

Original Article

Hexavalent chromium removal by titanium dioxide photocatalytic reduction and the effect of phenol and humic acid on its removal efficiency

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ABSTRACT

Aims: The aim of this study is Cr (VI) removal by titanium dioxide (TiO₂) photocatalytic reduction and the effect of phenol and humic acid (HA) on its removal efficiency are investigated.

Materials and Methods: The experiments were performed on both simulated synthetic wastewater and real wastewater. Various parameters such as pH, contact time, Cr (VI) and TiO₂ concentrations, and a constant concentration of phenol and HA were considered to perform the experiments.

Results: The removal value of Cr (VI) alone is 81% and in combination with HA and phenol is 89.7% and 96.2%, respectively. Cr (VI) removal efficiency was enhanced by decreasing pH and contact time. With increasing TiO₂ dosage, the removal of Cr (VI) increased, up to 0.5 g/L and then decreased at 1 g/L. Cr (VI) removal efficiency decreases with the increase of Cr (VI) initial concentration. Removal efficiency, in 10 mg/L initial concentration of phenol and HA, was enhanced as contact time increased. Equilibrium data and adsorption process kinetics obey Langmuir isotherm model and pseudo second-order kinetic model, respectively.

Conclusions: Heavy metal ions and organic pollutants are often present in real wastewater. This research suggests that the photocatalytic reaction TiO₂ could be applied to more effectively treat wastewaters containing both Cr (VI) and organic compounds.

Key words: Chromium, humic acid, phenol, titanium dioxide

INTRODUCTION

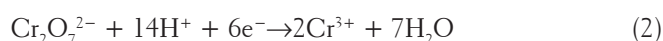
Hexavalent chromium (Cr) is one of particular concern due to its high-toxicity to human, animals, and plants. Presence of Cr (VI) in wastewater in high concentration could significantly inhibit biomass growth during biological treatment processes.^[1] Reduction of Cr (VI) to less mobile and toxic Cr(III) by a variety of inorganic and organic reduction's has been recognized as an important remediation strategy for Cr contaminant control.^[2] Cr (VI) has been widely used in several industries, such as

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metal plating, military purposes, and tanning of leather, as well as in the pigment and refractory industries.^[3] World Health Organization has confirmed that Cr (VI) is carcinogen in human.^[4] Craggregation in tissues of animals and plants can cause serious hazards. In concentrations higher than 50 µg/L, Cr (VI) causes lung and skin cancer, as well as kidney, liver and even allergic damages. In the other hand environmental problems arising from natural organic matter, such as humic acids (HAs) and fulvic acids, ect., are caused by the increased mobility of toxic heavy metals due to complication and the formation of trihalomethane precursor during the treatment of potable waters.^[5] Various methods have been developed to remove these pollutants from industrial wastewater, e.g., filtration, coagulation — flocculation, reverse osmosis, biological treatment, and distillation, etc.^[6] Cr (VI) usually exists in wastewater as chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) anions and does not precipitate easily using conventional methods.^[7] However, these methods also have problems, such as requiring a high capital cost and the formation of secondary pollutants. To overcome these problems, advanced oxidation processes (AOP) have been studied, and are suggested to be promising techniques. In general, AOPs use highly oxidizing hydroxyl radical to breakdown organic compounds into CO_2 and H_2O . The hydroxyl radical can be generated in aqueous solutions using O_3 /ultraviolet (UV), hydrogen peroxide (H_2O_2)/UV, Fe (II)/ H_2O_2 and titanium dioxide (TiO_2)/UV.^[8] Using TiO_2 /UV, can simultaneously treat organic compounds and heavy metals, as well as transform non-biodegradable to biodegradable organic compounds. Therefore, this technique can be used as a pre-/post- treatment method to other wastewater treatment methods, as it is convenient to install and economical to operate.^[7] The photo-reduction of Cr (VI) to Cr(III) can be achieved via a photocatalytic process with a simplified mechanism as follows:



UV light illumination on TiO_2 produces hole — electron pairs reaction (1) at the surface of the photocatalyst. After the hole — electron pairs being separated, the electrons can reduce Cr (VI) to Cr(III) reaction (2), and the holes may lead to generation of O_2 in the absence of any organics reaction (3). Therefore, in a completely inorganic aqueous solution, the net photocatalytic reaction is the three-electron-reduction of Cr (VI)Cr (VI) to Cr(III) with oxidation of water to oxygen, which is a kinetically slow four-electron process and hence the photocatalytic reduction

of Cr (VI)Cr (VI) alone is quite slow. Alternatively, the photocatalytic reduction of Cr (VI)Cr (VI) can be carried out in couple with the photocatalytic oxidation of organic pollutants by adding some amount of organic pollutants in solution. In the presence of degradable organic pollutants, the holes can produce OH radicals reaction (4), which can further degrade the organics to CO_2 and H_2O reaction (5). Of course, the holes can also directly oxidize the organic molecules reaction (6).^[9] TiO_2 , as a nontoxic material, satisfies these requirements. Another advantage of TiO_2 is that high concentration of hydroxyl groups (OH) are present on the surface, and the pollutants in water can be adsorbed on the TiO_2 surface via interacting with surface OH.^[10] The surface properties of TiO_2 such as surface OH, surface area, and particle size in crystalline phase play a critical role in determination of the efficiency and mechanism of the photocatalytic reactions.^[7] Wang *et al.* reported that the TiO_2 photocatalytic reduction process can effectively remove various toxic metal ions, such as Hg(II), Se(IV), Cd(II), Zn(II), Cu(II), and Cr (VI)Cr (VI).^[8]

It has been demonstrated that two pollutants Cr (VI)Cr (VI) and methyl tertiary-butyl ether (MTBE) could be eliminated simultaneously by UV/ TiO_2 process. The system containing Cr (VI)Cr (VI) and MTBE by UV/ TiO_2 process demonstrated the synergic effect between oxidation of MTBE and reduction of Cr (VI)Cr (VI).^[11] The objective of this research is the removal of Cr (VI) by TiO_2 photocatalytic reduction and the effect of phenol and HA on its Cr (VI) removal efficiency.

MATERIALS AND METHODS

This research is a laboratory-experimental study, which was performed during 6 months (October-March 2012). The experiments were performed on both simulated synthetic wastewater and paint industry wastewater. Real wastewater sample was taken from equalization tank of Binalood Paint Industry. All required chemicals were purchased from Merck (Germany) and Aldrich Companies. TiO_2 nanoparticle with size of 20 nm, surface area of 40 m^2/g , and 99% purity was prepared from Nano Pars Lima Company.

Adsorption experiments

Standard solutions for experiments were prepared by dilution of potassium $\text{Cr}_2\text{O}_7^{2-}$ stock solution (1,000 mg/L). HCl and NaOH solutions (1N) were used to adjust pH. There were six different parameters: pH (3, 5, 7, and 9), TiO_2 dosages (0.25, 0.5, 0.75, 1, 1.5 mg/L), contact time (30, 60, 90, 120, 150 min), initial concentration of Cr (VI) (10, 20, 40, 60, 80, 100 mg/L) and HA and phenol concentration (10 mg/L).

The experiments were performed at $19 \pm 1^\circ\text{C}$ in a closed reactor equipped circulating cooling water system and magnetic stirrer with 300 rpm speed. In this study, a Plaxi glass reactor with effective volume of 500 mL and 10 cm × 15 cm × 20 cm dimensions was prepared for photocatalytic

oxidation and a mercuric UV source by mean pressure was located in 10 cm distance of reactor surface with 280 W/cm² intensity and maximum wave-length of 360 nm. Every 30 min, 10 mL of the reaction mixture was taken and to remove catalyst particles, samples were centrifuged in at 4,000 rpm for 15 min then supernatant fluid by filtering 0.45 µm filtered. Then 2 mL of the filtered sample was analyzed. In all experiments, one parameter was changed while the others were constant. All steps of experiment were performed using UV ray intensity of 280 W/cm² with maximum wave-length of 360 nm, speed of 300 rpm, and constant temperature of 19 ± 1°C. The remaining Cr (VI) was measured by 1,5-diphenylcarbazide method at a wave-length of 540 nm using a UV — Visible light spectrophotometer (VIS) (Schimadzu UV-1800).^[12] After performing synthetic reactions and gaining the conditions in which the most removal yield was obtained at the least time and catalyst amount, the experiments were carried out on real wastewater under optimized conditions.

RESULTS

The experiments of wastewater chemical quality

Table 1 shows the average of three raw wastewater samples before 1 h settling and after transferring to the laboratory.

Determination of optimum pH

Effect of pH value on the photocatalytic reduction of Cr (VI) in the UV/TiO₂ system was studied and the results are shown in Figure 1. The amounts of Cr (VI) removed by UV/TiO₂ photocatalytic reduction varied markedly with

Table 1: Raw wastewater characteristics of binalood paint industries

| Parameter | Unit | Maximum | Minimum | SD |
|-----------|------|---------|---------|-------------|
| pH | — | 6 | 5.5 | — |
| Cr | mg/L | 51 | 48.5 | 50 ± 0.0011 |
| Cd | mg/L | 6 | 5.7 | 5.9 ± 0.144 |
| Pb | mg/L | 2 | 1.7 | 1.7 ± 0.118 |

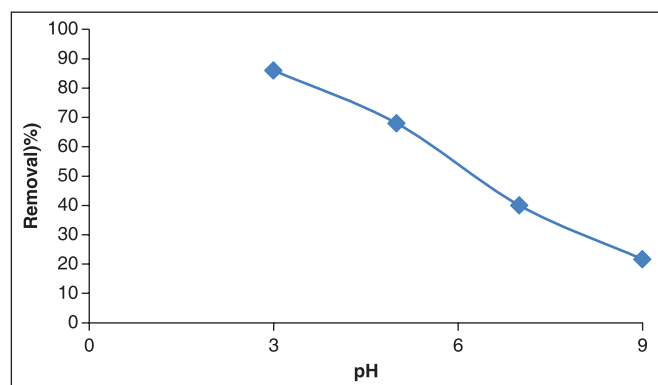


Figure 1: The effect of different amount pH on the photocatalytic reduction of chromium Cr (VI). Cr (VI) = 30 mg/L, Time = 60 min. Titanium dioxide = 1(g/L)

solution pH. At pH 3.0 there was a reduction of Cr (VI) concentration about 86% and Cr (VI) removal efficiency decreases with the increase of pH. The optimum pH for the photocatalytic reduction of Cr (VI) in the UV/TiO₂ system was found to be 3.

Determination of optimum contact time

Figure 2 show that adsorption of Cr (VI) on TiO₂ surface reached saturation in about 30 min. So that, removal efficiency for Cr (VI) at contact times 30 min was 86%. The removal rate of of Cr (VI) gradually decreased with increase in contact time. The optimum contact time for the photocatalytic reduction of Cr (VI) in the UV/TiO₂ system was found to be 30 min.

The effect of initial Cr (VI) concentration on the photo-reduction of Cr (VI)

Figure 3 show the removal of Cr (VI) different concentrations in the contact time 30 min and at pH 3 value. As the Cr (VI) concentration was increased to 100 mg/L, the fraction of removed Cr (VI) gradually decreased. The result showed that the Cr (VI) removal efficiency in Cr (VI) concentration 10 and 100 mg/L was 96.99 and 76.66% respectively.

The effect of TiO₂ loading on the photo-reduction of Cr (VI)

Figure 4 show the removal of Cr (VI) by varying the TiO₂ dosage from 0.25 to 1.5 g/L. With increasing TiO₂ dosage, the removal of Cr (VI) increased, up to 0.5 g/L, but decreased at 1.5 g/L. At 0.5 g/L, the fraction of removed Cr (VI) after 30 min was 91.6%. As no significant removal of Cr (VI) was observed above 1.5 g/L TiO₂, the optimum TiO₂ dosage was determined as being 0.5 g/L.

Photocatalytic reduction of Cr (VI) in the presence phenol and HA

There is an enhancement of Cr (VI) removal efficiency in the presence of phenol and HA. Figure 5 show that with

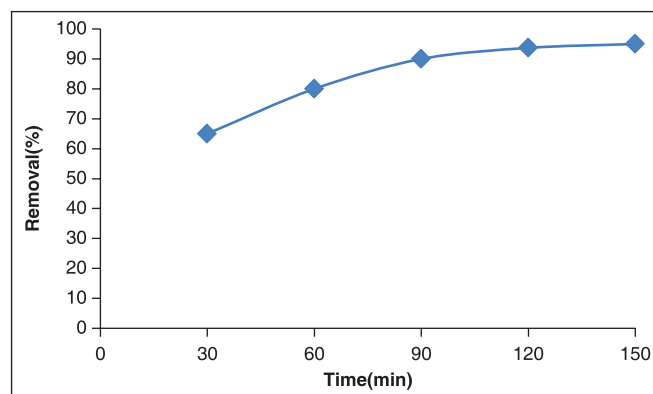


Figure 2: The effect of contact time on the photocatalytic reduction of chromium Cr (VI). Cr (VI) = 60 mg/L, titanium dioxide = 1 g/L, pH = 3

increasing contact time up to 150 min in pH 3 Cr (VI) Cr (VI) photocatalytic reduction increase in the presence of phenol and HA. The maximum Cr (VI) removal efficiency in the presence HA and phenol in the UV/TiO₂ system was 95 and 97.2% respectively.

Photocatalytic reduction of Cr (VI) on the real waste water sample

After performing synthetic reactions and obtain the optimized conditions the experiments were carried out on real wastewater. Figure 6, shows that experiments were carried out on real wastewater under optimized conditions. According to the Figure 6 removal efficiency was less than the synthetic tests and for Cr (VI), HA and phenol on real samples was 81, 89.7 and 96.2% respectively.

The experiment of sorption isotherms

Sorption experiments are performed to determine adsorption kinetics coefficients and isotherm constants. Adsorption capacity is obtained from equation below:

$$Q_t = \frac{V(C_i - C_t)}{M}$$

Where Q_t is the amount of metal adsorbed per unit mass of adsorbent, C_i is initial metal concentration (mg/g), C_t is metal concentration at time t (mg/g), V is solution volume (L), and M is adsorbent mass (g). For modelling of the Cr (VI) adsorption from wastewater, two models (Langmuir and Freundlich) were used.

Original form

1. Langmuir model

$$q = \frac{q_m K_1 C}{1 + K_1 C}$$

2. Freundlich model

$$q = K_f C^{1/n}$$

where,

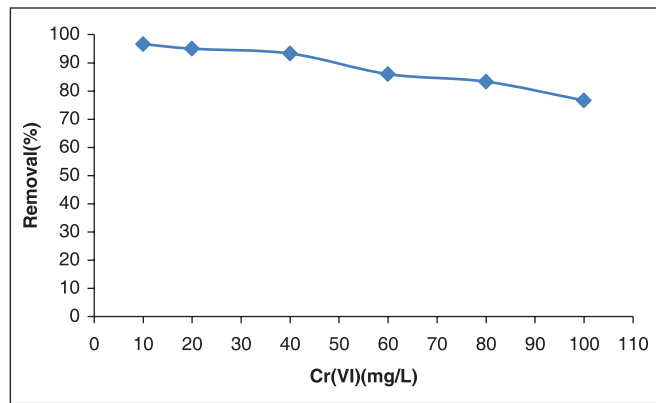


Figure 3: The effect of Chromium(VI) concentration on the photocatalytic reduction of Cr (VI), Cr (VI) = 60 mg/L, pH = 3, Time = 30 min

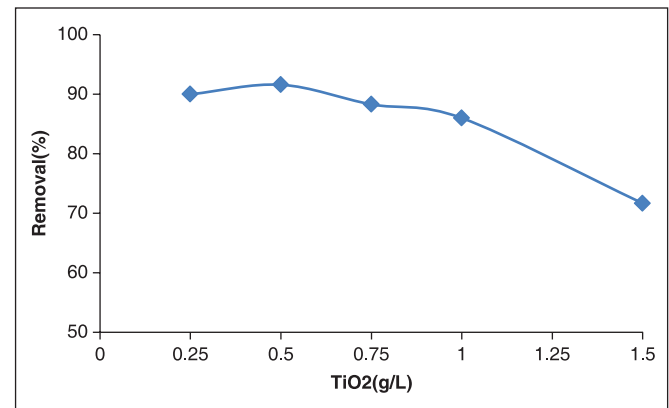


Figure 4: The effect of TiO₂ concentration on the photocatalytic reduction of, Chromium(VI) = 60 mg/L, pH = 3, Time = 30 min

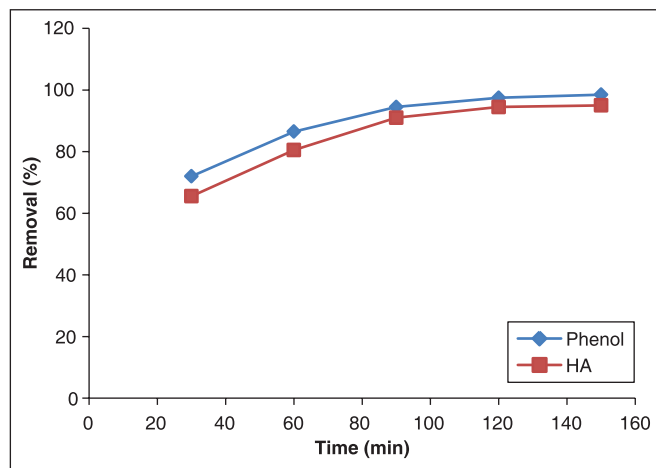


Figure 5: The effect of phenol and humic acid concentration on the photocatalytic reduction of Cr (VI), Cr (VI) = 60 mg/L, pH = 3, Time = 30 min

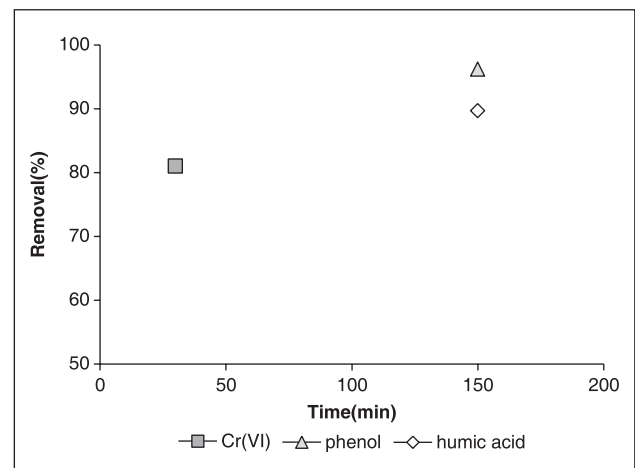


Figure 6: photocatalytic reduction of Cr (VI) on the real waste water sample. Cr (VI) = 50 mg/L. Phenol = 10 mg/L, HA = 10 mg/L, pH = 3. Titanium dioxide = 1 g/L

q : The amount of metal ions adsorbed per specific amount of adsorbent (mg/g).

C : Equilibrium concentration (mg/L or mmol/L).

q_m : The amount of metal ions required to form a monolayer (mg/g).

K_f : Langmuir equilibrium constant.

(K_f) and ($1/n$) are indicative isotherm parameters of sorption capacity and intensity, respectively.^[13] As Figures 7 and 8 show, the adsorption of Cr (VI) by Langmuir isotherm is better explained ($R^2 = 0.824$). The value of Freundlich and Langmuir constant was presented in Table 2. According to the obtained results, maximum amount of adsorbate is 23.8 mg/g.

Kinetic studies

The adsorption kinetics of Cr (VI) on TiO₂ nanoparticle can be determined by the pseudo first order and pseudo second order.

$$\log(q_e - q_t) = \log(q_e) - k_1 t / 2.303$$

where q_t and q_e are the amounts of Cr (VI) adsorbed (mg/g) at any time t and at equilibrium, respectively; k_1 (min⁻¹) is the rate constant of the pseudo first order adsorption.^[14] The values of q_e and k_1 can be determined from the intercept and slope of the plot of $\log(q_e - q_t)$ versus t [Figure 9] respectively, and are listed in Table 3.

The pseudo second order model:

$$t/q_t = 1/K_2 q_e^2 + t/q_e$$

Where K_2 (g⁻¹/mg/min) is the rate constant of the pseudo second order model.^[15] The plot of t/q versus t is presented in Figure 10. The values of q_e and K_2 can be calculated from the slope and intercept of the plot, respectively, and are shown

in Table 3. The pseudo second order model shows a better fitting model than the pseudo first order model because of the higher coefficient correlation ($R^2 = 0.965$).

DISCUSSION

Removal of Cr (VI) obviously increased in the UV/TiO₂ system, possibly due to effective reduction of the Cr (VI) to Cr(III) by the electrons in the conduction band of the TiO₂, as well as adsorption of the Cr (VI) onto the TiO₂ surface. As the standard redox potential of Cr (VI) is positive compared to the conduction band of TiO₂, the potential difference between the conduction band of TiO₂ and the Cr (VI) is a thermodynamic driving force for the reduction of Cr (VI). Therefore, the enhanced removal of Cr (VI) in the UV/TiO₂ system is related to the reduction of Cr (VI).^[16] Photocatalytic reduction of Cr (VI) using TiO₂ as the catalyst was also reported by Liu *et al.*^[17] and Wang *et al.*^[18] At pH 3.0 there was a higher reduction of Cr (VI) concentration during the 1st h of photoreaction. This may indicate that the adsorption played a significant role on the photocatalytic degradation, since the photoreaction mainly occurred on the surface of catalyst, but not in the bulk solution. When pH was 9, almost low photo-reduction of Cr (VI) was detected. According to

Table 2: Freundlich and langmuir isotherm constants

| Langmuir | | Freundlich | |
|----------|-------|------------|-------|
| 36.9 | K_f | -0.189 | K_f |
| 11.9 | N | 23.8 | Q_f |
| 0.78 | R^2 | 0.82 | R^2 |

Cr (VI)

Table 3: Kinetic parameters for Cr(VI) adsorption by TiO₂ nanoparticle

| Model | q_e (mg/g) | Rate constant | R^2 |
|---------------------|--------------|-----------------------------------|-------|
| Pseudo first order | -1.51 | k_1 (min ⁻¹), 13.88 | 0.938 |
| Pseudo second order | 58.4 | k_1 (g/mg/min), 0.002 | 0.965 |

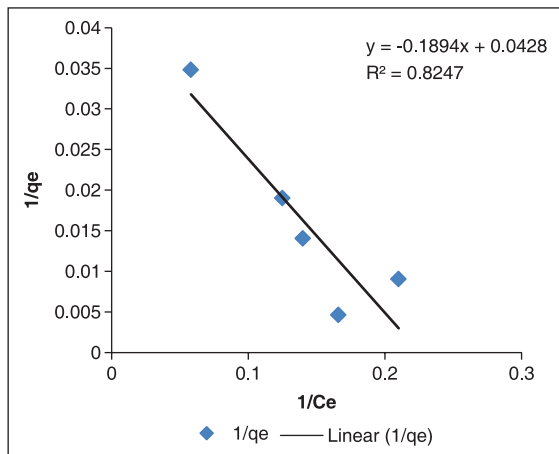


Figure 7: Langmuir adsorption isotherm for Chromium(VI) photocatalytic reduction

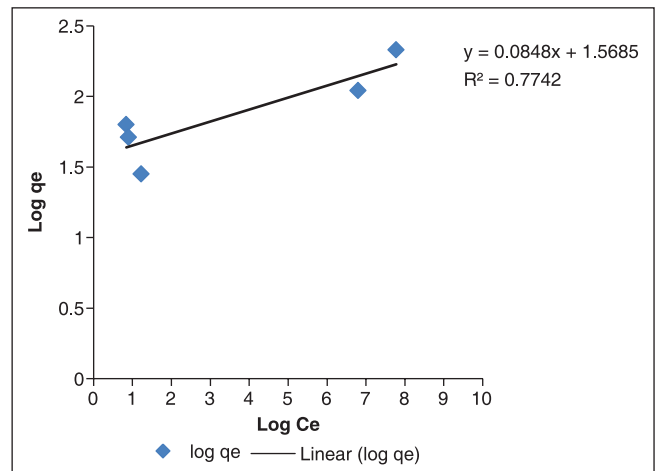


Figure 8: Freundlich adsorption isotherm for Chromium(VI) photocatalytic reduction

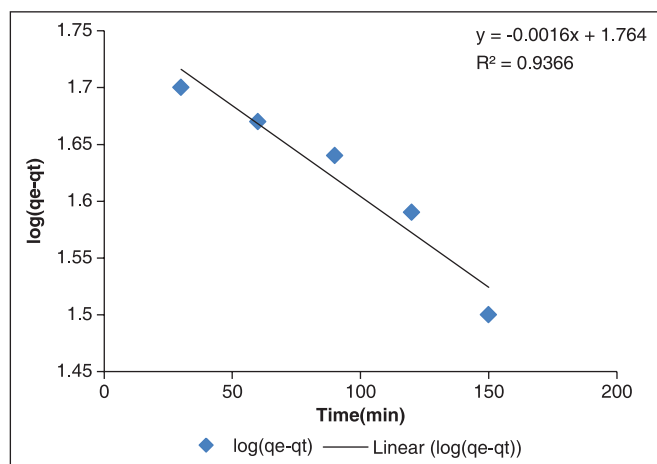


Figure 9: Pseudo first order kinetic plots for Chromium(VI) adsorption by titanium dioxide nanoparticle

previous study, the concentration of the surface OH of TiO₂ strongly depends on solution pH.^[19]

When the solution pH is low, they are mainly present in the forms of Ti-OH and/or Ti-OH₂⁺, when the solution pH is high, on the other hand, the surface OH of TiO₂ will be dissociated to form TiO⁻. In the case of Cr (VI) adsorption, the electrostatic attraction or repulsion between the surface OH of TiO₂ and CrO₄²⁻ or Cr₂O₇²⁻ dominate the adsorption. When the solution pH is low, negatively charged CrO₄²⁻ or Cr₂O₇²⁻ can associate with TiO₂ surfaces via electrostatic attraction with positively charged Ti-OH₂⁺, leading to adsorption. In the high pH region, there will be an electrostatic repulsion between negatively charged CrO₄²⁻ and TiO⁻, resulting in the decrease in the Cr (VI) removal efficiency. So that, under the acidic pH, the presence of negatively charged Cr (VI) ions lead to the more removal of Cr (VI) by TiO₂ particles than neutral pH.^[11] The results match Asuha *et al.*^[20] studies. Tel *et al.* illustrated that the Cr (VI) removal efficiency shows an increase from 20% for pH 10-99% for pH 3.^[21]

Figure 2, show that Cr (VI) photocatalytic reduction increased in about initial 30 min. This difference in removal amount at various times could be explained by considering the fact that removal capability is affected by change of the amount of OH⁻ on the surface of TiO₂ and number of metal species. At the initial minutes, Cr (VI) reduction increase due to surface changes, and negative charges on the surface.^[22] On the other hand, hydroxyl radicals concentration production due to photocatalysis process in the TiO₂ surface in initial minute is more than last minutes, which caused is remove more Cr (VI). Xu *et al.* experimental results showed that adsorption of Cr (VI) on TiO₂ surface reached saturation in about 20-30 min.^[11] Yoon *et al.* showed that with increasing contact time up to 120 min in different pH, Cr (VI) removal efficiency decreases.^[23]

Figure 3, show that the Cr (VI) removal efficiency decreases with the increase of Cr (VI) initial concentration. One reason

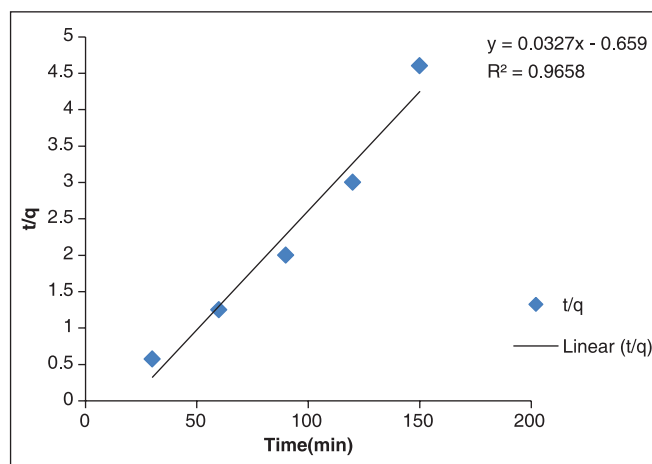


Figure 10: Pseudo second order kinetic plots for Chromium(VI) adsorption by titanium dioxide nanoparticle

for this is that, concentration of hydroxyl radicals surface TiO₂ and pairs of electrons-holes produced by the photocatalytic process decreases at Cr (VI) high concentrations. Thus, hydroxyl radical's surface TiO₂ and electrons-holes generated in TiO₂ surface saturated and Cr (VI) removal value diminishes. Furthermore, the change of the amount of OH⁻ on the surface of TiO₂ may be another reason for Cr (VI) removal efficiency decreases with the increase of Cr (VI) initial concentration. The obtained result is in accordance with the results of Karthikeyan *et al.* studies on the Cr (VI) removal by sawdust activated carbon.^[24] Figure 4 show that the with increasing TiO₂ dosage, the removal of Cr (VI) increased, up to 0.5 g/L, but decreased at 1 g/L. This can be explained via the combined results of three different effects with increase of TiO₂ dosage. As Positive effects, the adsorption sites on the TiO₂ surface, the generation of free electrons in the conduction band, should increase with increasing TiO₂ dosage. As a negative effect blockage of the incident UV light used for the photocatalytic reaction also gradually increased with increasing TiO₂ dosage with up to 0.5 g/L TiO₂. The positive effects may be greater than the negative, showing increased removal of Cr (VI). However, above 0.5 g/L TiO₂, the blocking of the incident UV light may be greater than the positive effects; Because of increased turbidity caused by high concentration of catalyst. Hence, the decreased removal of Cr (VI) at 1 g/L. The optimum TiO₂ dosage was determined as being 0.5 g/L. However, controversial results observed by Yang *et al.* indicating that the reduction rate of Cr (VI) by UV/TiO₂ process increased with increasing amount TiO₂ 2 g/L.^[25] Khailil *et al.* also reported reduced removal of Cr (VI) at higher TiO₂ dosages.^[3]

There is an enhancement of Cr (VI) removal efficiency in the presence of phenol and HA at acidic pH [Figure 5]. As described in introduction, the mechanism the photo-reduction of Cr (VI) over TiO₂ may follow a general mechanism being composed of reactions (1)-(6). In general, adding some organic compounds into the solution is favorable to further increasing of the charge separation by scavenging

holes via reactions (4)-(6). Through scavenging of positive hole in the valence band of TiO_2 , which is able to sufficiently compensate any reduced adsorption of Cr (VI) due to the competitive adsorptions between Cr (VI), HA and phenol onto TiO_2 . This is due to the enhancement of potential between conduction band of TiO_2 , (Cr (VI)/Cr(III) ratio as well as the anionic-type adsorption of Cr (VI) onto the TiO_2 surface. The results illustrate that HA and phenol act as sensitizers in photocatalytic reduction of Cr (VI)-Cr(III). However, the photocatalytic reduction of Cr (VI) couple with the photo oxidation of the added organics, leading to a great promotion of the photocatalytic reduction of Cr (VI) due to the significant synergistic effect of photocatalytic treatment of Cr (VI) and organic pollutants. Wang *et al.*, demonstrated this synergistic effect is increased with increase of the specific surface area of TiO_2 photocatalyst, being less dependent on its crystalline structure.^[8] Vohra and Davis showed that the adsorption of organic acids such as ethylenediamine tetra acetic acid and nitrilotriacetic acid into TiO_2 is usually anionic.^[26] Lee *et al.* reported that (Cr (VI) removal efficiency increases by increasing the concentration of phenol.^[27] Ku and Jung, showed that the Cr (VI) can be reduced almost completely by UV/ TiO_2 process within 5 h of reaction time in the presence of 0.5% ethanol at pH 3.^[28]

According to Figures 7 and 8, equilibrium and experimental data of Freundlich and Langmuir isotherms illustrated that the results are in good accordance with Langmuir isotherm. The adsorption on TiO_2 surface occurs through electrostatic attraction between TiO_2 surface OH and CrO_4^{2-} . Therefore, the identical nature of surface OH leads to follow Langmuir isotherm. Maximum adsorbent capacity determined 23.8 mg/g using Langmuir model. Study of adsorption kinetics is useful to predict adsorption rate for process design and modeling.^[29] The adsorption kinetics fitted well with the pseudo second order model [Figures 9 and 10]. This suggested that the adsorption of Cr (VI) on TiO_2 nanoparticle involved a chemisorption process.^[30] After performing synthetic reactions and obtain the optimal conditions, the experiments were carried out on real wastewater under optimum conditions [Figure 6]. Result showed real tests that, removal efficiency was less than the synthetic tests. This reason is that, chemical quality real wastewater and presence of interfering factors in wastewater Cr (VI) removal efficiency decreases.

CONCLUSION

It was confirmed that the photocatalytic reduction of Cr (VI) enhanced in the system UV/ TiO_2 when system contained both organic compounds and Cr (VI) compared to Cr (VI) alone. The results showed that Cr (VI) reduction by UV/ TiO_2 photocatalytic process is more effective for solution pH below 6. The experimental results indicated that the pH of the aqueous solution is critical to the adsorption of Cr (VI) possibly since the presence of various Cr (VI)

species and the surface charge of TiO_2 particles are highly pH dependent. With increasing TiO_2 dosage, the removal of Cr (VI) increased, up to 0.5 g/L, because of increased turbidity caused by high concentration of catalyst, hence the decreased removal of Cr (VI). At the initial minutes, Cr (VI) reduction increase due to surface changes, and negative charges on the surface. At Cr (VI) high concentrations, scavenging holes generated in TiO_2 surface saturated and Cr (VI) removal value diminishes. The results showed in the presence of appropriate organic compounds, however, the photocatalytic reduction of Cr (VI) couple with the photo oxidation of the added organics, leading to a great promotion of the photocatalytic reduction of Cr (VI). This trend could be explained by the increased photocatalytic efficiency due to the reduced recombination between positive holes in the valence band and the electrons in the conduction band of the TiO_2 . Equilibrium data and adsorption process kinetics obey Langmuir isotherm model and pseudo second-order kinetic model, respectively. Because heavy metal ions and organic pollutants often present in real wastewater, this research suggests that the photocatalytic reaction TiO_2 could be applied to more effectively treat wastewaters containing both Cr (VI) and organic compounds than those containing a single species only.

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