where } k_{red} = 1.217 pH^{-0.6}$$

Photocatalytic degradation of TEP by UV/ TiO_2

During TEP oxidation process, intermediate materials such as diethyl phosphate and ethanol can be produced from TEP photocatalytic degradation, subsequently monoethyl phosphate can be formed from TEP and diethyl phosphate. At the final step, TEP and intermediate products degrade to phosphate which is

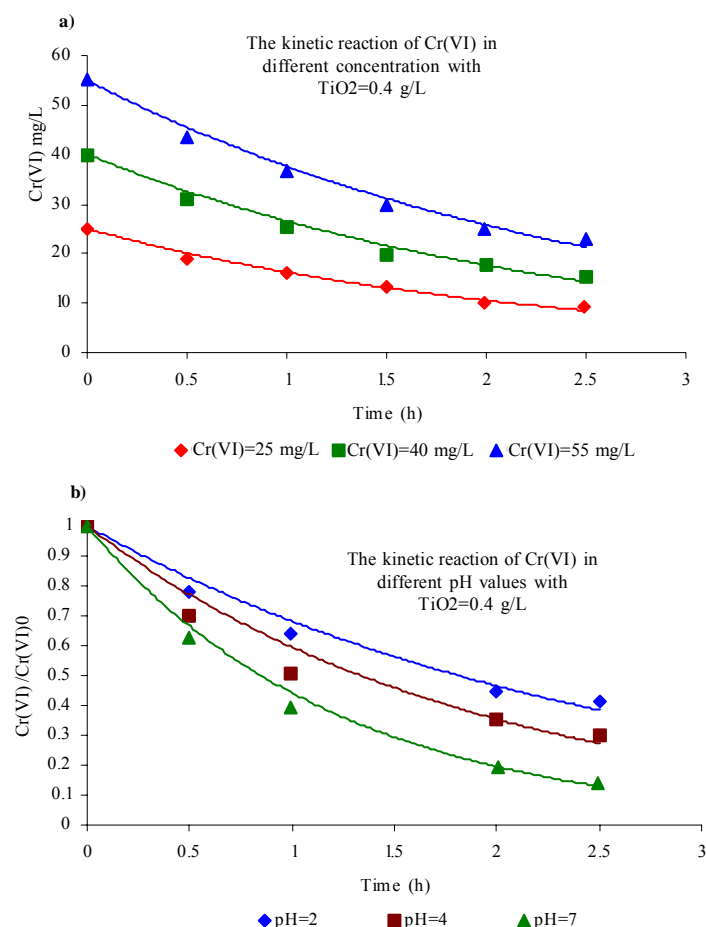


Fig. 4: The kinetic reaction of Cr(VI) in different a) concentration and b) pH

known as the end of TEP degradation. At lower pH values, TEP is more stable; therefore, it hardly reached the criteria for ready photocatalytic degradation. The effect of pH values on reaction rates is shown in Fig. 5a. The experimental results showed the natural pH has a higher reaction rate. Degradation rate of TEP at higher pH values was lower than pH 7.0. This can be explained by the less adsorption amount of TEP on the TiO_2 at acidic pH compared pH 7; therefore, the adsorption process plays an important role in photocatalytic reactions.

In Fig. 5b, the effect of TEP concentration on kinetic degradation was studied at the pH level of 7. A little trace phosphate were observed at earlier stage of the photocatalytic reaction; because, phosphate is formed

after the degradation of TEP, diethyl phosphate and monoethyl phosphate. After lag time, phosphate amount suddenly increased up to final concentration. These lags were 21.1, 35, and 47 min for 10, 30 and 50 mg/L of TEP concentration in solution, respectively. Also, the zero-order kinetic can be fitted in different concentrations of TEP at the pH value of 7. The final equation is:

$$\frac{dC_{phosphate}}{dt} = k_{red} \quad t > t_{lag} \quad (3)$$

$$\text{Where, } k_{red} = 0.756 C_{TEP_0}^{-0.29} \quad (h/r)$$

$$\text{And } t_{lag} = 0.112 C_{TEP_0}^{0.492} \quad (hr)$$

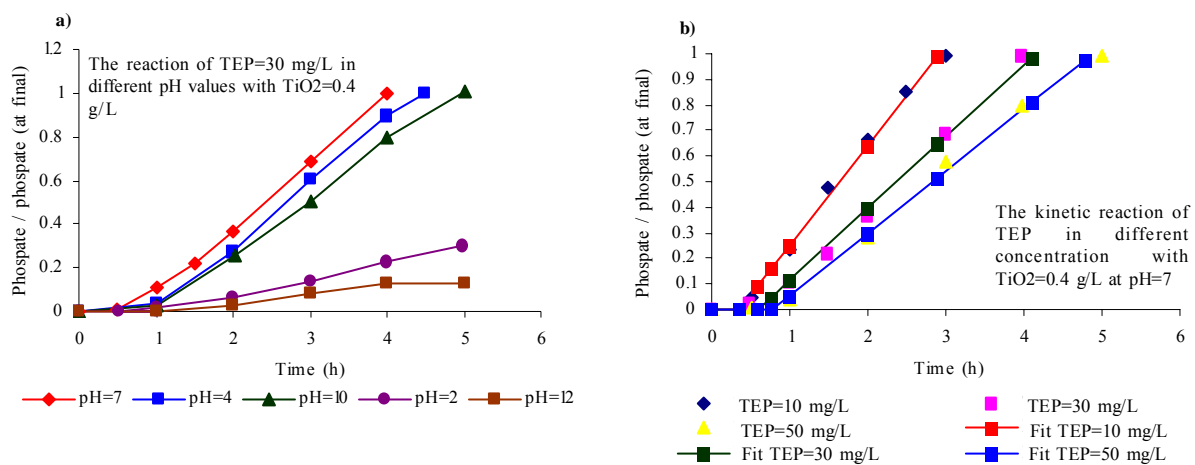


Fig. 5: The kinetic reaction of TEP in different a) concentration and b) pH

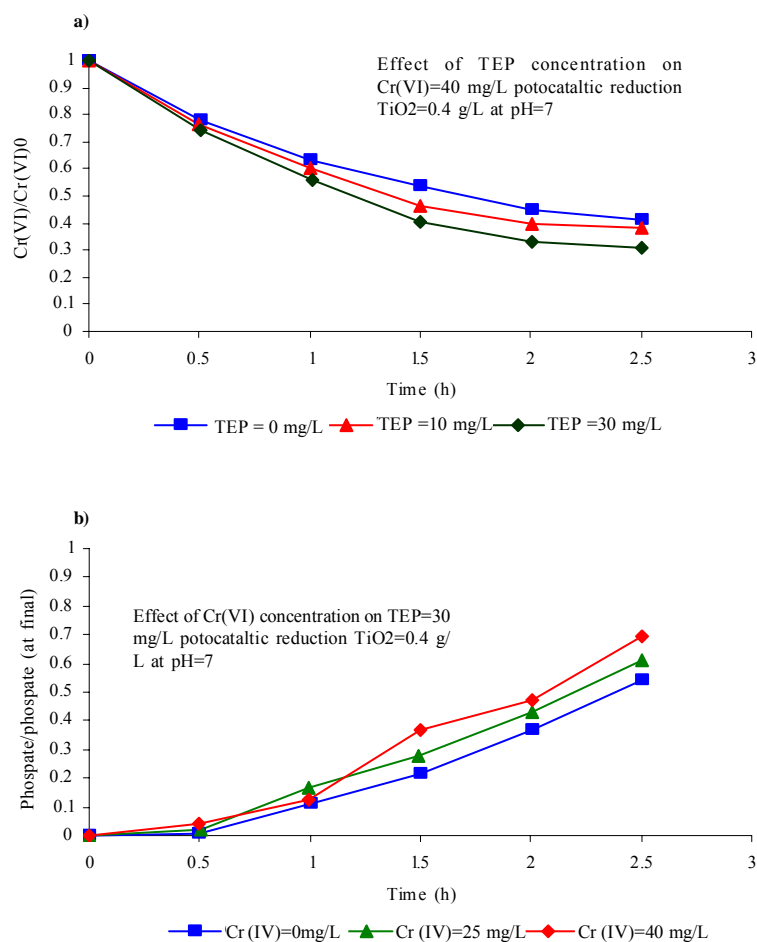


Fig. 6: Effect of TEP on a) Cr(VI) photocatalytic reduction and b) Cr(VI) on TEP photocatalytic

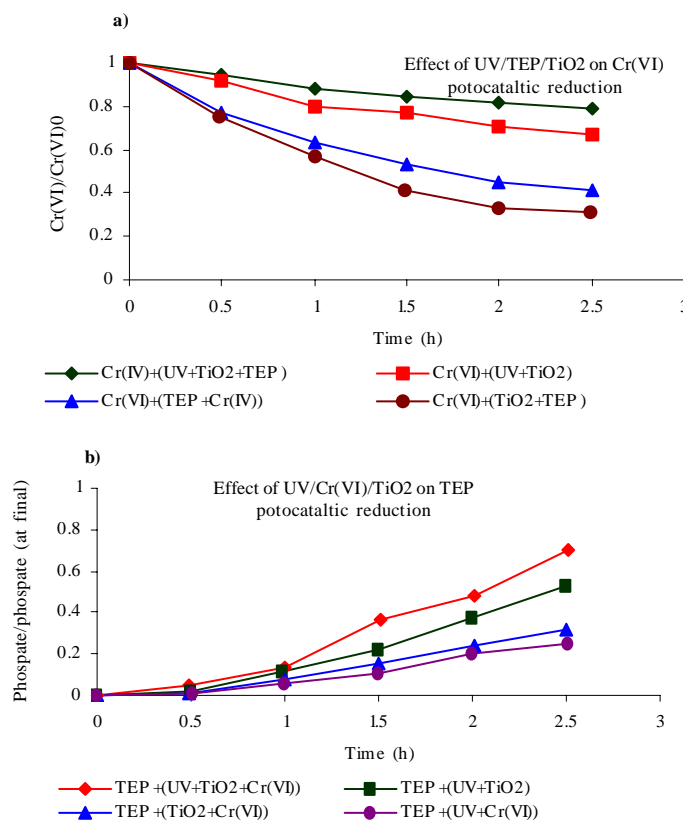


Fig. 7: Effect of parameter conditions on a) Cr(VI) photocatalytic reduction and b) TEP photocatalytic degradation

Photocatalytic oxidation on TEP/Cr(VI) mixture

The photocatalytic degradation of the TEP/Cr (VI) mixture was investigated at the pH value of 7.0 using the UV/TiO₂ process with TiO₂. A decreasing in TEP and Cr (VI) concentration with time and synergic effect was observed as shown in Fig. 6. The rate constants of Cr (VI) photocatalytic reduction were 0.38, 0.44 and 0.51 h/r at TEP concentrations of 0, 10 and 30 mg/L, respectively. Results showed the photocatalytic reduction rate of Cr (VI) subsequently increased. When TEP was mixed with Cr(VI) in a UV/TiO₂ system, the possibility of the capture of an electron by Cr(VI) could be promoted while the parts of the hole could be scavenged by TEP and produced intermediate materials such as ethanol. The effect of Cr(VI) concentration on the photocatalytic degradation of TEP at the pH value of 7, are shown in Fig. 6b. The photocatalytic degradation of TEP in the Cr(VI)/ TEP system was faster in compared to the TEP single system conducted with the UV/TiO₂ process. When Cr(VI) concentrations in solution

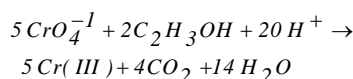
increased, the rate constants of TEP degradation increased from 0.201 to 0.33 h/r.

Siemon *et al.* (2002) explained an electron-shuttle mechanism which Cr(VI) is continuously reduced and reoxidized by valence band holes, he was previously invoked to explain the results in pure water. This mechanism is non-operative in the presence of a reducing agent that can strongly compete for the holes with reduced Cr(VI) species, producing a synergistically cooperative effect. A synergetic effect between the photocatalytic reduction of Cr(VI) and the TEP degradation was observed. Previous researches have reported this accelerating effect (Colon *et al.*, 2001).

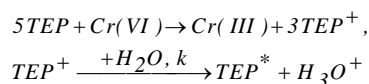
Reactions on TEP/Cr(VI)/UV/TiO₂ mixture

The photocatalytic reaction rate in the Cr(VI)/TEP mixture solution without TiO₂ under the irradiation of UV light and with TiO₂ under visible light were investigated at the pH value of 7 with continuous stirring. Results are shown in Fig. 7 which indicate that

the reaction rate of TEP under visible light with TiO_2 and the reduction rate of Cr(VI) under UV light without TiO_2 had the lowest rates. In the case of TiO_2 present, adsorption had most important role on removing of Cr(VI) and also, the thermal reaction between produced intermediate materials and Cr(VI) can cause Cr(VI) to reduce:



The main degradation process for TEP in water is hydrolysis which may increase with the irradiation of UV light in a Cr(VI)/TEP system in the absence of TiO_2 . Photocatalytic degradation of TEP and intermediates on the surface of titanium dioxide in water suspension can be done via reactions between Cr(VI) and hole:



CONCLUSION

The following results may be achieved from the above work in which the photocatalytic oxidation of the Cr(VI)/TEP mixture have been studied in different conditions. It was found that the capacity of adsorption is increased with the decreasing of pH for Cr(VI) and the increasing of pH for TEP. Also, co-adsorption of TEP/Cr(VI) can cause to increasing the Cr(VI) adsorption on the TiO_2 surface. The highest photocatalytic reaction rate was observed at neutral pH and acidic pH for TEP and Cr(VI), respectively. The synergic effect between the degradation of TEP and the reduction of Cr(VI) is demonstrated in a system containing Cr(VI) and TEP by UV/ TiO_2 . The results show that the reaction rate between Cr(VI) and TEP in the absence of TiO_2 and UV light is at pH level 7.

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