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Chromium (VI) removal using nano-TiO_2/chitosan film in photocatalytic system

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Abstract: TiO_2/chitosan film was fabricated by chitosan flake from crab shell and TiO_2 (Degussa P25) and immobilised on a glass plate for chromium (VI) removal. Adsorption and photocatalytic activity of chromium (VI) removal and chelating ability of chitosan to enhance photocatalytic activity were investigated. The effect of chitosan and TiO_2 contents of film property was conducted. The chitosan concentration 1.5% w/w with different TiO_2 concentration was homogenous solution leading to smooth TiO_2/chitosan film with high ability in chromium (VI) removal. The adsorption of TiO_2/chitosan film with ratio 0.8% TiO_2 and 1.5% chitosan resulted in chromium (VI) removal up to 64.05%. With photocatalytic process, the TiO_2/chitosan can remove all of residual chromium (VI) in wastewater. The kinetics of the photocatalytic process using Langmuir-Hinshelwood model were also discussed. The TiO_2/chitosan film can be a potential catalyst for heavy metal removal in photocatalytic process.

Keywords: TiO_2; chitosan; TiO_2/chitosan film; photocatalytic process; chromium; waste management.

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Tra Van Tung received his Master degree from Asian Institute of Technology, Thailand. His main topic was investigation of membrane technology based industrial wastewater reuse application. Currently, he is a PhD student at Naresuan University, Thailand. His topic is focusing on the use of photocatalytic process with a couple of membrane unit for application in wastewater treatment.

Puangrat Kajitvichyanukul is an Associate Professor in Environmental Engineering, Department of Civil Engineering, Naresuan University, Thailand. She has more than 15 years of experience in the applications of nanomaterials (especially TiO_2 and iron oxide) for contaminant removal from water and wastewater.

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1 Introduction

Chromium has been widely used in several industries, such as metal plating military purposes and tanning of leather, as well as in the pigment and refractory industries. Normally chromium can exist in the form of several oxidation states. Chromium occurs in two common oxidation states in nature as chromium (III) and chromium (VI). Hexavalent chromium with concentrations higher than 0.05 ppm is toxic to most organisms, carcinogenic in animals, and causes irritation and corrosion of the skin in humans (Khalil et al., 1998) while trivalent chromium is easily precipitated or adsorbed on a variety of inorganic substances at neutral or basic pH (Kajitvichyanukul et al., 2004). Treatment of contaminated chromium (VI) can be achieved by chemical precipitation, ion exchange, bioremediation and adsorption on coal or activated carbon.

Nevertheless, most of these methods require either high energy or large quantities of chemicals.

Chitosan known as a biopolymer of polyaminosaccharide is used to synthesis film to Chromium from wastewater (Sivakami et al., 2013). The amino and the hydroxyl group in the chitosan structure can lead to its great potential to adsorb metal ions in removal (Jayakumar et al., 2007). Chitosan as sorbent is totally renewable, low cost, no risk, and biodegradation (Bajpai and Rai, 2010). However, chitosan film is physical instability (Batista et al., 2011).

Photocatalysis is a novel technology for environmental abatement. As an efficient means for pollution treatment, this technology is widely investigated to remove organic and inorganic contaminants from water and wastewater. Titanium dioxide (TiO_2) has been widely used as a photocatalyst due to its activity, photostability, non-toxicity and commercial availability. There are previous studies show that the chromium (VI) can undergo photocatalytic reduction and deposit on the surface of titanium dioxide (Lin et al., 1993; Ku and Jung, 2001; Kajitvichyanukul and Watcharenwong, 2003). Harmful chromium (VI) undergoes photocatalytic process reducing to less harmful chromium (III) (Shaban, 2013). However, there are some problems when TiO_2 is used as catalytic in photocatalytic process that are low adsorption activity and the difficulty in separating the catalyst from the effluent. The latter problem could be avoided by using the TiO_2 films applied on different types of substrates (Fujishima, 2000). As results, many research works have been used the TiO_2 in an immobilised form to treat pollutants from water/wastewater. Recently, many research works were focused on the improvement of adsorption ability of TiO_2. In this work, the synthesis of new composite material as TiO_2/chitosan film was purposed with the major objective was to enhance the adsorption ability of TiO_2 in photocatalytic process. Chitosan is a biopolymer material produced from N-deacetylation of chitin. It has a superb ability in adsorption of various pollutants especially metal ions. It is a powerful chelating agent, which is easy to form complexes with the combination of chitosan on TiO_2 film. It was expected that the adsorption ability of TiO_2 would be enhanced with our new composite material.

In this work, new composite material as TiO_2/chitosan film was synthesised by sol-gel method. The chromium removal was investigated by the performance of TiO_2/chitosan film such as adsorption ability and photocatalytic oxidation under UV light. The performance of TiO_2/chitosan film was compared with TiO_2 powder and neat chitosan film. The effect of different TiO_2 concentration on TiO_2/chitosan film preparation, the stability of the obtained films, and the chromium removal percentage were reported.

2 Experimental

2.1 *Materials*

Chitosan of medium molecular weight (600,000 g/mol) with moisture content (6%), sulphated ash (0.3%) and viscosity (411 mPas), TiO_2 (Degussa P25) were obtained from Fluka, Sigma-Aldrich Co. Acetic acid, potassium chromate (K_2CrO_4), sodium hydroxide (NaOH) and sulphuric acid (H_2SO_4) were purchased from Merck chemical company. Ultra-pure water was used throughout this study.

2.2 Preparation TiO_2/chitosan film and chitosan film

Nano-TiO_2 was mixed to chitosan in different ratios of TiO_2 to chitosan, and then the mixture was added to acetic acid solution 20%. The above mixture solution was constantly stirred for 24 h at room temperature, and then 5 g slurry was taken and spread on a glass plate with dimension 5 cm × 6 cm. Then the mixed TiO_2/chitosan solution was dried at room temperature for 48 h. Subsequently, the obtained solution was casted on a glass plate at room temperature. The weight of different TiO_2/chitosan film was weighted by weight balance, and the thickness was measured by micrometer at eight points on each film. The average weight and thickness of TiO_2/chitosan film were calculated. The average weight ranged from 0.0896 to 0.1649 g, and the average thickness ranged from 0.027 to 0.056 mm.

2.3 Characterisation and analysis

The surface morphology of TiO_2/chitosan film was observed by using scanning electron microscopy (SEM). The X-ray Diffraction (XRD) with monochromatised Cu Kα characteristic radiation (in the 2θ range of 9°–60°) was used to obtain XRD patterns of TiO_2/chitosan film at room temperature.

Stock chromium solution was prepared by dissolving approximated 141.1 mg $K_2Cr_2O_7$ in double distilled water and diluting up to 100 mL (1 mL = 500 μg Cr^{+6}). Diphenylcarbazide solution was obtained from a dissolubility of 250 mg 1, 5-diphenylcarbazide in 50 ml acetone. Samples from each experiment were equilibrated in the dark condition and adjusted pH to 1.0 ± 0.3 by 2N H_2SO_4, and adding 2.0 mL diphenylcarbazide solution in the sample, then mixing until full colour was developed. The concentration of chromium was monitored at different time interval using UV-Vis spectroscopy at 540 nm.

2.4 Evaluation of photocatalytic performance

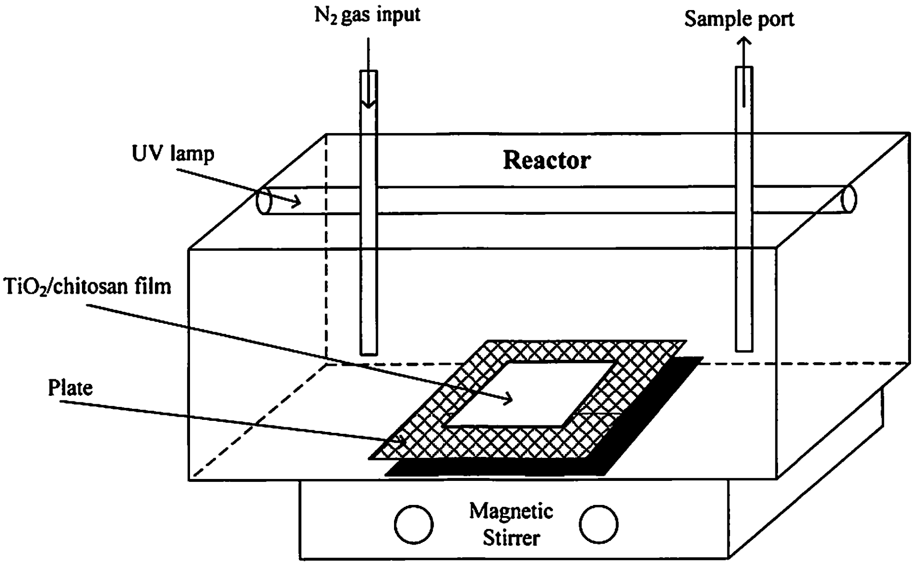
The photoreactor consisted of 1.5 L reactor, a UV lamp (10 W, 254 nm), nitrogen (N_2) gas supply, TiO_2/chitosan film, and a magnetic stirrer (Figure 1). The UV lamp was placed on the top of the reactor. The TiO_2/chitosan film with 30 cm^2 surface area was soaked in distilled water for 30 min to adjust from dry to wet film, and then placed on the screen before putting in the reactor.

The adsorption experiments were carried out in a batch mode. One litre of synthetic chromium (VI) solution at pH 3 was poured into the reactor and mixed by magnetic stirrer in 150 min for adsorption equilibrium in the dark condition. The samples were taken at 0, 10, 15, 30, 45, 60, 90, 120 and 150 min to measure residual chromium concentration in each sample.

In the photocatalytic process, the UV lamp was turned on, and nitrogen gas was supplied to the reactor. Each sample was syringed out with different setting time for the measurement of residual chromium (VI) concentration. The effects of different initial chromium concentrations (50, 100, 150, 200, 250 and 300 ppm), and different TiO_2/chitosan films obtained from different TiO_2 concentrations (0, 0.2, 0.4, 0.6 and

0.8% with 1.5% chitosan) on adsorption and photocatalytic oxidation were studied. Photocatalysis experiments using composite TiO_2/chitosan film and TiO_2 powder with the same amount of catalyst in both materials were conducted to obtain the effect of different forms of TiO_2 on the photocatalytic activity. It is noted that the removal of chromium (VI) using chitosan films in photocatalysis is not significantly different from that in the adsorption process. Thus, in this work, we varied only the TiO_2 content in the film.

Figure 1 Reactor set up



Langmuir and Freundlich equations, given by equations (1) and (2), respectively, were used to describe adsorption of TiO_2/chitosan films.

$$\frac{C_e}{x/m} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0 b} \tag{1}$$

where C_e (mg/L) is the equilibrium concentration of chromium (VI), x/m (mg/g) is the amount of adsorbed chromium (VI) at equilibrium per unit mass of TiO_2/chitosan film, Q_0 (mg/g) is maximum adsorption at monolayer coverage, and b (L/mg) is Langmuir constant related to the affinity of binding sites.

$$\log\left(\frac{x}{m}\right) = \left(\frac{1}{n}\right)\log C_e + \log k_f \tag{2}$$

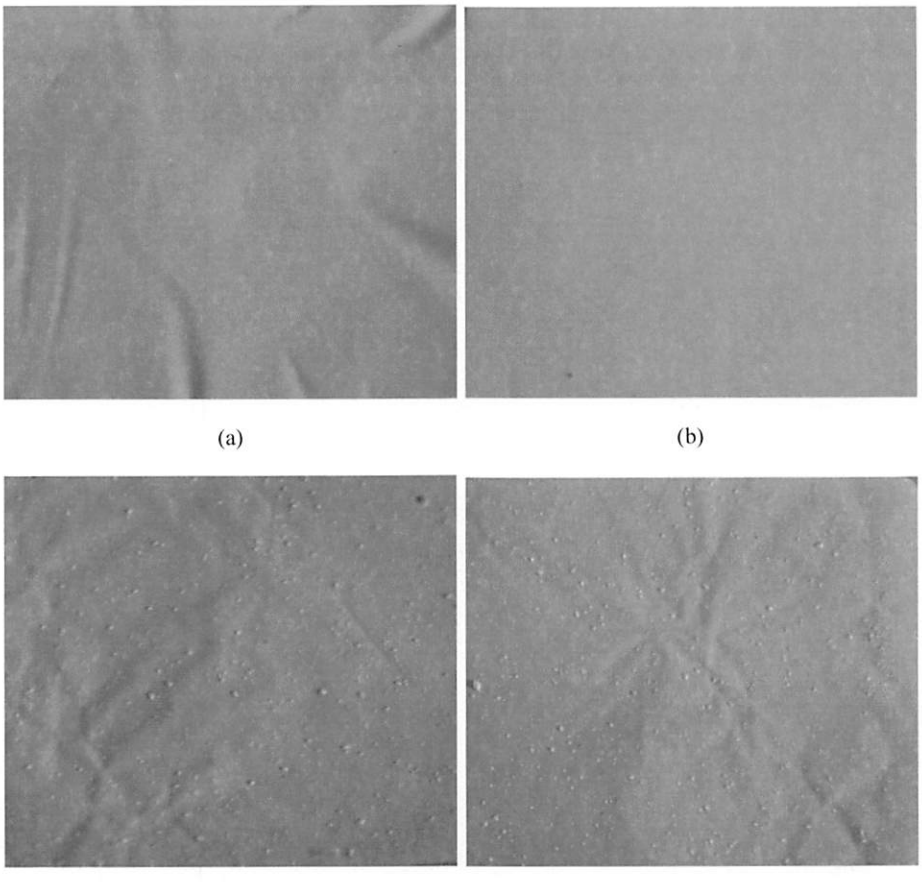
where C_e (mg/L) is the equilibrium concentration of chromium (VI), x/m (mg/g) is the amount of adsorbed chromium (VI) at equilibrium per unit mass of TiO_2/chitosan film, k_f, and n are the Freundlich constants.

3 Results and discussion

3.1 TiO_2/chitosan film preparation

TiO_2/chitosan films were prepared from different TiO_2 concentrations (0.2%, 0.4%, 0.6% and 0.8%) and different chitosan concentration (1.0%, 1.5%, 2.0% and 2.5%). The results indicated that at high chitosan concentrations (2.0% and 2.5%), the slurry was not homogeneous and the surface of TiO_2/chitosan films with were not smooth. The low chitosan concentration (1.0% and 1.5%) could well fabricate smooth TiO_2/chitosan films resulting in a homogeneous film surface. The film obtained from 0.8% TiO_2 and 1.5% chitosan provided the best physical property as considered from its smoothness and homogeneous appearance (Figure 2).

Figure 2 Surface view of TiO_2/chitosan films with different TiO_2 and chitosan concentrations, (a) 0.6% TiO_2, 1.5% chitosan (b) 0.8% TiO_2, 1.5% chitosan (c) 0.6% TiO_2, 2.5% chitosan (d) 0.8% TiO_2, 2.5% chitosan



(a) (b)

(c) (d)

3.2 Surface observation

3.2.1 SEM

SEM analysis was used to study the morphology of TiO_2/chitosan films. The surface SEM images of TiO_2/chitosan film were obtained from the different TiO_2 and chitosan concentrations. The results indicated that the surface of chitosan film (0% TiO_2) was flat and smooth with a homogeneous surface. With the addition of TiO_2 to the chitosan slurry, the different surface morphology of the composite film was obtained as shown in Figure 3. The TiO_2 was impregnated into the chitosan surface.

Figure 3 SEM micrographs of TiO_2/chitosan films, (a) surface view of TiO_2/chitosan film with 0% TiO_2 and 1% chitosan (b) surface view of TiO_2/chitosan film 0.4% TiO_2 and 1.5% chitosan

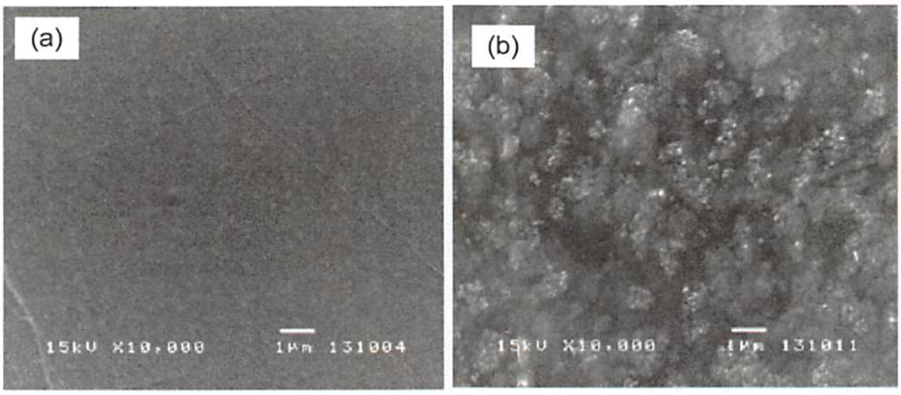
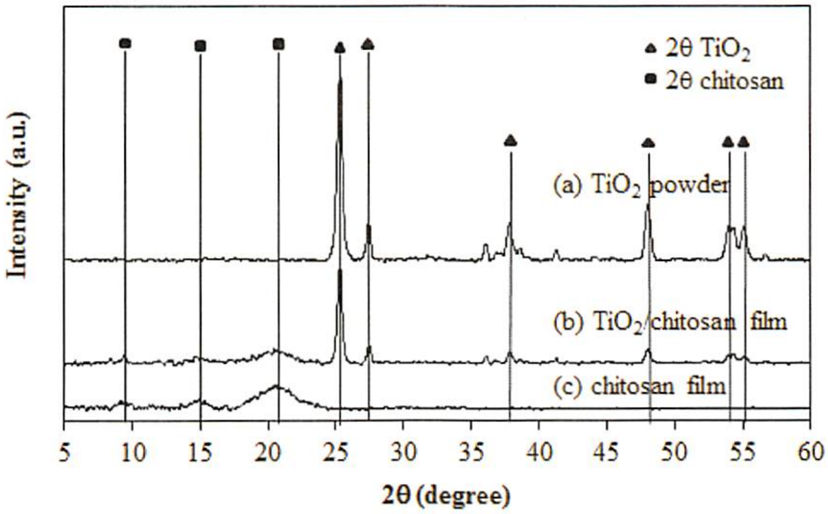


Figure 4 X-ray diffraction patterns of the comparison among of (a) TiO_2 powder, (b) TiO_2/chitosan film with 0.8% TiO_2 and 1.5% chitosan and (c) chitosan film



3.2.2 XRD

The XRD diffraction patterns of TiO_2 particle, chitosan film (0% TiO_2 and 1.5% chitosan) and TiO_2/chitosan film (0.8% TiO_2 and 1.5% chitosan) were shown in Figure 4. XRD pattern of TiO_2 powder shown characteristic crystalline peaks at 25.3° and 27.5°, in which peak of 25.3° was anatase phase and 27.5° was rutile phase. The characteristic crystalline peaks of chitosan film with 2θ at 9.5°, 15.0° and 20.5°. The 2θ at 9.5° and 20.5° was amino acid structure that was an agile group that reacted with chitosan reaction. The TiO_2/chitosan film provided five characteristic crystalline peaks of 2θ at 9.5°, 15.5°, 20.5°, 25.3° and 27.5°. The 2θ at 9.5°, 15.0°, 20.5° were the chitosan peaks, and the 2θ at 25.3° and 27.5° were the TiO_2 crystalline peaks. The results indicated that both TiO_2 and chitosan did not change in their identities, and TiO_2 particles were well distributed on TiO_2/chitosan film.

3.3 Photocatalytic batch experiments

3.3.1 *Effect of TiO_2 concentration on chromium adsorption on TiO_2/chitosan film*

Figure 5 shows the adsorption of chromium (VI) and TiO_2/chitosan films surface that occurred during the dark equilibration period. The amount of chromium (VI) adsorption was increased with time and attained equilibrium at 120 min. This result indicates the required equilibration time for a maximum chromium (VI) adsorption onto TiO_2/chitosan film surface. The percentage of chromium adsorption onto TiO_2/chitosan film (varied Ti content with 1.5% chitosan) ranged from 29.01% to 64.50% after reaching equilibrium. TiO_2/chitosan film with 0.8% TiO_2 and 1.5% chitosan provided the highest adsorption. The lowest chromium adsorption (29.01%) was obtained from the TiO_2/chitosan film with 0.2% TiO_2 and 1.5% chitosan. The results illustrate that the high amount of TiO_2 in the composite TiO_2/chitosan film tentatively lead to the increasing of chromium adsorption on TiO_2/chitosan film.

Figure 5 Adsorption percentages of 100 mg/L chromium (VI) on TiO_2/chitosan film with different TiO_2 contents (0.2, 0.4, 0.6 and 0.8%) and 1.5% chitosan

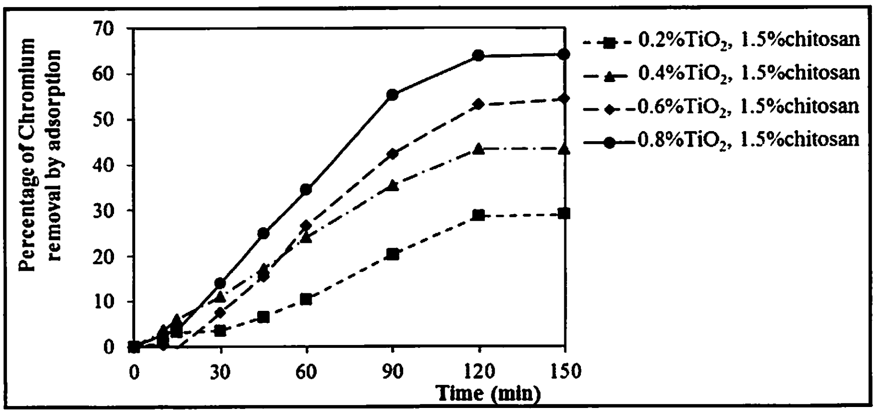


Table 1 demonstrates the adsorption of 100 mg/L of chromium (VI) concentration on TiO_2/chitosan, chitosan film, and TiO_2 powder surface. Percentages of chromium (VI) removal using TiO_2/chitosan film (varied Ti content and fixed 1.5% chitosan) were in the range of 29.01%–64.50%. The TiO_2 powder with varied contents and the chitosan film can remove chromium (VI) with the percentage in the range of 0.33%–2.38% and 18.64%, respectively. Apparently, chromium (VI) removal efficiency using TiO_2/chitosan film was higher than that using chitosan film and TiO_2 powder. The TiO_2/chitosan film with 0.8% TiO_2 and 1.5% chitosan provided the highest efficiency for chromium (VI) removal.

Table 1 Percentage removals of 100 mg/L chromium (VI) using TiO_2/chitosan films, TiO_2 powder with different TiO_2 content, and chitosan film in the adsorption process

Types of film	*Chitosan contents (%)*	*TiO_2 contents (%)*	*Initial concentration of chromium (VI) (mg/L)*	*x/m at the end of the adsorption process (mg of Cr (VI)/g of film)*	*% Removal*
TiO_2/chitosan film	1.5	0.2	100	304. 05	29.01
	1.5	0.4	100	420.12	43.36
	1.5	0.6	100	430.85	54.35
	1.5	0.8	100	433.23	64.05
TiO_2 powder	0	0.2	100	21.25	0.33
	0	0.4	100	28.72	0.84
	0	0.6	100	30.83	1.40
	0	0.8	100	37.72	2.38
Chitosan film	1.5	0	100	252.23	18.64

3.3.2 Adsorption isotherm

Equilibrium isotherm of chromium was investigated by using the pilot scale of batch experiment. Langmuir and Freundlich equations were used to model the equilibrium data of chromium adsorption (Table 2). The correlation coefficient (R) of all tested models by Langmuir was ranged from 0.9792 to 0.9872 depending on TiO_2 concentration while the correlation coefficient for Freundlich plot was ranged from 0.8725 to 0.9373. The value of the correlation coefficient of chromium (VI) adsorption indicates that the adsorption behaviour of chromium (VI) onto TiO_2/chitosan film tends to be a monolayer adsorption as described by Langmuir model with a better fit than Freundlich.

Thus, the adsorption of chromium on TiO_2/chitosan film surface in each condition obeys Langmuir adsorption isotherm. The correlation coefficient for the linear regression fits the Langmuir plot. All the models tested indicated a good correlation coefficient (0.9792 to 0.9872) depending on concentration TiO_2 on TiO_2/chitosan film. The reason for the increasing of chromium removal by TiO_2/chitosan film ion sorption could be the synergistic effect of chelation of chitosan that is enhancing the adsorption ability of chromium (VI) onto the composite film. In addition, it is reported previously that the formation of macro-pores on the immobilised TiO_2, the top layer of the TiO_2/chitosan, is responsible for more chromium ions adsorption over this porous structure (Nawi et al., 2011; Nawi et al., 2012).

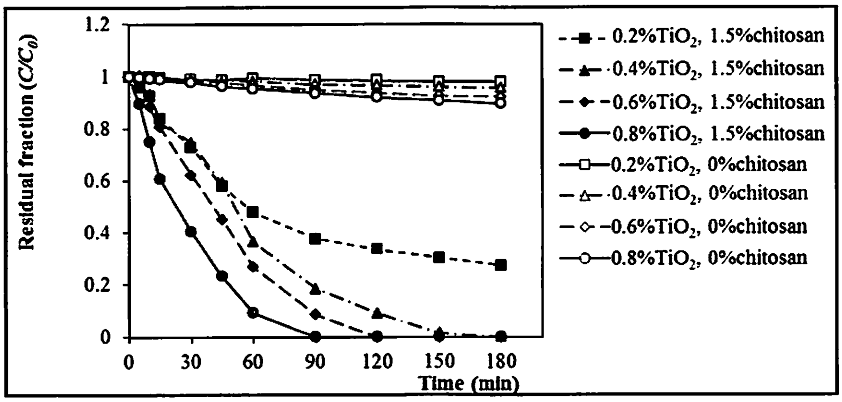
Table 2 Langmuir and Freundlich adsorption isotherms for TiO_2/chitosan film that prepared from 0.2, 0.4, 0.6 and 0.8% TiO_2 with 1.5% chitosan

Adsorption isotherms	*Chitosan contents (%)*	*TiO_2 contents (%)*	*Equations*	R^2
Langmuir	1.5	0.2	$C_e/(x/m) = 0.0023\,C_e + 0.0598$	0.9838
	1.5	0.4	$C_e/(x/m) = 0.0018\,C_e + 0.0310$	0.9824
	1.5	0.6	$C_e/(x/m) = 0.0017\,C_e + 0.0209$	0.9872
	1.5	0.8	$C_e/(x/m) = 0.0016\,C_e + 0.0172$	0.9792
Freundlich	1.5	0.2	$log(x/m) = 0.1794\,C_e + 2.1685$	0.9373
	1.5	0.4	$log(x/m) = 0.1403\,C_e + 2.383$	0.9352
	1.5	0.6	$log(x/m) = 0.0992\,C_e + 2.5066$	0.8725
	1.5	0.8	$log(x/m) = 0.0923\,C_e + 2.5445$	0.9039

3.3.3 Photocatalytic reduction of chromium (VI) using TiO_2/chitosan film and kinetics

The photocatalytic reduction of 100 mg/L chromium (VI) concentration in the irradiation process for TiO_2/chitosan film with different TiO_2 contents and TiO_2 powder were compared. The ratio of residual to the initial concentration of chromium (VI) in term of C/C_0 as a function of irradiation time was illustrated in Figure 6.

Figure 6 Residual fraction of chromium (VI) in different TiO_2 content under photocatalytic reduction reaction



The TiO_2/chitosan film provided the higher efficiency in chromium (VI) removal than that obtained from the TiO_2 powder. Higher TiO_2 concentration of TiO_2/chitosan film gave higher chromium removal efficiency. Under photocatalytic process, the chromium (~100 mg/L) in solution after adsorption process was completely removed by TiO_2/chitosan film with 0.8%, 0.6% and 0.4% TiO_2 and 1.5% chitosan after 90, 120 and 180 min, respectively. Chromium removal by TiO_2/chitosan film with the lowest TiO_2 content (0.2%) was 80.61% after 180 min. While TiO_2 powder provided relatively low chromium removal efficiency. Chromium removal efficiency by TiO_2 powder with concentration of 0.2%, 0.4%, 0.6% and 0.8% was 2.25%, 5.08%, 9.01% and 12.53% after

180 min, respectively. In addition, chromium was not removed by chitosan film under photocatalytic process. The TiO_2/chitosan film with 0.8% TiO_2 and 1.5% chitosan provided the highest efficiency of chromium (VI) removal. The explanation might come from the fact that chitosan that composed with TiO_2 could enhance adsorption ability of TiO_2/chitosan film in photocatalytic process. Chitosan is biopolymer material produced from N-deacetylation of chitin that has a superb ability in adsorbing pollutants especially metal ions. The combination of TiO_2 and chitosan leads to powerful chelating agent that is easy to form complexes with chromium (VI) (Ramnani et al., 2006). For this reason, the adsorption ability of TiO_2 would be enhanced by composed with chitosan.

To obtain the kinetic information from the photocatalytic reduction of chromium (VI) using TiO_2/chitosan film, the experiments with the initial concentration of chromium varied from 50–300 mg/L were conducted. The pH was fixed at values 3. It was found that TiO_2/chitosan films were excellence in chromium removal to compare with chitosan film or TiO_2 powder separately. Higher TiO_2 concentration of TiO_2/chitosan film gave higher chromium removal efficiency. Results are shown in Figure 7.

The Langmuir-Hinshelwood rate expression has been used for heterogeneous photocatalytic degradation to determine the relationship between the initial degradation rate and the initial concentration of chromium (VI),

$$\frac{1}{k_{obs}} = \frac{1}{k * K_{Cr(VI)}} + \frac{[Cr(VI)]_0}{k} \tag{3}$$

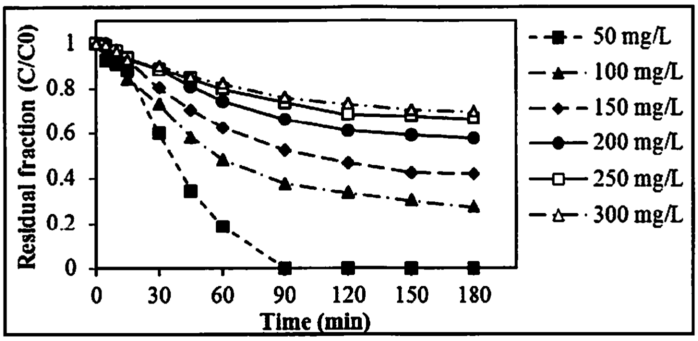
where $[Cr\ (VI)]_0$ is the initial concentration of chromium (VI) in the unit of mg/L, k is the rate constant of surface reaction in the unit of mg/(L min), and $K_{Cr\ (VI)}$ is the Langmuir-Hinshelwood adsorption equilibrium constant in the unit of L/mg.

The kinetics of different chromium concentration in the range of 50 to 300 mg/L fitted well to the Langmuir-Hinshelwood model ($R^2 \approx 0.98$). The Langmuir-Hinshelwood equations for each TiO_2/chitosan film are shown in Table 3.

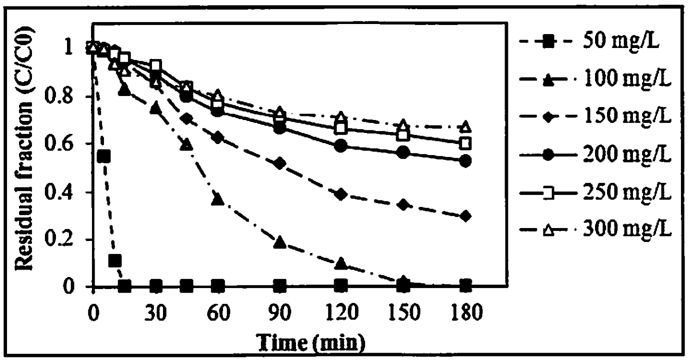
Table 3 Langmuir-Hinshelwood equations for photocatalytic process using TiO_2/chitosan films in variation of TiO_2 contents

Chitosan contents (%)	*TiO_2 contents (%)*	*Langmuir-Hinshelwood Equation*
1.5	0.2	$\frac{1}{k_{obs}} = \frac{1}{(0.409)(-0.024)} + \frac{[Cr(VI)]_0}{0.409}$
1.5	0.4	$\frac{1}{k_{obs}} = \frac{1}{(0.623)(-0.058)} + \frac{[Cr(VI)]_0}{0.623}$
1.5	0.6	$\frac{1}{k_{obs}} = \frac{1}{(0.646)(-0.039)} + \frac{[Cr(VI)]_0}{0.646}$
1.5	0.8	$\frac{1}{k_{obs}} = \frac{1}{(0.732)(-0.039)} + \frac{[Cr(VI)]_0}{0.732}$

Figure 7 Residual fraction of chromium (VI) in different initial concentrations for TiO_2/chitosan film that prepared from (a) 0.2% TiO_2 and 1.5% chitosan, (b) 0.4% TiO_2 and 1.5% chitosan and (c) 0.6% TiO_2 and 1.5% chitosan



(a)



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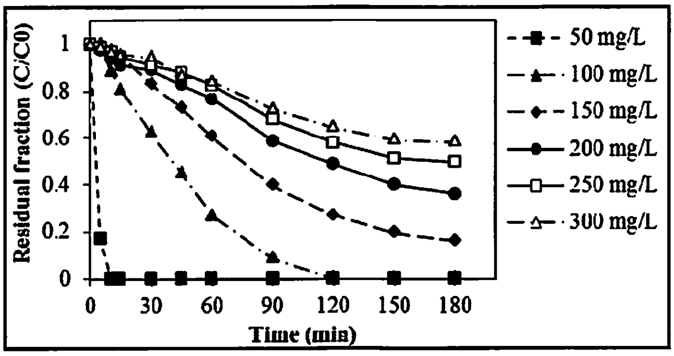
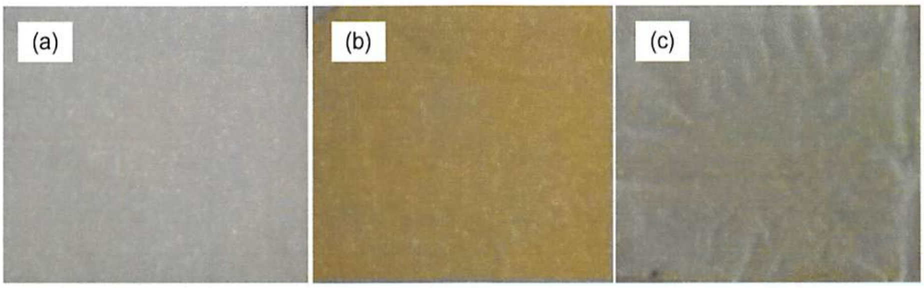


(c)

After carried out the experiments, TiO_2/chitosan film was taken out of the reactor and investigated TiO_2 particles absorption on the surface of the film. It was found that the colour of TiO_2/chitosan film was changed from grey to yellow after dark adsorption process, and the colour changed from yellow to light-green after photocatalytic process (Figure 8). It was demonstrated that chromium had absorbed on TiO_2/chitosan film, and the reduction of chromium from chromium (VI) (yellow) to chromium (III) (light-green) occurred.

Figure 8 Changing colour of TiO_2/chitosan film before and after photocatalytic process, (a) the colour of TiO_2/chitosan film before treated chromium (b) the colour of TiO_2/chitosan film after dark adsorption process (c) the colour of TiO_2/chitosan film changing from Cr (VI) to Cr (III) after photocatalytic process (see online version for colours)

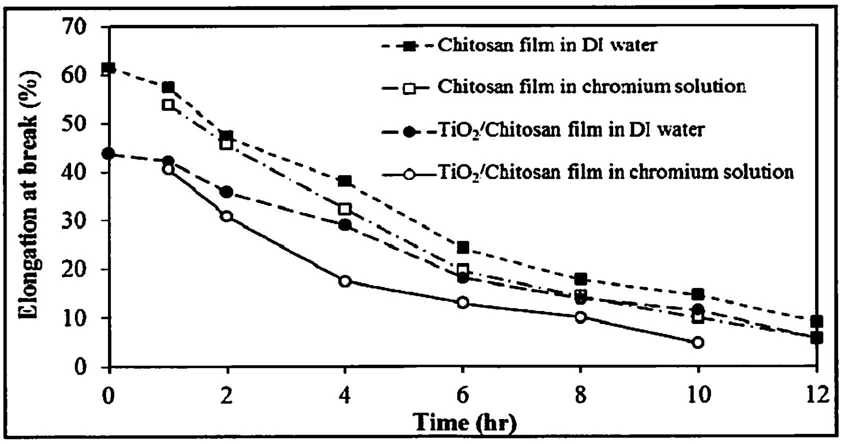


3.4 *Effect of the photocatalytic process on mechanical properties of the film*

Photocatalytic reaction of 100 mg/L chromium solution was conducted to investigate the stability of TiO_2/chitosan film. TiO_2/chitosan film with 0.8% TiO_2 and 1.5% chitosan was used. The mechanical properties of TiO_2/chitosan and chitosan films included of tensile strength and elongation at break. The measurement was conducted after both films were used in photocatalytic process for 0, 2, 4, 6, 8, 10 and 12 hours with either in DI water (pH7) or chromium solution (pH3). It was found that tensile strength of chitosan and TiO_2/chitosan films at beginning were 4.127 N/mm^2 and 0.914 N/mm^2, respectively. While the elongation at break of chitosan film and TiO_2/chitosan film before photocatalytic test were 61.35% and 46.63%, respectively. The tensile strength and elongation at break of TiO_2/chitosan were lower than chitosan film.

After UV irradiation under photocatalytic process, tensile strength and elongation at break of two types of film tended to decrease from time to time (Figure 9). The chitosan structure of both films may be destroyed under UV light. Both tensile strength and elongation at break of TiO_2/chitosan film were reduced faster than the chitosan film. In addition, the films in a chromium solution were deformed faster than those in DI water under UV irradiation. This result indicated that under acidic chromium solution, chitosan that protonated amino group ($-NH_{3+}$) as a functional of the chitosan biopolymer might capture negatively charged (chromium (VI) existed as $HCrO_4^-$) causing the destroying intramolecular hydrogen bonding of chitosan polymer. In addition, under photocatalytic reduction of chromium (VI), the hydroxyl radical ($^{\bullet}OH$) was highly generated from the photocatalytic oxidation of water. This radical is known for its powerful and high reactivity. The reaction of the hydroxyl radical with chitosan film may the results of the increasing of deformable and degradable of both chitosan and TiO_2/chitosan films.

Figure 9 Relationship between elongation at break (%) of films and UV illumination time (hr)



4 Conclusions

The present study focused on application of TiO_2/chitosan film in adsorption and photocatalytic process for chromium (VI) removal from synthetic wastewater. The results found that TiO_2/chitosan films can efficiently remove chromium (VI) from the wastewater. Both TiO_2 and chitosan contents are the major factors that affect on film properties, adsorption percentage, and photocatalytic activities for chromium (VI) removal. The obtained chitosan film surface was flat and smooth while TiO_2/chitosan film was non-uniform with TiO_2 scattering on the surface of the composite film.

In the adsorption process, chromium removal efficiency using TiO_2/chitosan film was higher than that using chitosan film and TiO_2 powder. The TiO_2/chitosan film with 0.8% TiO_2 and 1.5% chitosan provided the highest removal efficiency (64.05%) of 100 mg/L of chromium (VI) in the adsorption process. The adsorption behaviour of chromium (VI) onto all of TiO_2/chitosan film tends to be a monolayer adsorption as described by the Langmuir isotherm..

Under photocatalytic process with 100 mg/L chromium concentration in solution before irradiation, the chromium in solution was completely removed by TiO_2/chitosan film with 0.8%, 0.6% and 0.4% TiO_2 and 1.5% chitosan after 90, 120 and 180 min, respectively. While TiO_2 powder provided relatively low chromium removal efficiency. Chromium removal efficiency by TiO_2 powder with concentration of 0.2%, 0.4%, 0.6% and 0.8% was 2.25%, 5.08%, 9.01% and 12.53% after 180 min, respectively. In addition, chromium was not removed by chitosan film under photocatalytic process. The TiO_2/chitosan film with 0.8% TiO_2 and 1.5% chitosan provided the highest efficiency of chromium (VI) removal. The photocatalytic reduction reactions of TiO_2/chitosan films could be described by pseudo-first order pattern. The chitosan structure of both films may be destroyed after photocatalytic process. Both tensile strength and elongation at break of TiO_2/chitosan film were reduced faster than the chitosan film. In addition, the films in a chromium solution were deformed faster than those in DI water under UV irradiation. The deformation of the both films by ultraviolet light and pH of the solution was found. This TiO$_2$/chitosan film provided high efficiency in chromium (VI) removal. However, the deformation of films under ultraviolet light and acidic pH is the important limitation of the application of this composite film.

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