# CHAPTER IV

# RESULTS AND DISCUSSIONS

## 4.1 Role of chitosan content on $TiO_2$/chitosan and chitosan films preparation.

In this experiment, $TiO_2$/chitosan film prepared by mixing $TiO_2$ (Degussa P-25) with chitosan flake from crab shells which was highly viscosity in acetic acid solution. The physical and chemical properties of chitosan flake present in table 4.1.For $TiO_2$ powder (Degussa P-25) and chitosan flake that used in this research were shown in figure 4.1.

**Table 4.1** Physical and chemical properties of chitosan flake(Fluka, Sigma-aldrich co., plc.)

| Physical and chemical properties | Values |
|---|---|
| Moisture content (%) | 6 |
| Sulfated ash(%) | 0.3 |
| Viscosity(mPas) | 411* |
| Deacetylation (%) | 85-90 |
| Molecular weigh(gram/mole) | ~600,000 |

* 1% chitosan in 1% acetic acid at 20 C°

$TiO_2$/chitosan films in different conditions were prepared by dissolving 1, 1.5, 2 and 2.5% w/w of chitosan flake with 0.4% Ti from $TiO_2$ powder in 20% acetic acid solution for 24 hr So $TiO_2$/chitosan slurry which were similar to glue. After that 5 g of slurry were taken and spread them on 5x6 cm glass plate then placed its in room temperature to dry for 48 hr Next step, the film was peeled out from glass plate. And stored in the confined space.

For chitosan films were prepared by dissolving 1, 1.5, 2 and 2.5% w/w of chitosan flake in 20% acetic acid solution without $TiO_2$ power in same method of $TiO_2$/chitosan films preparation.

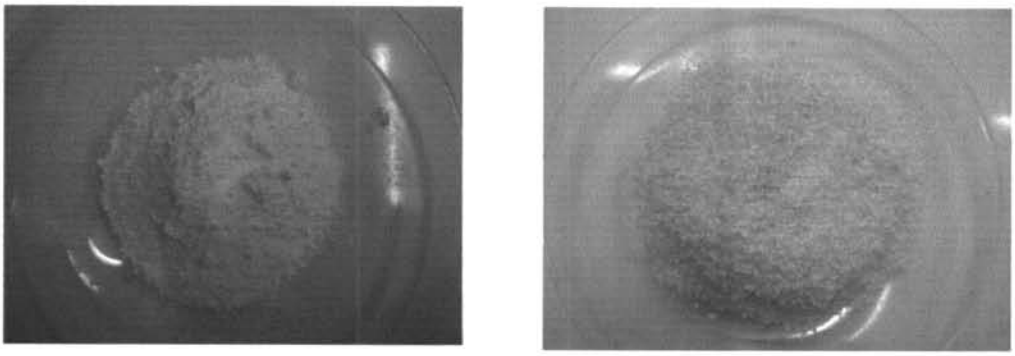
### 4.1.1 Results of film weight, thickness and characteristic

Effect of varying chitosan content on properties of film show in table 4.2 – 4.4 so, chitosan content was important factor that influence on chitosan and $TiO_2$/chitosan films properties such as weight, thickness and characteristics of film. Weight of film results represent in table 4.2. In this study, the weight of $TiO_2$/chitosan film was obtained in ranged of 0.0896-0.1649 g ± 0.029 whereas the weight of chitosan film was in ranged of 0.0534-0.1295 g. ± 0.030 This result could be compared between $TiO_2$/chitosan and chitosan film weight and it was found that the weight of $TiO_2$/chitosan film was heavier than weight of chitosan film because of the addition of 0.4% Ti on $TiO_2$/chitosan film. When consideration about the relation between the films which prepared in difference of chitosan contents, the result shown that trend of film weight of all samples were increased if increased chitosan content and weight of film that prepared from 1% chitosan was the lightest weight.

Regarding film thickness (Table 4.3), the thickness of $TiO_2$/chitosan film was obtained in ranged of 0.027-0.056 mm ± 0.013 while the thickness of chitosan film was in ranged of 0.014-0.041 mm ± 0.011. When compared between chitosan content on films in different chitosan contents were found that the thickness of film that prepared from 1% chitosan was the thinnest of film and the trend thickness of all films were increased with increasing chitosan content.

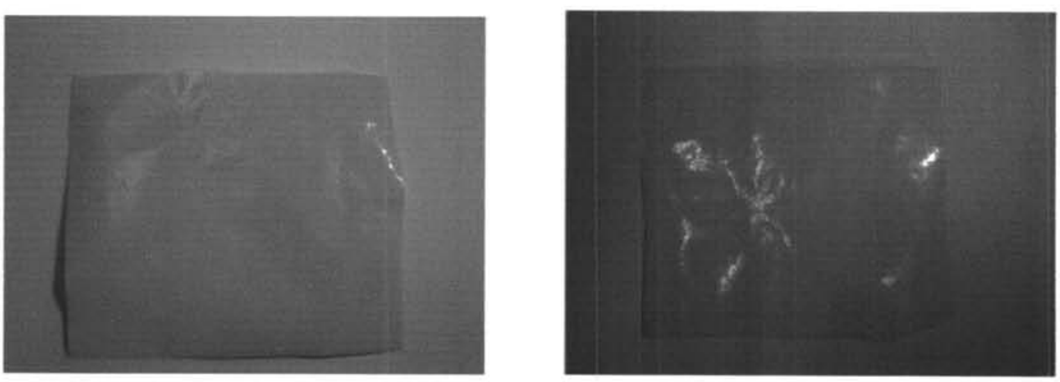
From this result, it could be concluded that the relation between chitosan content with weight and thickness of film, its weight and thickness tended to increase with the increasing of chitosan content. These results were similar to Sukkunta's research (2002).

The propertiesof prepared $TiO_2$/chitosan and chitosan films such as coarseness, transparent and acid odor of film were observed. The physical properties of film show in table 4.4. The film surface that exposed to the air was coarse, while the reverse surface touching glass was smooth and there were no acid odor after dry in room temperature for 48 hr.These results were similar to Sukkunta's research, 2002 which reported that drying of film could reduc the acidic odor and the transparent of film was observed. Chitosan films were transparent film which look like clear plastic on the other hand $TiO_2$/chitosan films look like dense plastic. Pictures of $TiO_2$/chitosan and chitosan films show in figure 4.2.



a) $TiO_2$ powder (Degussa P-25) b) Chitosan flake

**Figure 4.1** $TiO_2$ powder (Degussa P-25) and chitosan flake that used in this research



a) $TiO_2$/chitosan film b) Chitosan film

**Figure 4.2** Formation of $TiO_2$/chitosan and chitosan films

**Table 4.2** Weight of film that prepared from 1, 1.5, 2 and 2.5% chitosan with 0.4% Ti ($TiO_2$/chitosan film) and without Ti content(chitosan film)

| Types of film | Chitosan contents (%) | Ti contents (%) | Weight of film (g) | | | | | Average (g) | SD |
|---|---|---|---|---|---|---|---|---|---|
| $TiO_2$/ chitosan film | 1 | 0.4 | 0.0843 | 0.0955 | 0.0871 | 0.0901 | 0.0911 | 0.0896 | 0.0042 |
| | 1.5 | 0.4 | 0.1181 | 0.1134 | 0.1145 | 0.1132 | 0.1114 | 0.1141 | 0.0025 |
| | 2 | 0.4 | 0.1394 | 0.1413 | 0.1393 | 0.1419 | 0.1431 | 0.1410 | 0.0016 |
| | 2.5 | 0.4 | 0.1611 | 0.1639 | 0.1623 | 0.1681 | 0.1696 | 0.1649 | 0.0035 |
| Chitosan film | 1 | 0 | 0.0583 | 0.0514 | 0.0520 | 0.0542 | 0.0512 | 0.0534 | 0.0030 |
| | 1.5 | 0 | 0.0781 | 0.0811 | 0.0801 | 0.0800 | 0.0810 | 0.0801 | 0.0012 |
| | 2 | 0 | 0.1053 | 0.1060 | 0.1201 | 0.1113 | 0.1168 | 0.1119 | 0.0045 |
| | 2.5 | 0 | 0.1324 | 0.1371 | 0.1251 | 0.1282 | 0.1245 | 0.1295 | 0.0043 |

**Table 4.3** Thickness of film that prepared from 1, 1.5, 2 and 2.5% chitosan with 0.4% Ti ($TiO_2$/chitosan film) and without Ti content(chitosan film)

| Type of film | Chitosan contents (%) | Ti contents (%) | Thickness of film (mm) | | | | | Average (mm) | SD |
|---|---|---|---|---|---|---|---|---|---|
| $TiO_2$/ chitosan film | 1 | 0.4 | 0.030 | 0.035 | 0.027 | 0.025 | 0.020 | 0.027 | 0.006 |
| | 1.5 | 0.4 | 0.043 | 0.035 | 0.035 | 0.030 | 0.045 | 0.038 | 0.006 |
| | 2 | 0.4 | 0.050 | 0.040 | 0.045 | 0.050 | 0.050 | 0.047 | 0.004 |
| | 2.5 | 0.4 | 0.055 | 0.060 | 0.060 | 0.050 | 0.065 | 0.058 | 0.006 |
| Chitosan film | 1 | 0 | 0.013 | 0.015 | 0.013 | 0.015 | 0.010 | 0.013 | 0.002 |
| | 1.5 | 0 | 0.025 | 0.020 | 0.020 | 0.025 | 0.015 | 0.021 | 0.004 |
| | 2 | 0 | 0.025 | 0.035 | 0.025 | 0.035 | 0.035 | 0.031 | 0.005 |
| | 2.5 | 0 | 0.040 | 0.045 | 0.040 | 0.040 | 0.040 | 0.041 | 0.002 |

**Table 4.4** Physical characteristics of film that prepared from 1, 1.5, 2 and 2.5% chitosan with 0.4% Ti ($TiO_2$/chitosan film) and without Ti content(chitosan film)

| Types of film | Chitosan contents (%) | Ti contents (%) | Weight of slurry (g) | characteristics | | | |
|---|---|---|---|---|---|---|---|
| | | | | Transparency | Acid smell | Coarseness of film surface | |
| | | | | | | Exposed air | Contacted glass plate |
| $TiO_2$/ chitosan film | 1 | 0.4 | 5 | X | X | O | X |
| | 1.5 | 0.4 | 5 | X | X | O | X |
| | 2 | 0.4 | 5 | X | X | O | X |
| | 2.5 | 0.4 | 5 | X | X | O | X |
| Chitosan film | 1 | - | 5 | O | X | O | X |
| | 1.5 | - | 5 | O | X | O | X |
| | 2 | - | 5 | O | X | O | X |
| | 2.5 | - | 5 | O | X | O | X |

O = Showing characteristic

X = Not showing characteristic

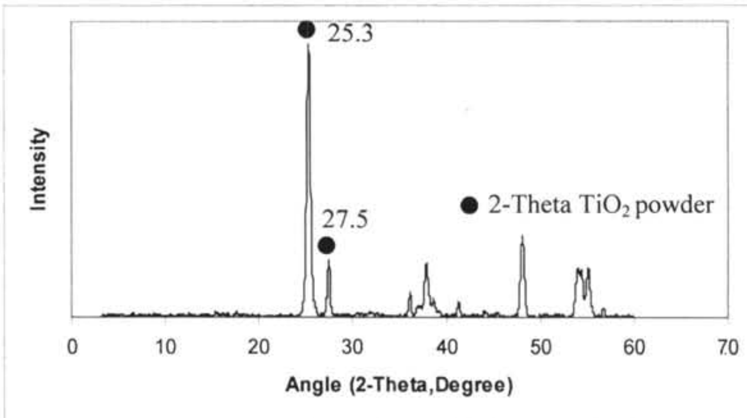
### 4.1.2 Crystal structures of $TiO_2$/chitosan and chitosan films

The XRD pattern of $TiO_2$ powder represent in figure 4.3 (a). $TiO_2$ crystalline was mainly composed of anatase phase as shown by the main peak of 2- Tetra at 25.3 degree was anatase phase and 2- Theta at 27.5 degree was rutile phase.

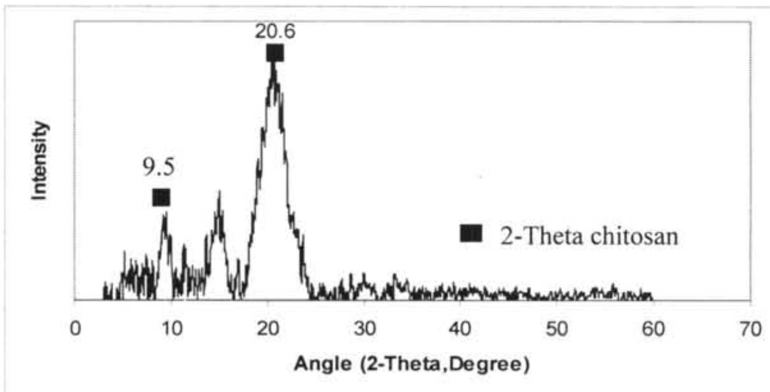
Crystallizations of $TiO_2$/chitosan and chitosan film were checked with Power X-Ray Diffractometer (XRD). Normally, chitin-chitosan was outstanding demonstrated peak of 2- Theta in two position were at 9 and 19 degree. So The 2-Theta at 9 and 19 degree were amino acid structure position which were a agile group to react with chitosan reaction (Sappawinyoo, 2002).

Results of crystallization of $TiO_2$/chitosan and chitosan films show in figure 4.3 (b - e) which could be described that peaks of 2-Theta. Chitosan film was outstanding demonstrated peaks of 2- Theta in three positions which were at 9.5, 15.5 and 20.5 degree(Figure 4.20). So The 2- Theta at 9.5 and 20.5 degree were amino acid structure position which was a agile group to react with chitosan reaction and 15 degree was a water crystallize structure 25.3 degree was anatase phase and 27.5 degree was rutile phase.

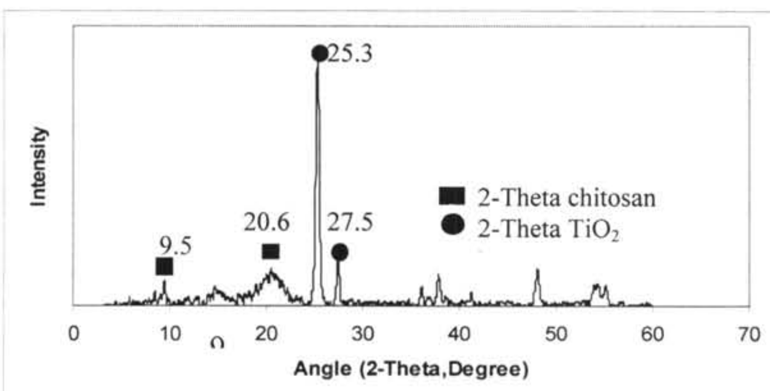
From synthesis XRD spectra results could be confirmed that chitosan and $TiO_2$/chitosan films that prepared from this method had no change in identity of chitosan and $TiO_2$ (Figure 4.4). However, $TiO_2$/chitosan and chitosan films that analyzed by XRD were prepared form 1% and 2.5% chitosan contents which were the minimum and maximum percentage of chitosan in this experiment and both of the films were maintained clear pattern of chitosan and $TiO_2$.




a)$TiO_2$ powder

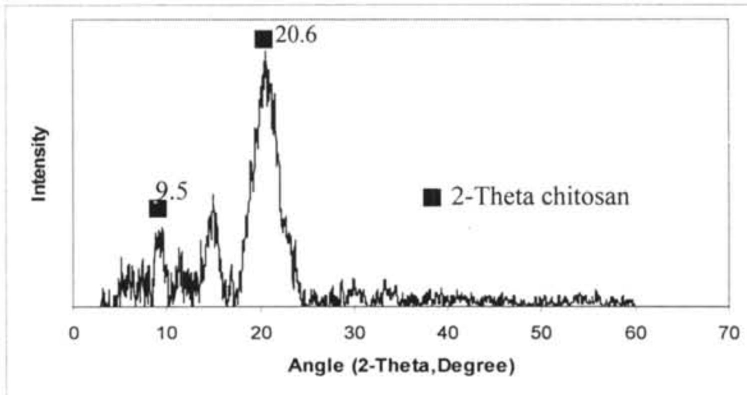



b) Chitosan film(1%chitosan, 0%Ti)

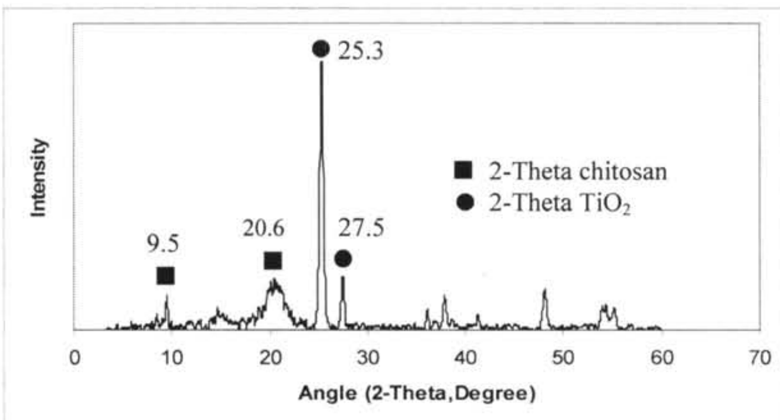



c) $TiO_2$/chitosan films(1%chitosan, 0.4%Ti)

**Figure 4.3** X-ray diffraction patterns of a) $TiO_2$ powder, b) Chitosan film (1% chitosan, 0% Ti), c) $TiO_2$/chitosan film (1% chitosan, 0.4%Ti) d) Chitosan film (2.5% chitosan, 0%Ti) and e) $TiO_2$/chitosan film (2.5% chitosan, 0.4%Ti)




d) Chitosan film(2.5%chitosan, 0%Ti)




e) $TiO_2$/chitosan films (2.5%chitosan, 0.4%Ti)

**Figure 4.3***(cont)* X-ray diffraction patterns of a) $TiO_2$ powder, b) Chitosan film (1% chitosan, 0% Ti), c) $TiO_2$/chitosan film (1% chitosan, 0.4% Ti) d) Chitosan film (2.5% chitosan, 0% Ti) and e) $TiO_2$/chitosan film (2.5% chitosan, 0.4% Ti)

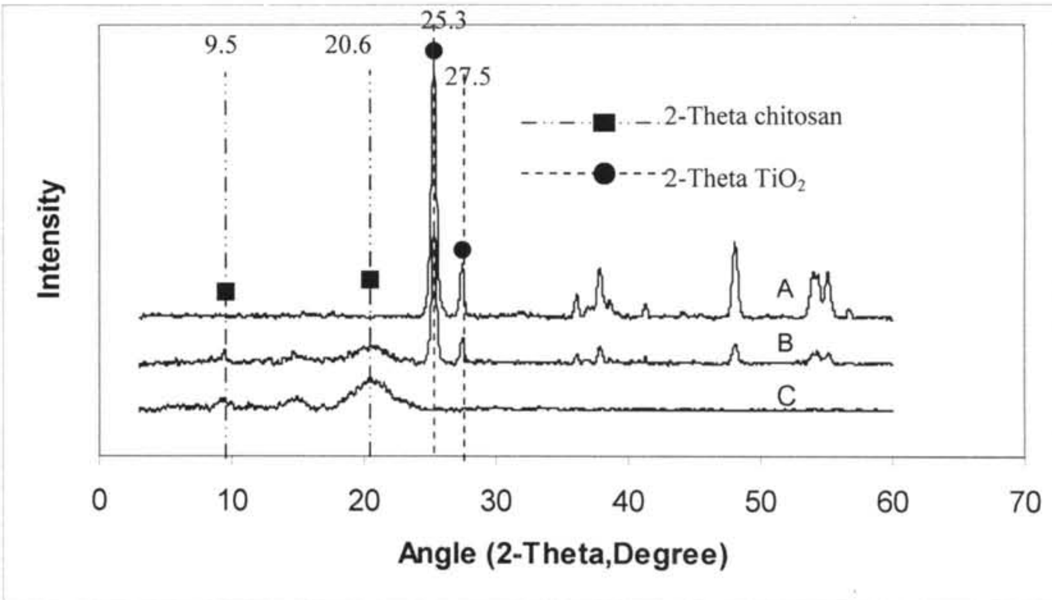
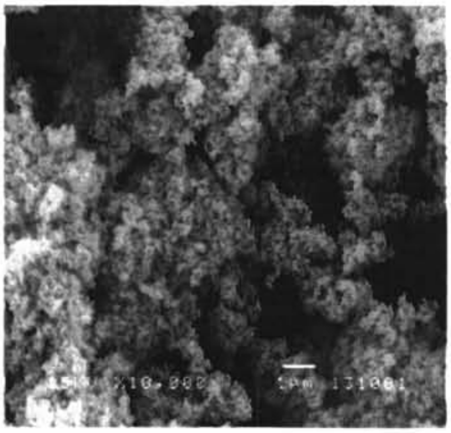


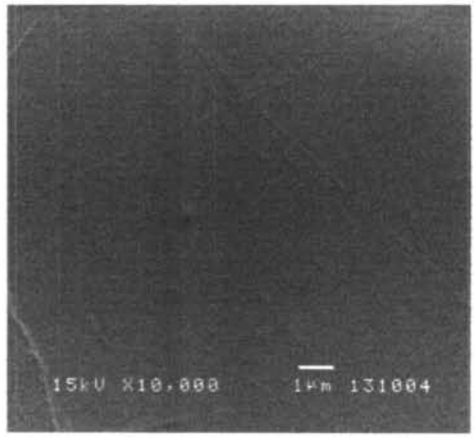

**Figure 4.4** X-ray diffraction patterns of the comparison between $TiO_2$ powder(A) and $TiO_2$/chitosan film(B) and chitosan film(C)

### 4.1.3 Surface morphology of $TiO_2$/chitosan and chitosan films analyzed by SEM

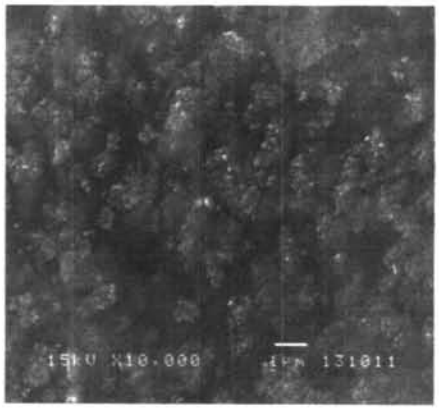
In this study, $TiO_2$ powder, $TiO_2$/chitosan and chitosan films were analyzed by using Scanning Electron Microscope (SEM) which was used at 10000 times in order to observe surface morphology (Figure 4.5). Results of this study shown that $TiO_2$ powder was agglomerated as particle. For chitosan film, the surface was flat and smooth which shows that chitosan was a homogeneous film before using for chromium(VI) removal. When $TiO_2$ composed with chitosan ($TiO_2$/chitosan film) which found that $TiO_2$ particles were non-uniform scattered into chitosan. In this study one condition of $TiO_2$/chitosan film has been shown since surface morphology of chitosan and $TiO_2$/chitosan films that prepared from variation of chitosan contents have no different in surface morphology.



a) $TiO_2$ powder




b) Chitosan film (1%chitosan,0%Ti)




c) $TiO_2$/chitosan film (1% chitosan,0.4% Ti)

**Figure 4.5** Scanning electron micrographs of a) $TiO_2$ powder, b) Chitosan film and c) $TiO_2$/chitosan film

### 4.1.4 Treating of chromium (IV) using synthesized $TiO_2$/chitosan and chitosan films

In this experimental set, chromium(IV) solution was prepared by dissolving potassium chromate in distilled water. The pH of the resultant solution was adjusted to pH 3 with diluted $H_2SO_4$. In this work, the treating of chromium was divided in to two process as follow: adsorption and photocatalytic processes.

Figure 4.6 shows about $TiO_2$/chitosan, chitosan film and $TiO_2$ powder for removing 100 mg/L chromium(VI)concentration. It was obvious that with $TiO_2$ powder alone (0% chitosan, 0.4% Ti), the removal efficiency was only 5.08 %. In addition, using chitosan only, the highest efficiency was 31.06 % with the maximum chitosan content (2.5% chitosan, 0%Ti). The $TiO_2$/chitosan film that the film which prepared from 2.5% chitosan with 0.4% Ti could completely remove 100 mg/L chromium(VI) concentration. It was clearly seen that the film with 2.5% chitosan, 0.4% Ti provided the performance (100% chromium(VI) removal) with the shortest treatment period.

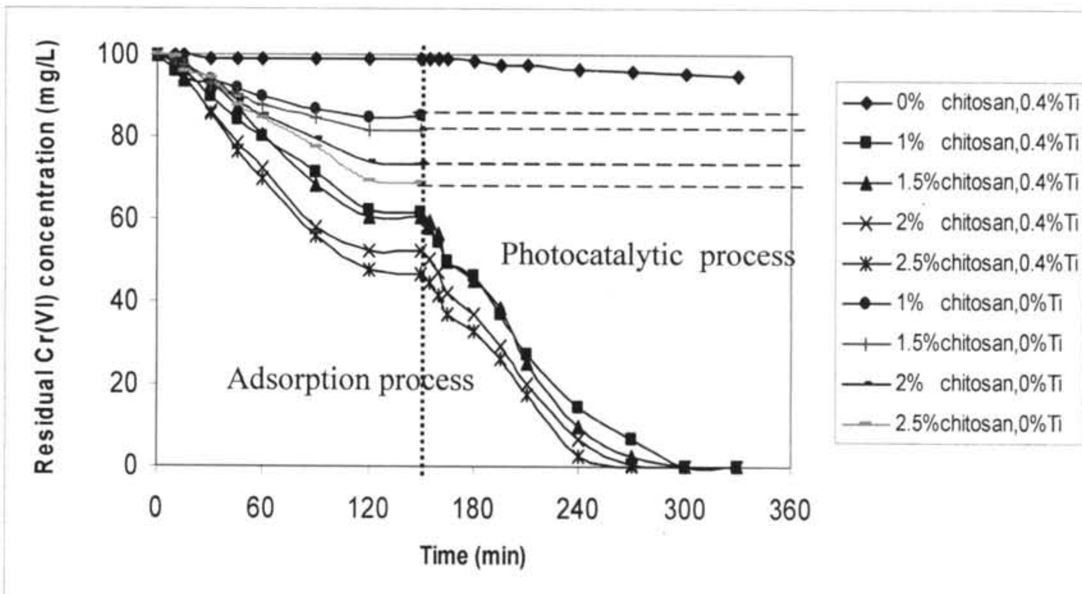



**Figure 4.6** Removal of 100 mg/L chromium(IV) concentration using synthesized films that prepared from 1, 1.5, 2 and 2.5% chitosan with 0.4% Ti ($TiO_2$/chitosan film) and without Ti content(chitosan film) in adsorption and photocatalytic processes

For chitosan films were used only adsorption process but the phenomenal of chitosan films for treating chromium(VI) in photocatalytic process were predicted that after illumination process, residual concentration of chromium(VI) in solution was not decreased because chitosan film is not semiconductor therefore photoreduction activity was not occurred. Efficiency of $TiO_2$/chitosan film in adsorption and photocatalytic processes show in table 4.5.

**Table 4.5** Percentage removals of 100 mg/L chromium(VI) by using synthesized films that prepared from 1, 1.5, 2 and 2.5% chitosan with 0.4% Ti ($TiO_2$/chitosan film) and without Ti content(chitosan film) in adsorption and photocatalytic processes.

| Types of film | Chitosan contents (%) | Ti contents (%) | Initial concentration of chromium(VI) (mg/L) | % Removal of chromium(VI) at the end of adsorption process | % Removal of chromium(VI) at the end of photocatalytic process |
|---|---|---|---|---|---|
| $TiO_2$/ chitosan film | 1 | 0.4 | 100 | 38.35 | 100 |
| | 1.5 | 0.4 | 100 | 43.36 | 100 |
| | 2 | 0.4 | 100 | 48.56 | 100 |
| | 2.5 | 0.4 | 100 | 53.22 | 100 |
| Chitosan film | 1 | - | 100 | 15.03 | - |
| | 1.5 | - | 100 | 18.64 | - |
| | 2 | - | 100 | 26.55 | - |
| | 2.5 | - | 100 | 31.06 | - |
| $TiO_2$ powder | 0 | 0.4 | 100 | 0.84 | 5.08 |

#### 4.1.4.1 Determination of adsorption isotherm of $TiO_2$/chitosan films in different chitosan contents

Table 4.6 demonstrats the adsorption of 100 mg/L chromium(VI) concentration on $TiO_2$/chitosan and chitosan films surface. Comparison between $TiO_2$ powder, $TiO_2$/chitosan film could remove chromium(VI) with efficiency as 38.35 - 53.22 % whereas chitosan film could remove with efficiency as 15.03 – 31.06% and $TiO_2$ powder could only remove at 0.84 %. Chromium removal efficiency range of $TiO_2$/chitosan film was higher than chromium removal efficiency range of chitosan film and $TiO_2$ powder. For $TiO_2$/chitosan film prepared in different chitosan contents (1, 1.5, 2 and 2.5%) with 0.4% Ti, the result shown that $TiO_2$/chitosan film was prepared from 2.5% chitisan, 0.4% Ti provided the highest efficiency(31.06%) for chromium(VI) removal. The reason that at the 2.5% of chitosan was the best efficiency for chromium (VI) removal. The reason might become the fact that the maximum quantity of chitosan which provided maximum protonated amino group ($-NH_3^+$) which was a functional of chitosan biopolymer, the sorbent was positively charged with protonated as amino group whereas the sorbate was negatively charged, (chromium (VI) existed as $HCrO_4^-$). In view of electrostatic interaction between the sorbent-sorbate systems. The pH should be maintained at pH 3 in further experiments (Sankararamakrishnan et al.,2005).

From 100 mg/L chromium (VI) removal experiment, the result shown that $TiO_2$/chitosan film could effectively adsorbed chromium (VI). This result was shown in same result as Ding et. al., 2006 with the fact that chitosan is a powerful chelating agent, which is easy to form complexes with transition metals and heavy metals such as $Cr^{+6}$ $Zn^{+2}$. Therefore, in this research it was necessary to study about $TiO_2$/chitosan film adsorption behavior.

The results depict in figure 4.7, the equilibration time for the physico-chemical reaction between chromium(VI) and $TiO_2$/chitosan film in each condition at pH 3. As seen from the graph, adsorption of chromium(VI) on $TiO_2$/chitosan film surface occur during the equilibration period. The amount of chromium(VI) adsorbed was increased with time and attained equilibrium within 120 min. This indicates the equilibration time required for maximum chromium(VI) adsorption on $TiO_2$/chitosan film surface.

**Table 4.6** Percentage removals of 100 mg/L chromium(VI) by using synthesized films that prepared from 1, 1.5, 2 and 2.5% chitosan with 0.4% Ti ($TiO_2$/chitosan film) and without Ti content(chitosan film) in adsorption process

| Types of film | Chitosan contents (%) | Ti contents (%) | Initial concentration of chromium(VI) (mg/L) | x/m at the end of adsorption process (mg of Cr(VI)/g of film) | % Removal |
|---|---|---|---|---|---|
| $TiO_2$/ chitosan film | 1 | 0.4 | 100 | 457.68 | 38.35 |
| | 1.5 | 0.4 | 100 | 420.11 | 43.36 |
| | 2 | 0.4 | 100 | 405.58 | 48.56 |
| | 2.5 | 0.4 | 100 | 351.82 | 53.22 |
| Chitosan film | 1 | - | 100 | 268.75 | 15.03 |
| | 1.5 | - | 100 | 252.23 | 18.64 |
| | 2 | - | 100 | 244.98 | 26.55 |
| | 2.5 | - | 100 | 230.70 | 31.06 |
| $TiO_2$ powder | 0 | 0.4 | 100 | 28.72 | 0.84 |

Langmuir equation was applied for adsorption equilibrium of chromium(VI) onto $TiO_2$/chitosan film surfaces. The Langmuir adsorption isotherm was based on these assumptions: (i) maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface: (ii) the energy of adsorption is constant: and (iii) there is no transmigration of adsorbate in surface plane (Kajitvichyanukul et al.,2004) . The Langmuir equation was shown below:

$$C_e/(x/m) = 1/(Q_o b) + C_e/Q_o \qquad \text{(Eq. 4.1)}$$

Where $C_e$ is the equilibrium concentration of chromium(VI), mg/L, $x/m$ is amount of adsorbed chromium(VI) at equilibrium per unit mass of $TiO_2$/chitosan film, mg/g , $Q_o$ is maximum adsorption at monolayer coverage, mg /g, and b is Langmuir constant related to the affinity of binding sites, L/mg and it is a measure of energy of adsorption. The linear plot of $C_e/(x/m)$ vs $C_e$ in figure 4.8 show that the adsorption of chromium(VI) onto $TiO_2$/chitosan film surface in each condition obeys Langmuir adsorption isotherm. The correlation coefficient for the linear regression fit of the Langmuir plot and the expressed equation present in table 4.10.

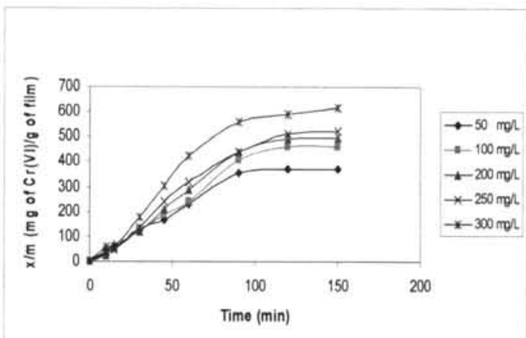
The essential characteristic of the Langmuir isotherm can be expressed in term of a dimensionless constant separation factor or equilibrium parameter, $R_L$, which is defined by (Mackay et al., 1982)

$$R_L = 1/(1 + bC_o) \qquad \text{(Eq. 4.2)}$$

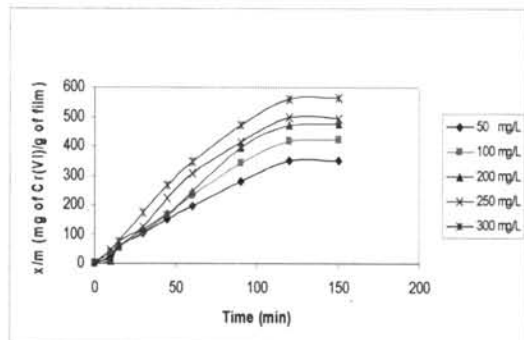
Where $b$ is Langmuir constant, and $C_o$ is initial concentration of chromium(VI). The parameter indicates the adsorption isotherms show in table 4.7. The values of $R_L$ in this experiment set were calculated (Table 4.8) and it was found that all $R_L$ values were between 0 and 1, indicating favorable chromium(VI) adsorption onto each $TiO_2$/chitosan film surface.

**Table 4.7** $R_L$ values and behaviors of Isotherm

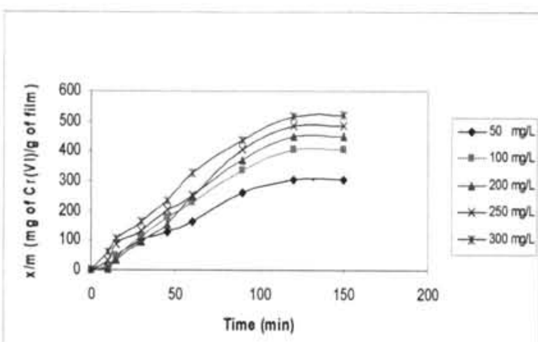
| $R_L$ Value | Behaviors of Isotherm |
|---|---|
| $R_L > 1$ | Unfavorable |
| $0 < R_L < 1$ | Favorable |
| $R_L = 0$ | Irreversible |



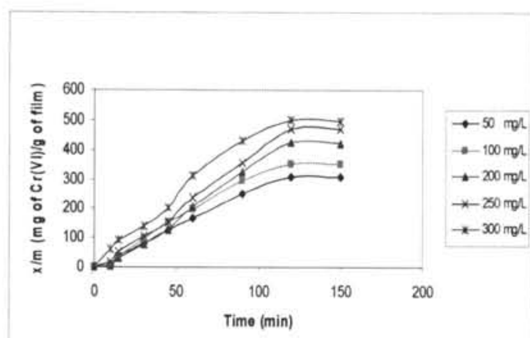

a) 1% chitosan, 0.4% Ti




b) 1.5% chitosan, 0.4% Ti

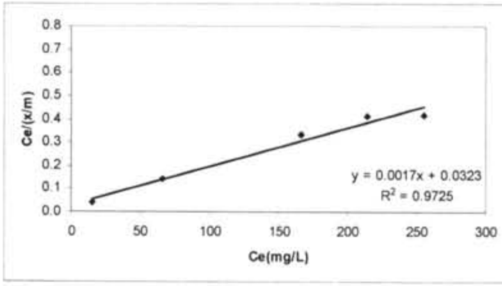



c) 2% chitosan, 0.4% Ti

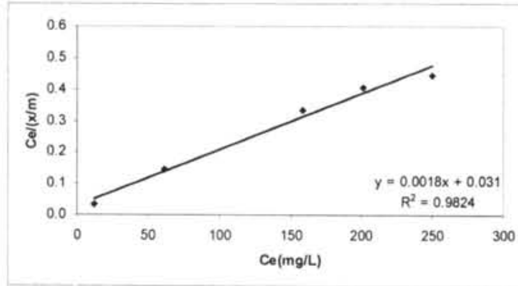



d) 2.5% chitosan, 0.4% Ti

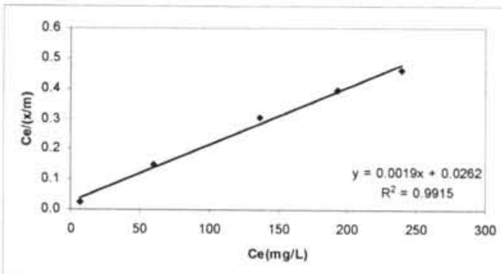
**Figure 4.7** Adsorption of chromium(VI) on $TiO_2$ /chitosan film that prepared from a) 1% chitosan, 0.4% Ti, b) 1.5% chitosan, 0.4% Ti, c) 2% chitosan, 0.4% Ti and d) 2.5% chitosan, 0.4% Ti in different initial concentrations of chromium(VI)



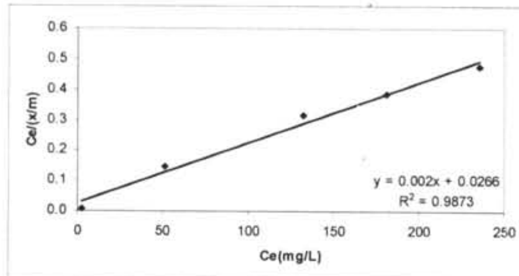

a) 1% chitosan, 0.4% Ti




b) 1.5% chitosan, 0.4% Ti




c) 2% chitosan, 0.4% Ti




d) 2.5% chitosan, 0.4% Ti

**Figure 4.8** Langmuir adsorption isotherms plot for adsorption of chromium(VI) on $TiO_2$ /chitosan film that prepared from a) 1% chitosan, 0.4% Ti, b) 1.5% chitosan, 0.4% Ti, c) 2% chitosan, 0.4% Ti and d) 2.5% chitosan, 0.4% Ti

**Table 4.8** $R_L$ Values for Langmuir adsorption isotherm for $TiO_2$/chitosan film that prepared from 1, 1.5, 2 and 2.5% chitosan with 0.4% Ti

| Initial concentrations of chromium(VI) (mg/L) | $R_L$ Values of $TiO_2$/chitosan film (1%chitosan, 0.4%Ti) | $R_L$ Values of $TiO_2$/chitosan film (1.5%chitosan, 0.4%Ti) | $R_L$ Values of $TiO_2$/chitosan film (2%chitosan, 0.4%Ti) | $R_L$ Values of $TiO_2$/chitosan film (2.5%chitosan, 0.4%Ti) |
|---|---|---|---|---|
| 50 | 0.275 | 0.256 | 0.216 | 0.210 |
| 100 | 0.160 | 0.147 | 0.121 | 0.117 |
| 200 | 0.087 | 0.079 | 0.065 | 0.062 |
| 250 | 0.071 | 0.064 | 0.052 | 0.051 |
| 300 | 0.060 | 0.054 | 0.044 | 0.042 |

**Table 4.9** $Q_0$ and $b$ values for Langmuir adsorption isotherm for $TiO_2$/chitosan film that prepared from 1 ,1.5,2 and 2.5% chitosan with 0.4% Ti

| Adsorption Isotherm | Chitosan contents (%) | Ti contents (%) | $Q_0$ (mg/g) | $b$ (L/mg) |
|---|---|---|---|---|
| Langmuir | 1 | 0.4 | 588 | 0.053 |
| | 1.5 | 0.4 | 555 | 0.058 |
| | 2 | 0.4 | 526 | 0.073 |
| | 2.5 | 0.4 | 500 | 0.075 |

Figure 4.9 shows about the relation between $Q_0$ ( the maximum adsorption at monolayer coverage, mg of chromium /g of film) and chitosan content which shown that the maximum adsorption at monolayer coverage was decreased with the increasing of chitosan content on $TiO_2$ /chitosan film. This phenomenon might come from the fact that increasing of chitosan content obvioued that x value was increased and m is also increased. However, the increase of m, g (mass of film) was much more higher than the increase of x, mg( amount of adsorbed chromium(VI)). Thus the x/m value for high concentration of percent chitosan (such as 1.5% chitosan) will be less than lower chitosan (1% chitosan) by on the $Q_o$ value as shown in the equation 4.1. On the other hand, figure 4.10 shows about the relation between $b$ which is a measure of the energy of adsorption.(L/mg) and chitosan content which found that measure of the energy of adsorption was increased with the increasing of chitosan content on $TiO_2$ chitosan film. This result might come from the fact that higher chitosan content, the more energy of chitosan film adsorption (Sappawinyoo, 2004). The Langmuir constants, $Q_0$ and $b$ values were determined form the Langmuir plot which show in table 4.9.

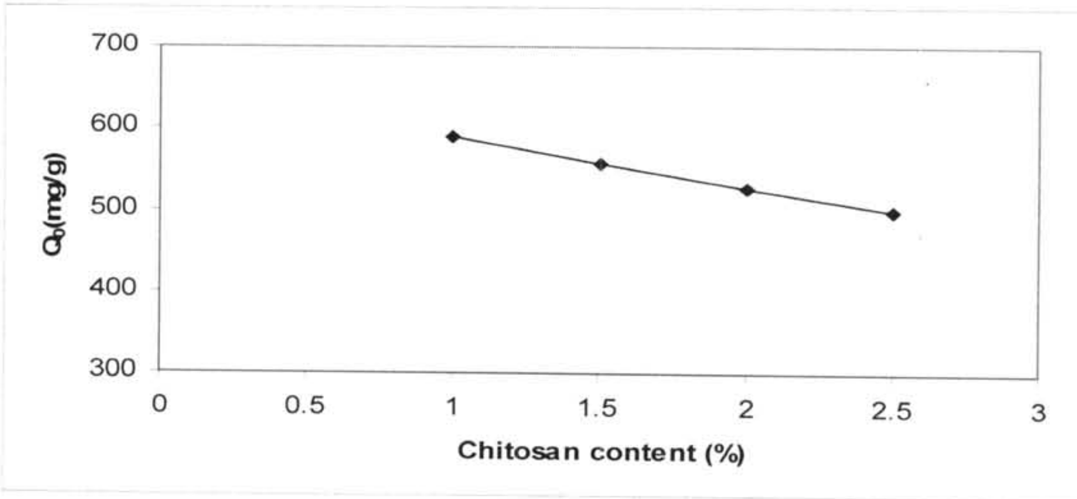



**Figure 4.9** Plotting of relation between $Q_0$ and chitosan contents

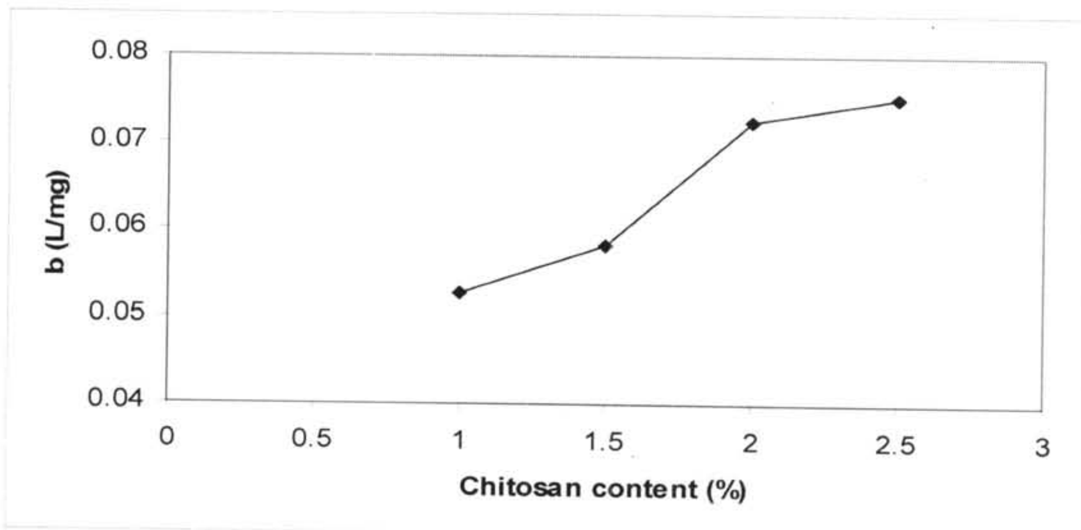



**Figure 4.10** Plotting of relation between *b* and chitosan contents

Freundlich equation was also applied to adsorption of chromium(VI) onto $TiO_2$/chitosan film surface. The Freundlich equation is basically empirical, and generally agrees with the experimental data over a moderate range of adsorbate concentrations. The Freundlich isotherm is represented by the equation (Mckay et., al 1982)

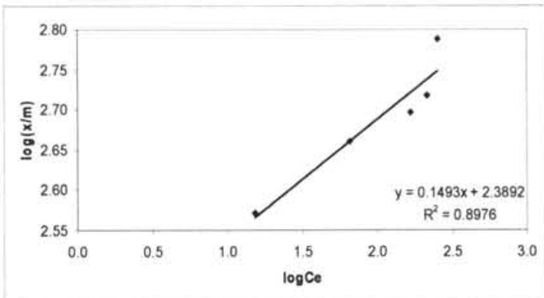
$$Log(x/m) = (1/n)\log C_e + \log k_f \qquad \text{(Eq. 4.3)}$$

Where $C_e$ is the equilibrium concentration of chromium(VI), mg/L, $x/m$ is the amount of adsorbed chromium(VI) at equilibrium per unit mass of $TiO_2$/chitosan film, mg/g, $k_f$, and $n$ are the Freundlich constants. The plot of $\log(x/m)$ versus $\log C_e$ based on equation was shown above for the same experimental results show in figure 4.11. The correlation coefficient for linear regression fit of the Freundlich plot and the expressed equations present in table 4.10.

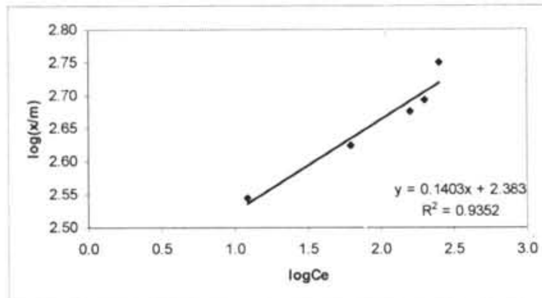
The correlation coefficient for linear regression fit of Langmuir plot in each condition of $TiO_2$/chitosan film (1, 1.5, 2 and 2.5% chitosan with 0.4% Ti) were found to be 0.9963, 0.9824, 0.9873 and 0.9757 while the correlation coefficient for the Freundlich plot in each condition of $TiO_2$/chitosan film(1, 1.5, 2 and 2.5% chitosan with 0.4% Ti) were found to 0.9931, 0.9352, 0.8271 and 0.7748, respectively which were less than that from Langmuir plot. The value of correlation coefficient of Chromium(VI) adsorption indicates that adsorption behavior of chromium(VI) onto $TiO_2$/chitosan film tends to be a monolayer adsorption as described by Langmuir isotherm rather than Freundlich isotherm.

**Table 4.10** Langmuir and Freundlich adsorption isotherms for $TiO_2$/chitosan film that prepared from 1, 1.5, 2 and 2.5% chitosan with 0.4 % Ti

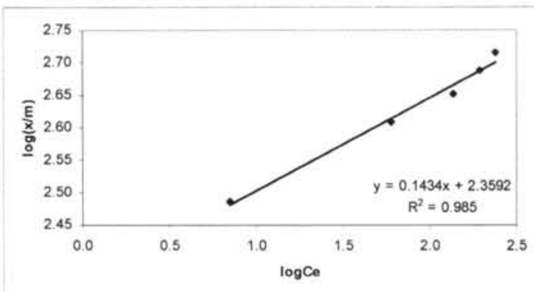
| Adsorption Isotherms | Chitosan contents (%) | Ti contents (%) | Equations | $R^2$ |
|---|---|---|---|---|
| Langmuir | 1 | 0.4 | $C_e/(x/m) = 0.0017C_e + 0.0323$ | 0.9963 |
| | 1.5 | 0.4 | $C_e/(x/m) = 0.0018C_e + 0.031$ | 0.9824 |
| | 2 | 0.4 | $C_e/(x/m) = 0.0019C_e + 0.0262$ | 0.9873 |
| | 2.5 | 0.4 | $C_e/(x/m) = 0.002C_e + 0.0266$ | 0.9757 |
| Freundlich | 1 | 0.4 | $\log(x/m) = 0.1493\log C_e + 2.3892$ | 0.9931 |
| | 1.5 | 0.4 | $\log(x/m) = 0.1403\log C_e + 2.383$ | 0.9352 |
| | 2 | 0.4 | $\log(x/m) = 0.1434\log C_e + 2.3592$ | 0.8271 |
| | 2.5 | 0.4 | $\log(x/m) = 0.1006\log C_e + 2.4257$ | 0.7748 |



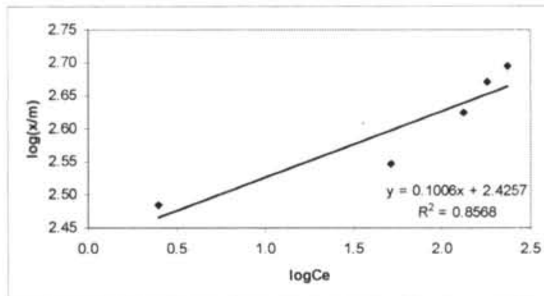

a) 1% chitosan, 0.4% Ti




b) 1.5% chitosan, 0.4% Ti




c) 2% chitosan, 0.4% Ti




d) 2.5% chitosan, 0.4% Ti

**Figure 4.11** Freundlich adsorption isotherm plot for adsorption of chromium(VI) on $TiO_2$/chitosan film that prepared from a) 1% chitosan, 0.4% Ti, b) 1.5% chitosan, 0.4% Ti, c) 2% chitosan, 0.4% Ti and d) 2.5% chitosan, 0.4% Ti

**4.1.4.2 Determination of kinetic values in photocatalytic reduction of chromium(VI) using $TiO_2$ /chitosan films in variation of chitosan contents.**

The photocatalytic reductions of chromium (VI) with $TiO_2$/chitosan film that prepared from 1, 1.5, 2 and 2.5% chitosan with 0.4% Ti in variation of initial concentrations of chromium(VI) in the range of 50 – 300 mg/L were conducted. The results of this experimental part were shown about residual fraction of chromium (VI) (Figure 4.13). It was obvious that the efficiency in chromium (VI) removal decreased with the increasing of initial concentration of chromium (VI) in solution. To explain the behavior of photocatalytic reduction of chromium (VI) by synthesized $TiO_2$/chitosan film for each condition in term of kinetic study, two patterns of kinetic orders, which are zero-order and pseudo-first order equations are considered. As seen in chromium (VI) declining pattern, the kinetic order to explain the existed reaction can be either zero order or pseudo first order. Thus, the value of $k_{obs}$ can be calculated by the both equations.

At $n$=0, the reaction is zero-order which is one in the rate of reaction independent of the concentration of solution. The zero-order equation can be derived a follow:

$$\frac{dc}{dt} = -k_{obs}[C]^n - k_{obs}[C]^0 = -k_{obs} \qquad \text{(Eq. 4.4)}$$

$$dc = -k_{obs}(dt) \qquad \text{(Eq. 4.5)}$$

$$\int_{c_0}^{c} dC = -k_{obs}\int_{0}^{t} dt \qquad \text{(Eq. 4.6)}$$

$$C - C_0 = -k_{obs}t \qquad \text{(Eq. 4.7)}$$

Where $k_{obs}$ is the apparent reaction rate constant, $n$ is the order of the reaction, $t$ is the reaction time, $C_0$ is the initial concentration of chromium (VI) in aqueous solution, and $C$ is the residual concentration of chromium (VI) at time $t$. Value of $k_{obs}$ was determined from the slope of graph which was plot between $C$-$C_o$ and reaction time, $t$. The value $R^2$ for linear regression was calculated to exhibit the tendency of the reaction pattern to be describe as a zero-order pattern. Values of $k_{obs}$ from zero-order equation were determined as show in table 4.11-4.14.

At $n$=1, the reaction first order which is the rate of reaction which can be obtained by the following relationship of concentration of solution and time.The first order equation can be derived a follow:

$$\frac{dc}{dt} = -k_{obs}[C]^n - k_{obs}[C]^1 \qquad \text{(Eq. 4.8)}$$

$$\frac{1}{[C]}d[C] = -k_{obs}dt \qquad \text{(Eq. 4.9)}$$

$$\frac{1}{[C]}\int_{c_0}^{c} dC = -k_{obs}\int_{0}^{t} dt \qquad \text{(Eq. 4.10)}$$

$$\ln(\frac{C}{C_o}) = -k_{obs}t \qquad \text{(Eq. 4.11)}$$

Where $k_{obs}$ is the apparent reaction rate constant, $n$ is the order of the reaction, $t$ is the reaction time, $C_0$ is the initial concentration of chromium (VI) in aqueous solution, and $C$ is the residual concentration of chromium (VI) at time $t$. Values of $k_{obs}$ was determined from the slope of graph which was plot between $-ln(C/C_0)$ and reaction time, $t$ (Figure 4.14). The value $R^2$ for linear regression was calculated to exhibit the tendency of the reaction pattern to be described as pseudo-first order. Values of $k_{obs}$ from pseudo-first order equation were determined as show in table 4.11-4.14.

The photocatalytic reduction of 100 mg/L chromium (VI) concentration under irradiation process for $TiO_2$/chitosan film with different chitosan contents were compared. The ratio of residual to initial concentration of chromium(VI) in term of $C/C_0$ as a function of irradiation time illustrate in figure 4.12. It is obvious that the $TiO_2$/chitosan film provided the higher efficiency in chromium(VI) removal comparing to $TiO_2$ powder or 0% chitosan,0.4%Ti.In consideration of treating efficiency of chromium(VI) using different chitosan contents that prepared from1, 1.5, 2 and 2.5% with 0.4%, the result shown that chitosan at 2.5% provided the highest efficiency for chromium (VI) removal and the lower chromium (VI) efficiency were 2, 1.5 and 1%, respectively.

Considering the pattern of kinetic equation, the photocatalytic reduction reactions of $TiO_2$/chitosan film in different chitosan contents can represented by pseudo-first order pattern for initial chromium(VI) concentration in range of 50-300 mg/L because the correlation coefficients ($R^2$) value of zero order less than that correlation coefficients value from pseudo-first order.

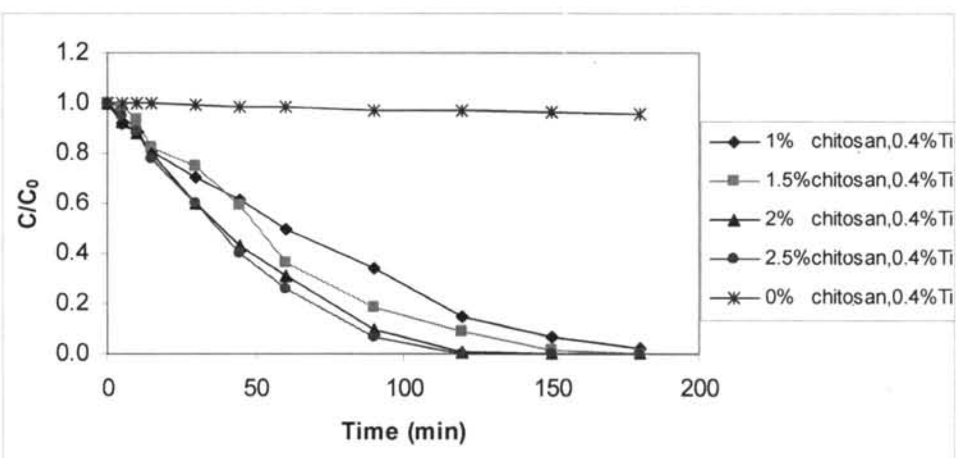
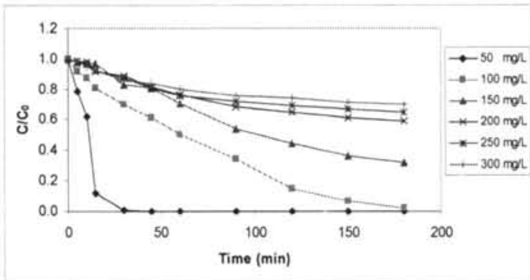
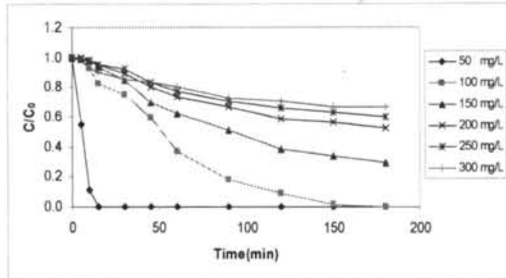


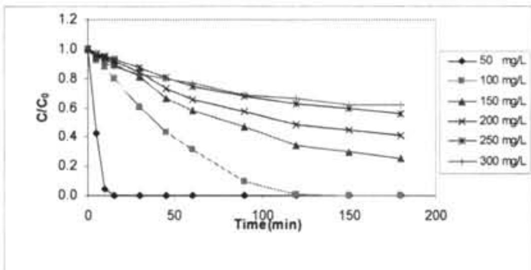

**Figure 4.12** Residual fraction of 100 mg/L chromium (VI) in different chitosan contents on $TiO_2$/chitosan film



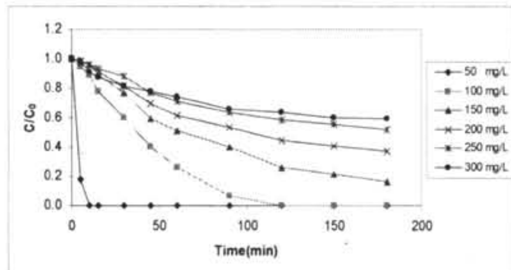

a) 1% chitosan, 0.4% Ti




b) 1.5% chitosan, 0.4% Ti




c) 2% chitosan, 0.4% Ti

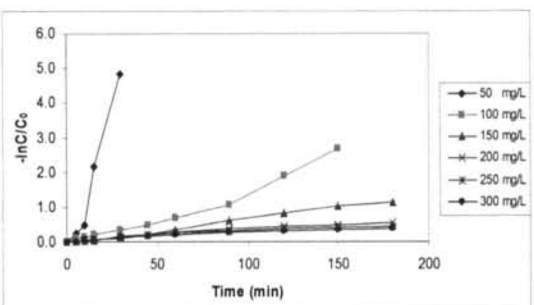



d) 2.5% chitosan, 0.4% Ti

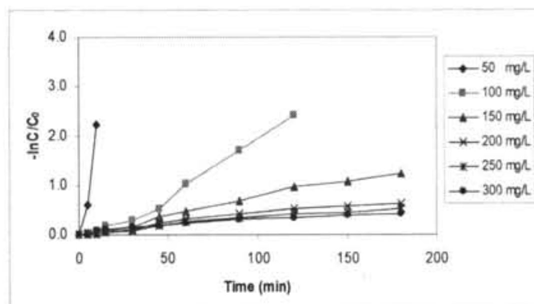
**Figure 4.13** Residual fraction of chromium (VI) in different initial concentrations for $TiO_2$/chitosan film that prepared from a) 1% chitosan, 0.4% Ti, b) 1.5% chitosan, 0.4% Ti, c) 2% chitosan, 0.4% Ti and d) 2.5% chitosan, 0.4% Ti

The photocatalytic reduction reactions of $TiO_2$/chitosan film in different chitosan contents were described by pseudo-first order pattern. As chromium(VI) concentrated increased with fixed dosage of $TiO_2$/chitosan film in the system, the reaction become depended on both concentration of chromium(VI) and reaction time. The plotting of $k_{obs}$ from pseudo-first order as a function of chitosan content on $TiO_2$/chitosan film form each condition that removed 100 mg/L chromium(VI) concentration show in figure 4.15. This figure shows that $k_{obs}$ obtained from $TiO_2$/chitosan film provided the higher than $k_{obs}$ from $TiO_2$ powder (0% chitosan, 0.4% Ti ), 0.0003 $min^{-1}$. While $k_{obs}$ of $TiO_2$/chitosan film from 2.5% chitosan with 0.4% Ti (0.0255 $min^{-1}$) was higher than $k_{obs}$ of $TiO_2$/chitosan films in other condition (Table 4.11-4.14). The reason for 2.5% chitosan with 0.4%Ti was the highest efficiency for chromium (VI) removal because $TiO_2$ /chitosan film that prepared from 2.5% chitosan with 0.4%Ti provide the maximum quantity of chitosan that mean it provide maximum protonated amino group ($-NH_3^+$) which was a functional of chitosan biopolymer that help for adsorbed chromium(VI) into $TiO_2$ /chitosan film surface. The photocatalytic reaction was confined mostly to adsorption capacity of media under illumination. Therefore, the more adsorption capacity, the more photocatalytic reaction occurs(Yu et al.,2001).

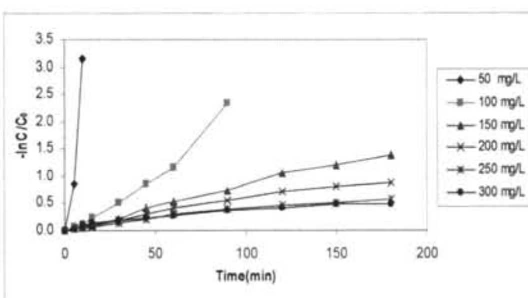
Upon photocatalyic reduction of chromium(VI), $TiO_2$ /chitosan film that prepared from 2.5% chitosan with 0.4% provided the highest efficiency (0.0255 $min^{-1}$) which could remove 100% chromium(VI) in 100 mg/L initial concentration wiyh the shortest period. Therefore 2.5% chitosan content was the best content for $TiO_2$ /chitosan film preparation and it was used in next experiment.



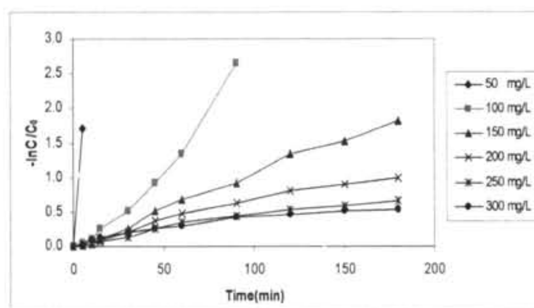

a) 1% chitosan, 0.4% Ti




b) 1.5% chitosan, 0.4% Ti




c) 2% chitosan, 0.4% Ti




d) 2.5% chitosan, 0.4% Ti

**Figure 4.14** Relation between $-ln(C/C_0)$ and time in different initial concentrations of chromium(VI) removal for $TiO_2$/chitosan film that prepared from a) 1% chitosan, 0.4% Ti, b) 1.5% chitosan, 0.4% Ti, c) 2% chitosan, 0.4% Ti and d) 2.5% chitosan, 0.4% Ti

**Table 4.11** Values of $k_{obs}$ from pseudo-first order equation for photocatalytic process using $TiO_2$ /chitosan film that prepared from 1%chitosan, 0.4% Ti with 20% acetic acid solution

| Initial concentrations of chromium(VI) (mg/L) | pseudo-first order | | % Removal |
|---|---|---|---|
| | $k_{obs}$ ($min^{-1}$) | $R^2$ | |
| 50 | 0.1462 | 0.9143 | 100.00 |
| 100 | 0.0155 | 0.9527 | 98.78 |
| 150 | 0.0065 | 0.9888 | 78.09 |
| 200 | 0.0034 | 0.9613 | 54.88 |
| 250 | 0.0029 | 0.8768 | 48.21 |
| 300 | 0.0024 | 0.8340 | 42.29 |

**Table 4.12** Values of $k_{obs}$ from pseudo-first order equation for photocatalytic process using $TiO_2$ /chitosan film that prepared from 1.5 %chitosan, 0.4% Ti with 20% acetic acid solution.

| Initial concentrations of chromium(VI) (mg/L) | pseudo-first order | | % Removal |
|---|---|---|---|
| | $k_{obs}$ ($min^{-1}$) | $R^2$ | |
| 50 | 0.2012 | 0.9434 | 100.00 |
| 100 | 0.0183 | 0.9598 | 100.00 |
| 150 | 0.0073 | 0.9892 | 79.92 |
| 200 | 0.0040 | 0.9685 | 60.74 |
| 250 | 0.0032 | 0.9610 | 53.05 |
| 300 | 0.0028 | 0.8621 | 46.30 |

**Table 4.13** Values of $k_{obs}$ from pseudo-first order equation for photocatalytic process using $TiO_2$ /chitosan film that prepared from 2 %chitosan, 0.4% Ti with 20% acetic acid solution.

| Initial concentrations of chromium(VI) (mg/L) | pseudo-first order | | % Removal |
|---|---|---|---|
| | $k_{obs}$ ($min^{-1}$) | $R^2$ | |
| 50 | 0.2868 | 0.9212 | 100 |
| 100 | 0.0226 | 0.9507 | 100 |
| 150 | 0.0081 | 0.9913 | 83.31 |
| 200 | 0.0055 | 0.9711 | 72.57 |
| 250 | 0.0036 | 0.9488 | 58.78 |
| 300 | 0.0033 | 0.8351 | 53.86 |

**Table 4.14** Values of $k_{obs}$ from pseudo-first order equation for photocatalytic process using $TiO_2$ /chitosan film that prepared from 2.5%chitosan, 0.4% Ti with 20% acetic acid solution.

| Initial concentrations of chromium(VI) (mg/L) | pseudo-first order | | % Removal |
|---|---|---|---|
| | $k_{obs}$ ($min^{-1}$) | $R^2$ | |
| 50 | - | - | 100 |
| 100 | 0.0255 | 0.9436 | 100 |
| 150 | 0.0104 | 0.9937 | 89.78 |
| 200 | 0.0062 | 0.9666 | 75.76 |
| 250 | 0.0041 | 0.9477 | 62.41 |
| 300 | 0.0036 | 0.8421 | 56.42 |

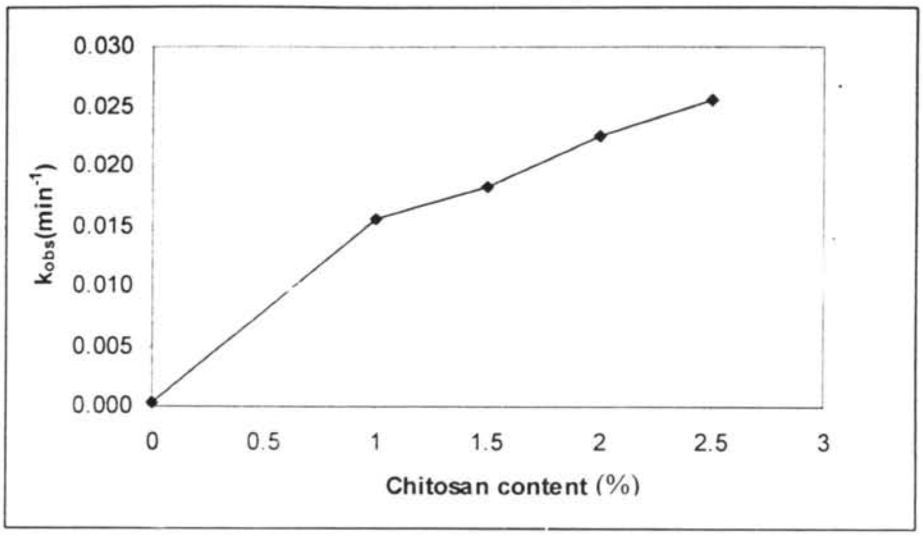



**Figure 4.15** Comparison of apparent reaction rate constant ($k_{obs}$) for 100 mg/L chromium(VI) removal by using different chitosan contents.

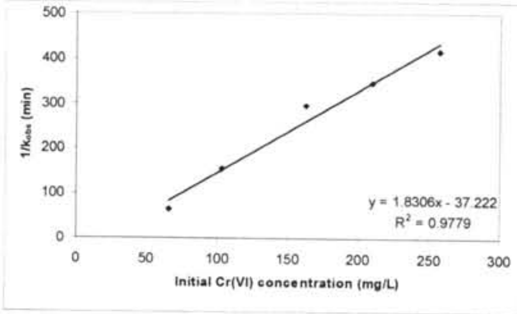
The Langmuir-Hinshelwood rate expression has been successfully used for heterogeneous photocatalytic degradation to determine the relationship between the initial degradation rate and the initial concentration of chromium (VI) (Chen et al., 1998):

$$\frac{1}{k_{obs}} = \frac{1}{k \cdot K_{cr(VI)}} + \frac{[Cr(VI)]_o}{k} \qquad \text{(Eq. 4.12)}$$

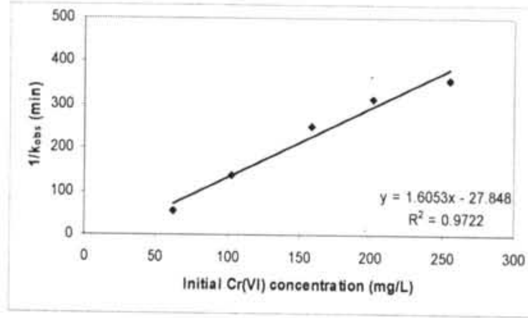
Where $[Cr(VI)]_o$ is the initial concentration of chromium (VI) in the unit of mg/L

$K_{cr(VI)}$ is the Langmuir-Hinshelwood adsorption equilibrium constant in the unit of L/mg

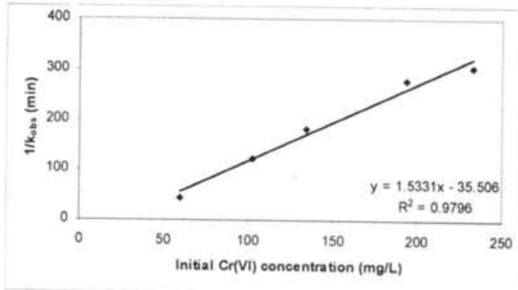
$k$ is the rate constant of surface reaction in the unit of mg/L.min



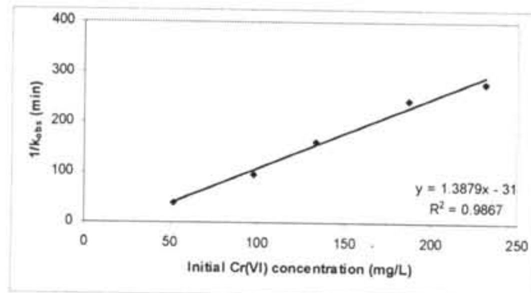

a) 1% chitosan, 0.4% Ti




b) 1.5% chitosan, 0.4% Ti




c) 2% chitosan, 0.4% Ti




d) 2.5% chitosan, 0.4% Ti

**Figure 4.16** Determination of adsorption equilibrium constants and degradation rate constants chromium(VI) by using $TiO_2$/chitosan film that prepared from a) 1% chitosan, 0.4% Ti, b) 1.5% chitosan, 0.4% Ti, c) 2% chitosan, 0.4% Ti and d) 2.5% chitosan, 0.4% Ti

Figure 4.16 shows the determination of the adsorption equilibrium constant and degradation rate constant for chromium (VI) in the range of initial concentrations 100 to 300 mg/L by plotting between $1/k_{obs}$ and initial chromium(VI) concentration. The Langmuir-Hinshelwood equations for photocatalytic process using $TiO_2$/chitosan films in variation of chitosan contents which show in table 4.15.

**Table 4.15** Langmuir-Hinshelwood equations for photocatalytic process using $TiO_2$/chitosan films in variation of chitosan contents

| Chitosan contents (%) | Ti contents (%) | Langmuir-Hinshelwood Equations $\frac{1}{k_{obs}} = \frac{1}{k \cdot K_{cr(VI)}} + \frac{[Cr(VI)]_o}{k}$ |
|---|---|---|
| 1 | 0.4 | $\frac{1}{k_{obs}} = \frac{1}{(0.546)(-0.049)} + \frac{[Cr(VI)]_o}{0.546}$ |
| 1.5 | 0.4 | $\frac{1}{k_{obs}} = \frac{1}{(0.623)(-0.058)} + \frac{[Cr(VI)]_o}{0.623}$ |
| 2 | 0.4 | $\frac{1}{k_{obs}} = \frac{1}{(0.652)(-0.043)} + \frac{[Cr(VI)]_o}{0.652}$ |
| 2.5 | 0.4 | $\frac{1}{k_{obs}} = \frac{1}{(0.721)(-0.045)} + \frac{[Cr(VI)]_o}{0.721}$ |

## 4.2 Role of Ti content on $TiO_2$/chitosan film preparation.

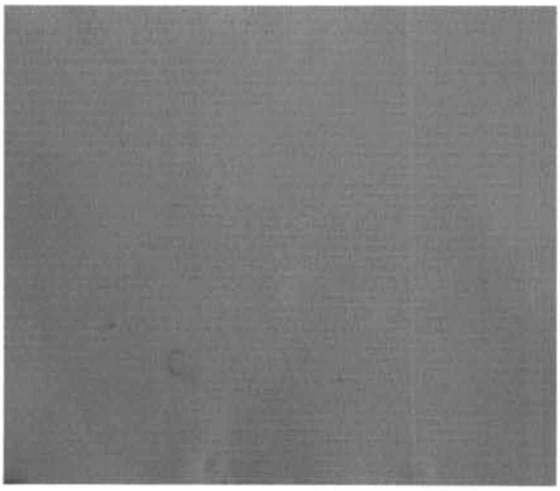
$TiO_2$/chitosan films in different Ti contents were prepared by dissolving 0.2, 0.4, 0.6 and 0.8 % w/w of Ti from $TiO_2$ powder with 2.5 % chitosan flake in 20% acetic acid solution for 24 hr. After that 5 g of slurry were taken and spread them on 5x6 cm glass plate then placed its in room temperature to dry for 48 hr. Next step peeled the film out from glass plate. However in step of mixing substances, the problem was occurred in condition 0.6% and 0.8% Ti with 2.5% chitosan which was the $TiO_2$/chitosan slurry could be not homogeneous and films that prepare from this condition were not smooth. While at 0.2 % and 0.4% Ti with 2.5% chitosan could be provided smooth films. The same problem existed when 2% of chitosan was used as show in table 4.16 but this problem was not occurred in using 1.5% of chitosan. The film is favorable with the mixing of $TiO_2$ in the range of 0.2-0.8% Ti. In step of mixing, all condition could be homogenous solution and provide smooth film (Figure 4.17-4.19).

**Table 4.16** Film formation in each condition

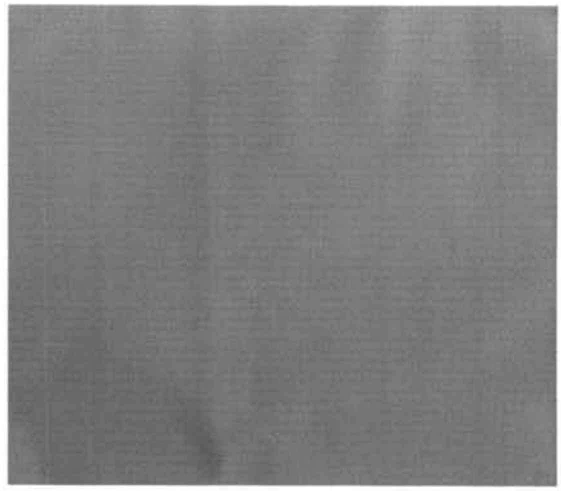
| Chitosan contents (%) | Ti contents (%) | Film formation |
|---|---|---|
| 2.5 | 0.2 | O |
| | 0.4 | O |
| | 0.6 | X |
| | 0.8 | X |
| 2 | 0.2 | O |
| | 0.4 | O |
| | 0.6 | X |
| | 0.8 | X |
| 1.5 | 0.2 | O |
| | 0.4 | O |
| | 0.6 | O |
| | 0.8 | O |

O = Can be used to prepare film

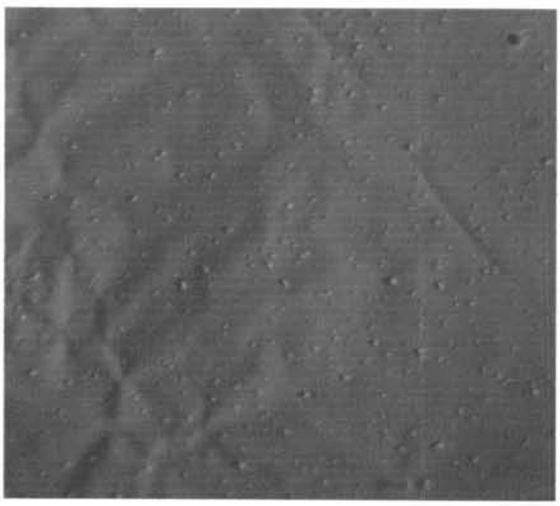
X = Can not be used to prepare film



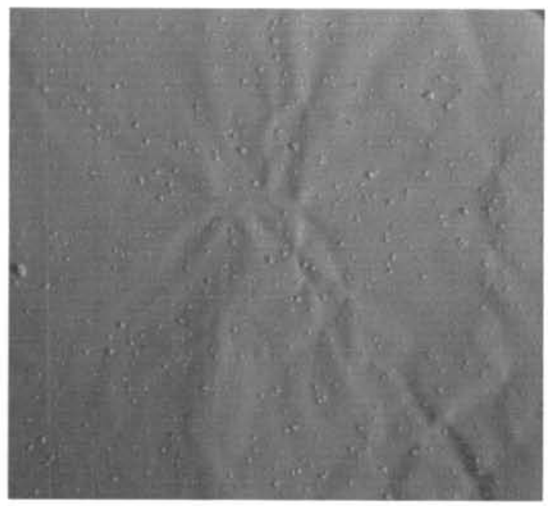
a) 0.2%Ti, 2.5% chitosan



b) 0.4%Ti, 2.5% chitosan

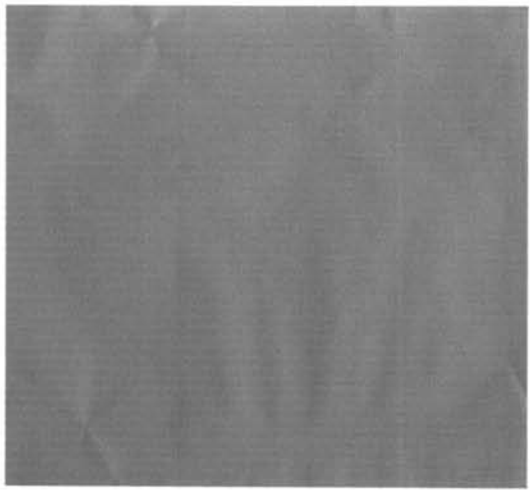


c) 0.6%Ti, 2.5% chitosan

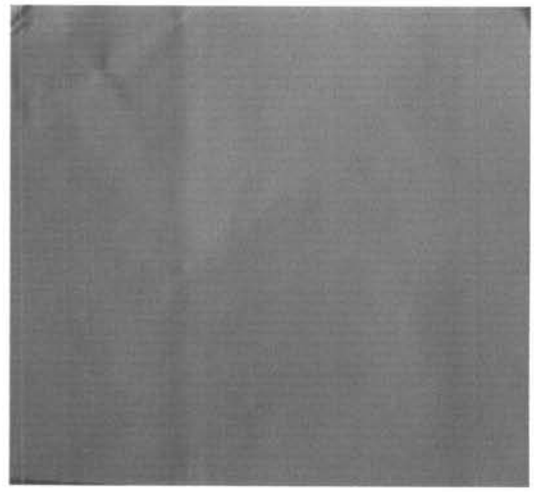


d) 0.8%Ti, 2.5% chitosan

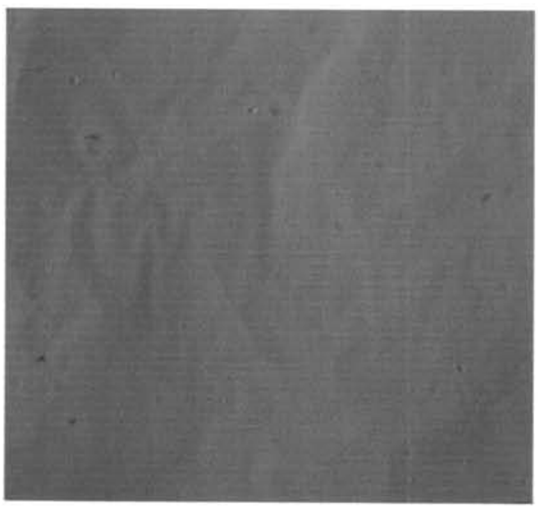
**Figure 4.17** Photographs of $TiO_2$/chitosan film that prepared from 2.5% chitosan with variation of Ti contents



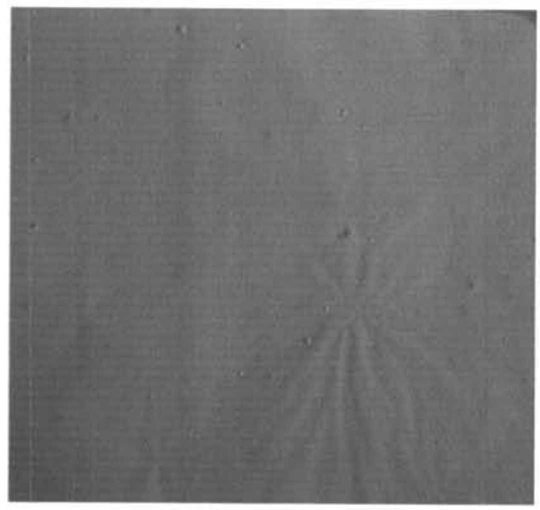
a) 0.2%Ti, 2.0% chitosan



b) 0.4%Ti, 2.0% chitosan

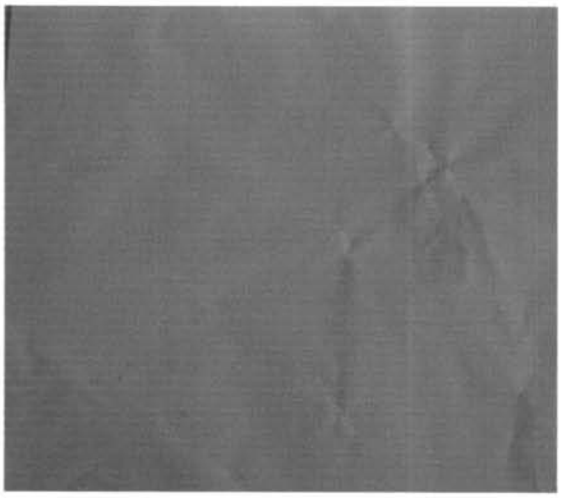


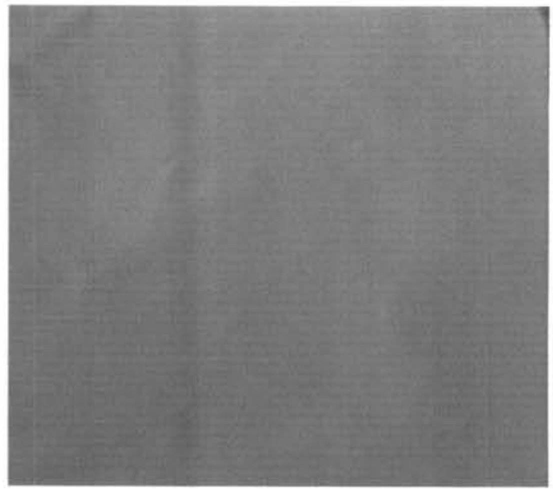
c) 0.6%Ti, 2.0% chitosan



c) 0.8%Ti, 2.0% chitosan

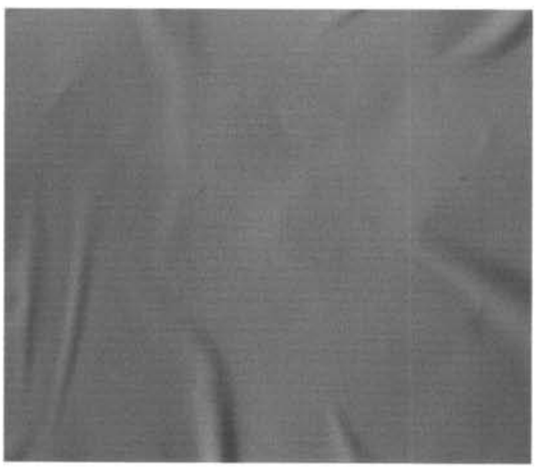
**Figure 4.18** Photographs of $TiO_2$/chitosan film that prepared from 2.0% chitosan with variation of Ti contents

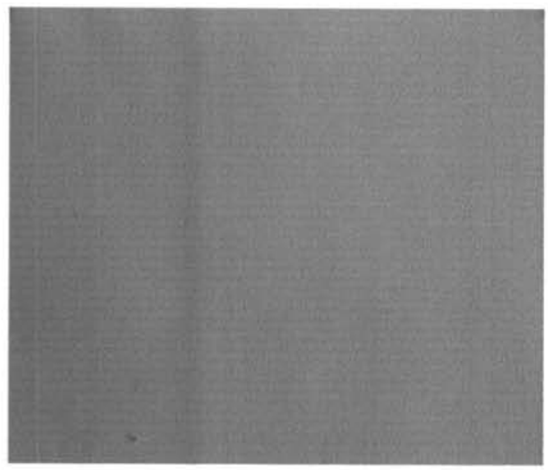




a) 0.2%Ti,1.5% chitosan

b) 0.4%Ti,1.5% chitosan





c) 0.6%Ti,1.5%chitosan

d) 0.8%Ti,1.5%chitosan

**Figure 4.19** Photographs of $TiO_2$/chitosan film that prepared from 1.5% chitosan with variation of Ti contents

Therefore, in this experiment, $TiO_2$/chitosan films were prepared from 1.5% chitosan in variation of Ti contents to investigate the effects of titanium quantity on film properties, adsorption and photocatalytic activity for chromium (IV) removal.

**4.2.1 Results of film weight, thickness and characteristic in variation of Ti contents**

Effect of chitosan content on properties of film show in table 4.17– 4.19 so, Ti content was important factor that influence on chitosan and $TiO_2$/chitosan film properties such as weight, thickness and characteristics of film.

Weight of film result represent in table 4.17. In this study, the weight of $TiO_2$/chitosan film that prepared from 0.2, 0.4, 0.6 and 0.8 % w/w of Ti with 1.5% chitosan was obtained in ranged of 0.0982-0.1489 g S.D. ± 0.019 whereas weight of chitosan dry film( 0%Ti,1.5% chitosan) was 0.0800 g S.D. ± 0.0012. This result could be compared between $TiO_2$/chitosan and chitosan films weight, and it was found that weight of $TiO_2$/chitosan film was heavier than weight of chitosan film because of addition of $TiO_2$ on $TiO_2$/chitosan film. When consideration about relation between films which prepared in variation of Ti contents, the result shown that trend of film weight of all samples were increased with increasing of Ti content and the weight of film that prepared from 0.8% chitosan was the heaviest weight.

Regarding film thickness (Table 4.18), thickness of $TiO_2$/chitosan film was obtained in ranged of 0.029-0.052 mm S.D. ± 0.010 while the thickness of chitosan film (0%Ti,1.5% chitosan) was 0.021 mm S.D. ± 0.004 . When compared between Ti content on film was found that the thickness of film that prepared from 0.8% Ti was the thickest. All samples, thickness of film trend to increase with increasing of Ti content.

From this result, it could be concluded that the relation between Ti content with weight and thickness of film, its weight and thickness tended to increase with the increasing in Ti content.

The properties of prepared $TiO_2$/chitosan and chitosan films such as coarseness, transparent and acid odor of film were observed. The physical properties of film show in table 4.19.The film surface that exposed to the air was coarse, while the reverse surface touching glass was smooth and there were no acid odor after dry in room temperature and the transparent of film were observed. Chitosan films were transparent films which look like clear plastic on the other hand $TiO_2$/chitosan films look like dense plastic.

**Table 4.17** Weight of films that prepared from 0, 0.2, 0.4, 0.6 and 0.8 % Ti with 1.5 % chitosan

| Types of film | Chitosan contents (%) | Ti contents (%) | Weigh of film (g) | | | | | Average (g) | SD |
|---|---|---|---|---|---|---|---|---|---|
| $TiO_2$/ chitosan film | 1.5 | 0.2 | 0.1010 | 0.0888 | 0.1006 | 0.0999 | 0.1007 | 0.0982 | 0.0053 |
| | 1.5 | 0.4 | 0.1181 | 0.1134 | 0.1145 | 0.1132 | 0.1114 | 0.1141 | 0.0025 |
| | 1.5 | 0.6 | 0.1290 | 0.1286 | 0.1301 | 0.1306 | 0.1285 | 0.1291 | 0.0009 |
| | 1.5 | 0.8 | 0.1455 | 0.1478 | 0.1571 | 0.1500 | 0.1441 | 0.1498 | 0.0020 |
| Chitosan film | 1.5 | 0 | 0.0781 | 0.0811 | 0.0801 | 0.0800 | 0.0810 | 0.0800 | 0.0012 |

**Table 4.18** Thickness of films that prepared from 0, 0.2, 0.4, 0.6 and 0.8 % Ti with 1.5 % chitosan

| Types of film | Chitosan contents (%) | Ti contents (%) | Thickness of film (mm) | | | | | Average (mm) | SD |
|---|---|---|---|---|---|---|---|---|---|
| $TiO_2$/ chitosan film | 1.5 | 0.2 | 0.030 | 0.025 | 0.030 | 0.035 | 0.025 | 0.029 | 0.004 |
| | 1.5 | 0.4 | 0.043 | 0.035 | 0.030 | 0.030 | 0.045 | 0.037 | 0.005 |
| | 1.5 | 0.6 | 0.050 | 0.045 | 0.040 | 0.050 | 0.045 | 0.046 | 0.004 |
| | 1.5 | 0.8 | 0.055 | 0.050 | 0.050 | 0.050 | 0.055 | 0.052 | 0.003 |
| Chitosan film | 1.5 | 0 | 0.025 | 0.020 | 0.020 | 0.025 | 0.015 | 0.021 | 0.004 |

**Table 4.19** Physical characteristics of film that prepared from 0, 0.2, 0.4, 0.6 and 0.8 % Ti with 1.5 % chitosan

| Types of film | Chitosan contents (%) | Ti contents (%) | Weight of slurry (g) | characteristics | | | |
|---|---|---|---|---|---|---|---|
| | | | | Transparency | Acid smell | Coarseness of film surface | |
| | | | | | | Exposed air | Contacting glass plate |
| $TiO_2$/ chitosan film | 1 | 0.4 | 5 | X | X | O | X |
| | 1.5 | 0.4 | 5 | X | X | O | X |
| | 2 | 0.4 | 5 | X | X | O | X |
| | 2.5 | 0.4 | 5 | X | X | O | X |
| Chitosan film | 1.5 | - | 5 | O | X | O | X |

O = Showing characteristic

X = Not showing characteristic

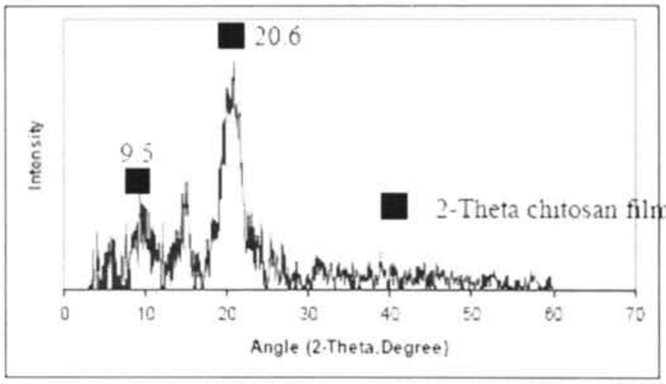
#### 4.2.2 Crystal structures of $TiO_2$/chitosan and chitosan films

XRD pattern of $TiO_2$ powder represent in figure 4.3 (a). $TiO_2$ crystalline was mainly composed of anatase phase as shown by the main peak of 2- Theta at 25.3 degree was anatase phase for 2- Theta at 27.5 degree was rutile phase.

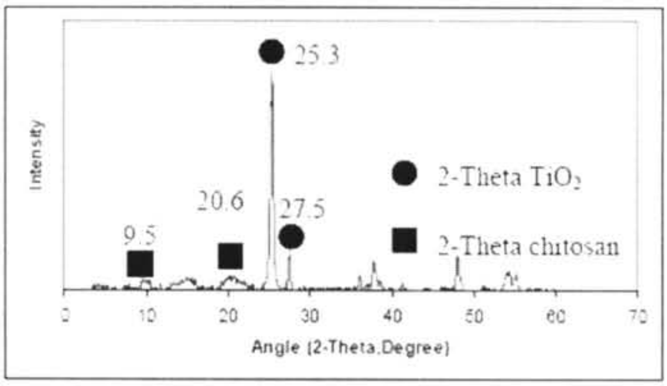
Crystallizations of $TiO_2$/chitosan (0.8% Ti, 1.5% chitosan) and chitosan film(0% Ti, 1.5% chitosan) was checked with Power X-Ray Diffractometer (XRD). Chitosan film was outstanding demonstrated peaks of 2- Theta in three positions which were at 9.5, 15.5 and 20.5 degree (Figure 4.20). So The 2- Theta at 9.5 and 20.5 degree were amino acid structure position which was a agile group to react with chitosan reaction and 15 degree was a water crystallize structure (Wanichpongpan, 2002).

In the other hand $TiO_2$/chitosan film was shown peak of 2-Theta at 9.5, 15.5, 20.5, 25.3 and 27.5 degree. The 2- Theta at 9,15.5and 19 degree which were the same peak position as chitosan and for 25.3 degree was anatase phase and 27.5 degree was rutile phase.

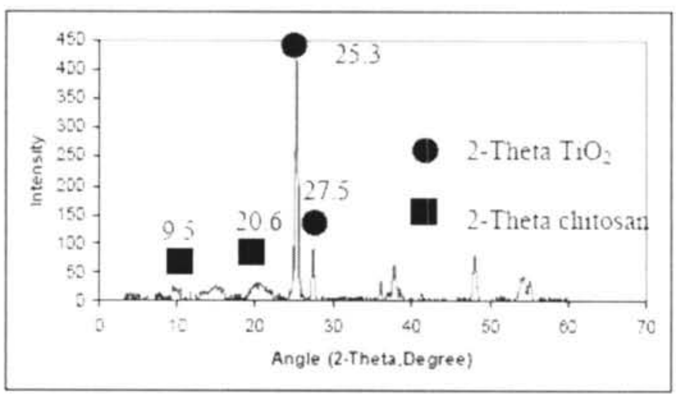
From XRD spectra, its result could be confirmed that chitosan and $TiO_2$/chitosan films in this study had no change in identity of chitosan and $TiO_2$ because chitosan and $TiO_2$ patterns were same pattern as chitosan and $TiO_2$/chitosan films (Figure 4.21).




a) Chitosan film(1.5%chitosan,0%Ti)

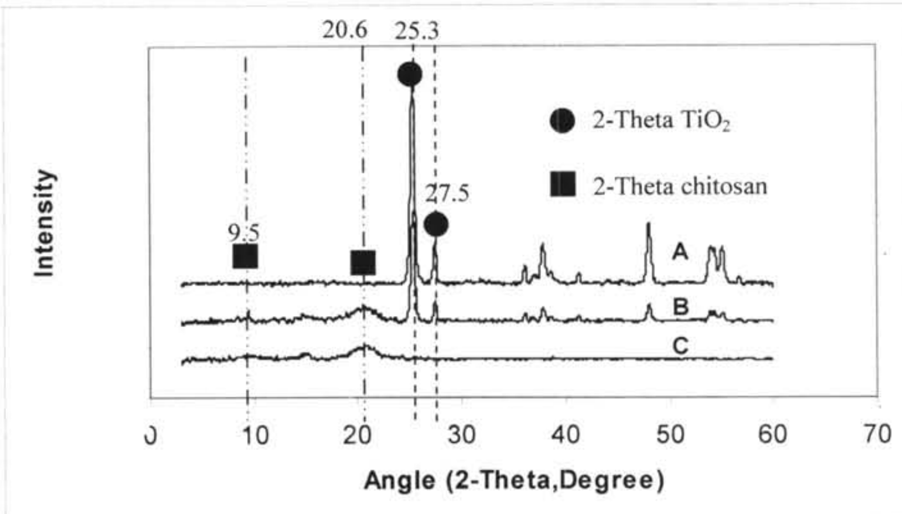



b) $TiO_2$/chitosan films(1.5%chitosan,0.2%Ti)




c) $TiO_2$/chitosan films(1.5%chitosan,0.8%Ti)

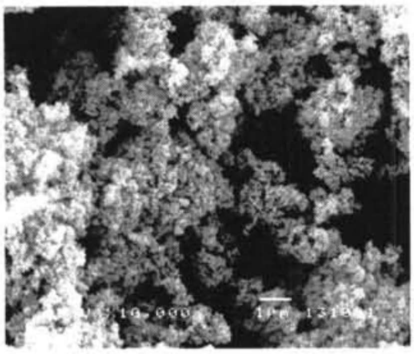
**Figure 4.20** X-ray diffraction patterns of a) Chitosan film and b) $TiO_2$/chitosan films (1.5%chitosan,0.2%Ti) and c) $TiO_2$/chitosan films(1.5%chitosan,0.8%Ti)



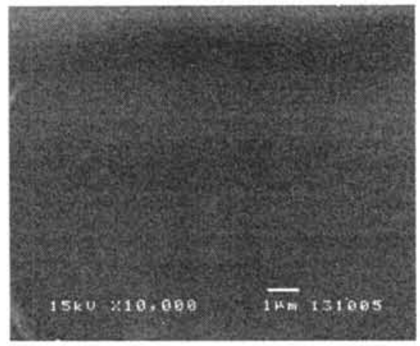

**Figue4.21** X-ray diffraction patterns of the comparison between $TiO_2$ powder(A) and $TiO_2$/chitosan film (B) and chitosan film(C)

### 4.2.3 Surface morphology of $TiO_2$/chitosan and chitosan films analyzed by SEM

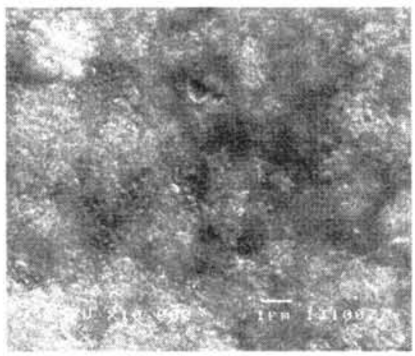
In this study, $TiO_2$ powder, $TiO_2$/chitosan and chitosan films were analyzed by using Scanning Electron Microscope (SEM) which was used at 10000 times in order to see surface morphology (Figure 4.22). Results of this study shown that $TiO_2$ powder was agglomerated as particle. For chitosan film, the surface was flat and smooth which shows that chitosan was a homogeneous film before using for chromium (VI) removal. When $TiO_2$ composed with chitosan ($TiO_2$/chitosan film) which found that $TiO_2$ particles were non-uniform scattered into chitosan. In this study, one condition of $TiO_2$/chitosan film has been shown since surface morphology of chitosan and $TiO_2$/chitosan film that prepared from variation of chitosan contents have no different in surface morphology.



a) $TiO_2$ powder




b) Chitosan film (1.5% chitosan, 0%Ti)



c) $TiO_2$/chitosan film (1.5% chitosan, 0.4%Ti)

**Figure 4.22** Scanning electron micrographs of a) $TiO_2$ powder, b) Chitosan film and c) $TiO_2$/chitosan film

### 4.2.4 Treating of chromium (IV) using synthesized $TiO_2$/chitosan and chitosan films

Figure 4.23 show about $TiO_2$ powder, $TiO_2$/chitosan and chitosan films in different $TiO_2$ quantities for removing 100 mg/L chromium (VI) concentration. This experiment was divided in two processes which were adsorption and photocatalytic processes. At the end of photocatalytic process, the result shown that chromium removal efficiency of $TiO_2$/chitosan film was higher than chromium removal efficiency of $TiO_2$ powder. The explanation of this result might become $TiO_2$ is as catalytic in photocatalytic process which were low adsorption activity in photocatalysis process. While $TiO_2$/chitosan film was combined with chitosan that is a powerful chelating agent, which is easy to form complexes with chromium(VI)

(Ramnani et al.,2005).Therefore, the adsorption ability of $TiO_2$ would be enhanced by composed with chitosan.

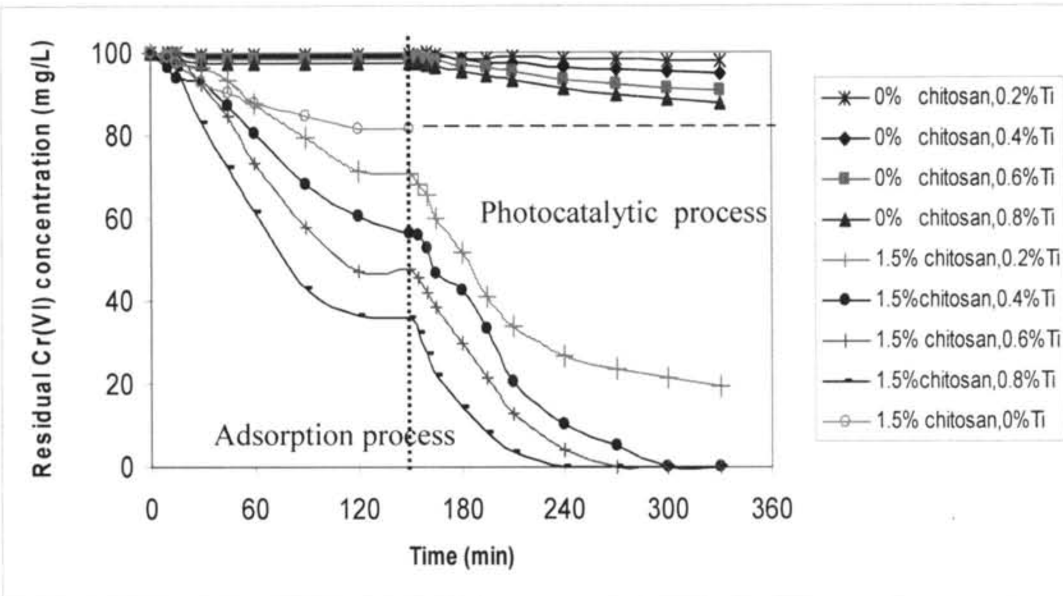



**Figure 4.23** Removal of 100 mg/L chromium (IV) concentration using synthesized $TiO_2$/chitosan, chitosan film and $TiO_2$ powder in adsorption and photocatalytic processes.

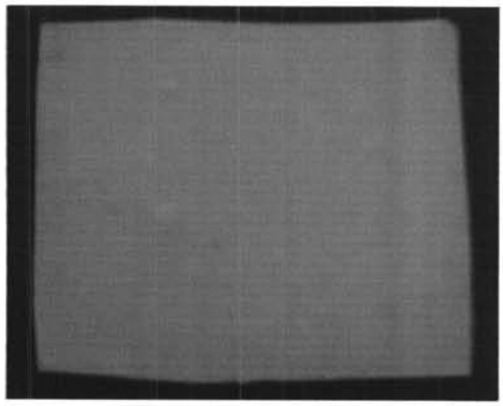
Table 4.20 shows about $TiO_2$/chitosan, chitosan film and $TiO_2$ powder for removing 100 mg/L chromium(VI)concentration. It was obvious that with $TiO_2$ powder alone (0% chitosan with 0.2, 0.4 0.6 and 0.8 % Ti), the removal efficiency is only 2.25, 5.08, 9.01 and 12.53%, recpectively. In addition, using chitosan only the highest efficiency was 18.65 % with the 1.5 % chitosan content (without Ti). $TiO_2$/chitosan film that prepared from 1.5% chitosan with 0.8 % Ti could completely remove 100 mg/L chromium(VI) concentration. It was clearly seen that the film with 1.5% chitosan, 0.8% Ti provided the performance (100% chromium(VI) removal) with the shortest treatment period.

**Table 4.20** Percentage removals of 100 mg/L chromium(VI) by using synthesized films that prepared from 0, 0.2, 0.4, 0.6 and 0.8% Ti with 1.5 % chitosan and $TiO_2$ powder in adsorption and photocatalytic processes

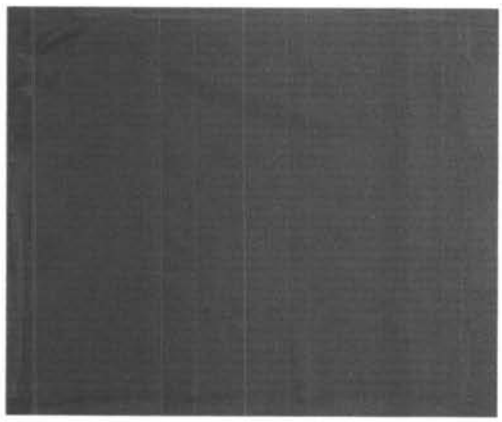
| Types of film | Chitosan content (%) | Ti content (%) | Initial concentration of chromium(VI) (mg/L) | % Removal at the end of adsorption process | % Removal at the end of photocatalytic process |
|---|---|---|---|---|---|
| $TiO_2$/ chitosan film | 1.5 | 0.2 | 100 | 29.01 | 81.28 |
| | 1.5 | 0.4 | 100 | 43.36 | 100.00 |
| | 1.5 | 0.6 | 100 | 54.35 | 100.00 |
| | 1.5 | 0.8 | 100 | 64.05 | 100.00 |
| $TiO_2$ powder | 0 | 0.2 | 100 | 0.33 | 2.25 |
| | 0 | 0.4 | 100 | 0.84 | 5.08 |
| | 0 | 0.6 | 100 | 1.40 | 9.01 |
| | 0 | 0.8 | 100 | 2.38 | 12.53 |
| Chitosan films | 1.5 | 0 | 100 | 18.64 | - |

**4.2.4.1 Determination of adsorption isotherm of $TiO_2$ /chitosan films in different Ti contents.**

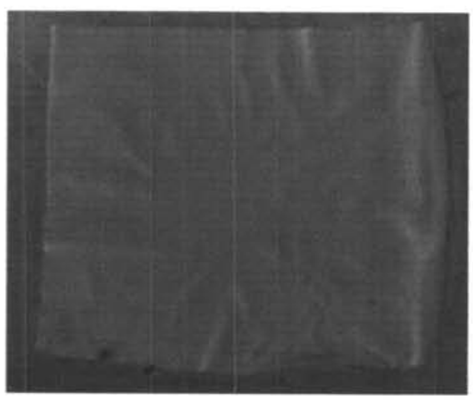
Table 4.21 demonstrates the adsorption of 100 mg/L of chromium(VI) concentration on $TiO_2$/chitosan, chitosan film and $TiO_2$ powder surface. Comparison between $TiO_2$ powder, $TiO_2$/chitosan film (varied Ti content and fixed 1.5% chitosan) could be removed chromium (VI) in range 29.01% - 64.50% whereas $TiO_2$ powder could only remove in range 0.33-2.38 % and chitosan film(0%Ti,1.5% chitosan) could remove 18.64 %. Chromium(VI) removal efficiency of $TiO_2$/chitosan film was higher than chitosan film and $TiO_2$ powder. For $TiO_2$/chitosan film was prepared in different Ti contents the result shown that 0.8%Ti with 1.5% chitosan provided the highest efficiency for chromium(VI) removal and lower chromium(VI) efficiency were 0.6, 0.4and 0.2% Ti, respectively.



a) $TiO_2$/chitosan film before treating of chromium(VI)



b) $TiO_2$/chitosan film at the end of adsorption process



c) $TiO_2$/chitosan film at the end of photocatalytic process

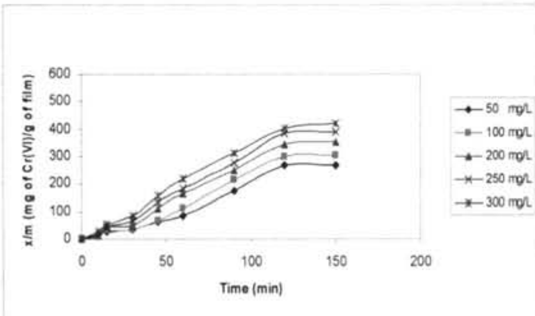
**Figure 4.24** Photographs of $TiO_2$/chitosan films in different conditions

**Table 4.21** Percentage removals of 100 mg/L chromium(VI) by using synthesized films that prepared from 0, 0.2, 0.4, 0.6 and 0.8% Ti with 1.5 % chitosan and $TiO_2$ powder in adsorption process

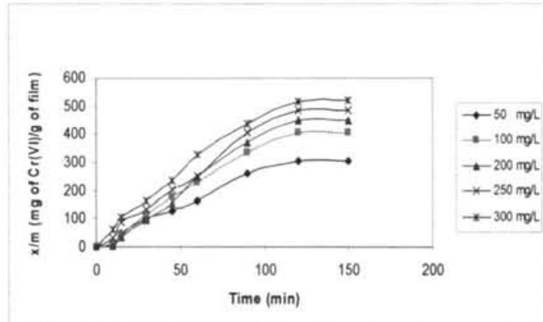
| Types of film | Chitosan contents (%) | Ti contents (%) | Initial concentration of chromium(VI) (mg/L) | x/m at the end of adsorption process (mg of Cr(VI)/g of film) | % Removal |
|---|---|---|---|---|---|
| $TiO_2$/ chitosan film | 1.5 | 0.2 | 100 | 304. 05 | 29.01 |
| | 1.5 | 0.4 | 100 | 420.12 | 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 |

The results depicted in figure 4.25, the equilibration time for the physico-chemical reaction between chromium(VI) and $TiO_2$/chitosan films in each condition at pH 3. As seen from the graph, adsorption of chromium(VI) and $TiO_2$/chitosan films surface occurred during the equilibration period. The amount of chromium(VI) adsorbed was increased with time and attains equilibrium within 120 min. This indicates the equilibration time required for maximum chromium(VI) adsorption on $TiO_2$/chitosan film surface.

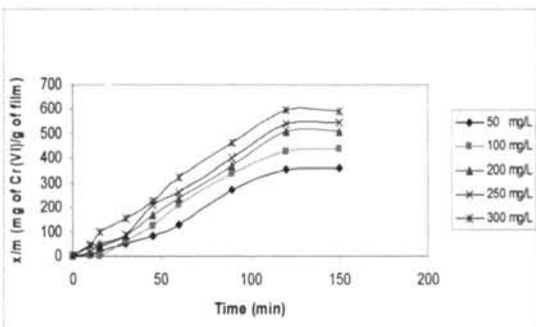
From figure 4.24 shows that the chitosan color was white color. After adsorption process chitosan color has changed from white to yellow It were demonstrated that chromium(VI) has adsorbed on $TiO_2$/chitosan. When photocatalytic process has been finished chitosan film color and turn in light-green color which shown that chromium(VI) has fixed on $TiO_2$/chitosan and change from chromium(VI) to chromium(III).



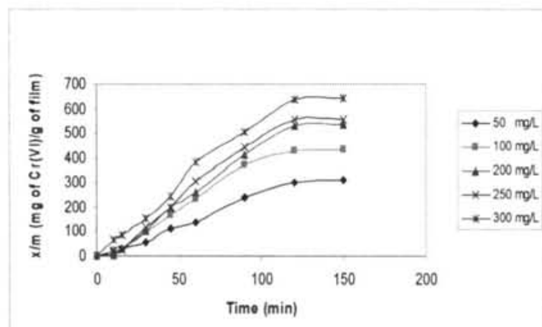

a) 1.5% chitosan, 0.2% Ti




b) 1.5% chitosan, 0.4% Ti




c) 1.5% chitosan, 0.6% Ti




d) 1.5% chitosan, 0.8% Ti

**Figure 4.25** Adsorption of chromium(VI) on $TiO_2$ /chitosan film that prepared from a) 1.5% chitosan, 0.2% Ti, b) 1.5% chitosan, 0.4% Ti, c) 1.5% chitosan, 0.6% Ti and d) 1.5% chitosan, 0.8% Ti in different initial concentrations of chromium(VI)

Langmuir equation was applied for adsorption equilibrium of chromium(VI) onto $TiO_2$/chitosan film surfaces. The Langmuir adsorption isotherm was based on these assumptions: (i) maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface: (ii) the energy of adsorption is constant: and (iii) there is no transmigration of adsorbate in surface plane. The Langmuir equation was shown below:

$$C_e/(x/m) = 1/(Q_o b) + C_e/Q_o \qquad \text{(Eq. 4.13)}$$

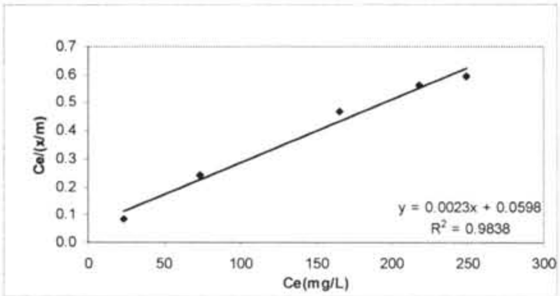
Where $C_e$ is the equilibrium concentration of chromium(VI), mg/L, $x/m$ is the amount of adsorbed chromium(VI) at equilibrium per unit mass of $TiO_2$/chitosan film, mg/g, $Q_o$ is the maximum adsorption at monolayer coverage, mg/g and b is Langmuir constant related to the affinity of binding sites, L/mg and it is a measure of the energy of adsorption. The linear plot of $C_e/(x/m)$ vs $C_e$ in figure 4.26 shown that adsorption of chromium(VI) onto the $TiO_2$/chitosan film surface in each condition obeys Langmuir adsorption isotherm. The correlation coefficient for the linear regression fit of Langmuir plot and expressed equation present in table 4.24

The essential characteristic of the Langmuir isotherm can be expressed in term of a dimensionless constant separation factor or equilibrium parameter, $R_L$, which is defined by (Mackay et al., 1982)

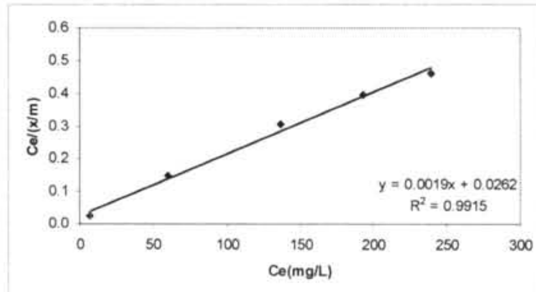
$$R_L = 1/(1 + bC_o) \qquad \text{(Eq. 4.14)}$$

Where $b$ is the Langmuir constant, and $C_o$ is the initial concentration of Chromium(VI). The parameter indicates the adsorption isotherm show in table 4.7. The values of $R_L$ in this experiment set were calculated (Table 4.22) and it was found that all $R_L$ values were between 0 and 1, indicating favorable chromium(VI) adsorption onto each $TiO_2$/chitosan film surface.

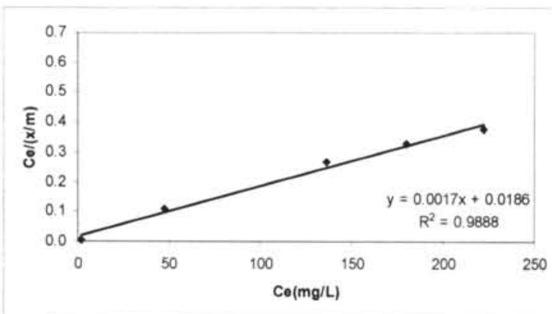
Figure 4.27 shows about the relation between $Q_0$ ( the maximum adsorption at monolayer coverage, mg of chromium /g of film) and chitosan content which shown that maximum adsorption at monolayer coverage was increased with increasing of Ti content on $TiO_2$/chitosan film. Figure 4.28 shows about the relation between $b$ which is a measure of the energy of adsorption.(L/mg) and chitosan content found that measure of the energy of adsorption was increased with the increasing of Ti content on $TiO_2$ chitosan film. From this result could be concluded that the relation between Ti content with $Q_0$ and $b$ tended to increased with increasing in Ti content. The Langmuir constants, $Q_0$ and $b$ values were determined form the Langmuir plotsshow in table 4.24.



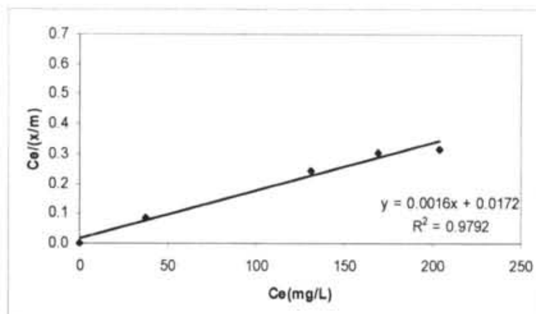

a) 1.5% chitosan, 0.2% Ti




b) 1.5% chitosan, 0.4% Ti




c) 1.5% chitosan, 0.6% Ti




d) 1.5% chitosan, 0.8% Ti

**Figure 4.26** Langmuir adsorption isotherm plot for adsorption of chromium(VI) on TiO2 /chitosan film that prepared from a) 1.5% chitosan, 0.2% Ti, b) 1.5% chitosan, 0.4% Ti, c) 1.5% chitosan, 0.6%Ti and d) 1.5% chitosan, 0.8% Ti

**Table 4.22** $R_L$ Values for Langmuir adsorption isotherm for TiO2/chitosan films in different Ti contents

| Initial concentrations of chromium(VI) (mg/L) | $R_L$ Value of $TiO_2$/chitosan film (1.5%chitosan, 0.2%Ti) | $R_L$ Value of $TiO_2$/chitosan film (1.5%chitosan,0.4%Ti) | $R_L$ Value of $TiO_2$/chitosan film (1.5%chitosan, 0.6%Ti) | $R_L$ Value of $TiO_2$/chitosan film (1.5%chitosan, 0.8%Ti) |
|---|---|---|---|---|
| 50 | 0.342 | 0.256 | 0.197 | 0.177 |
| 100 | 0.206 | 0.147 | 0.109 | 0.097 |
| 200 | 0.115 | 0.079 | 0.058 | 0.051 |
| 250 | 0.094 | 0.064 | 0.047 | 0.041 |
| 300 | 0.080 | 0.054 | 0.039 | 0.035 |

**Table 4.23** Langmuir and Freundlich adsorption isotherms for $TiO_2$/chitosan film that prepared from 0.2, 0.4, 0.6 and 0.8% Ti with 1.5 % chitosan

| Adsorption Isotherms | Chitosan contents (%) | Ti 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 |

**Table 4.24** $Q_0$ and $b$ values for Langmuir adsorption isotherm for $TiO_2$/chitosan film that prepared from 0.2, 0.4, 0.6 and 0.8% Ti with 1.5 % chitosan

| Isotherm | Chitosan contents (%) | Ti contents (%) | $Q_0$ (mg/g) | $b$ (L/mg) |
|---|---|---|---|---|
| Langmuir | 1.5 | 0.2 | 434 | 0.038 |
| | 1.5 | 0.4 | 555 | 0.058 |
| | 1.5 | 0.6 | 588 | 0.081 |
| | 1.5 | 0.8 | 625 | 0.093 |

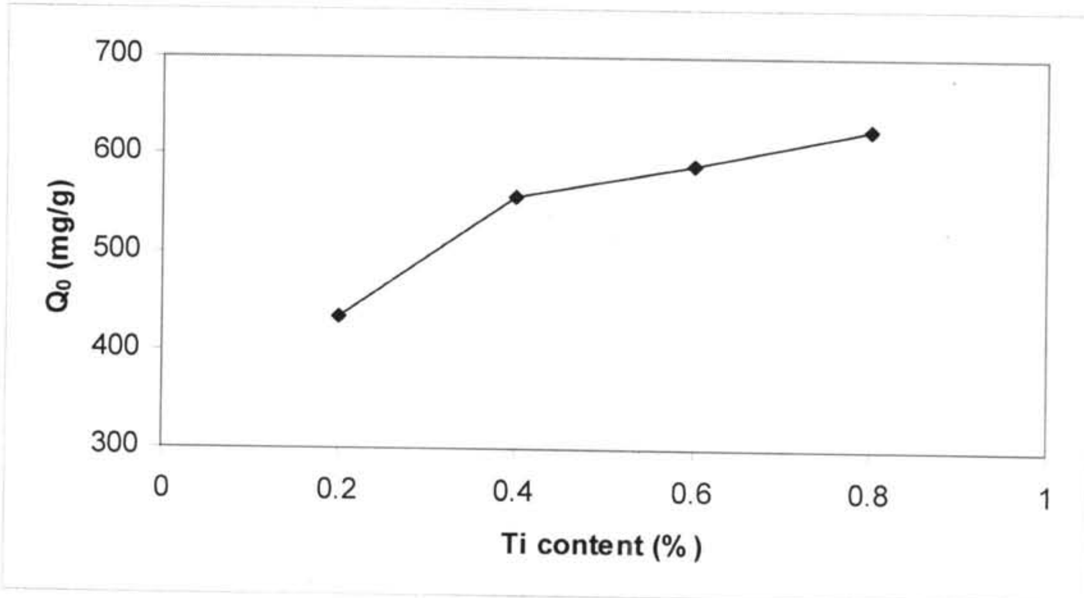



**Figure 4.27** Plotting of relation between $Q_0$ and Ti contents

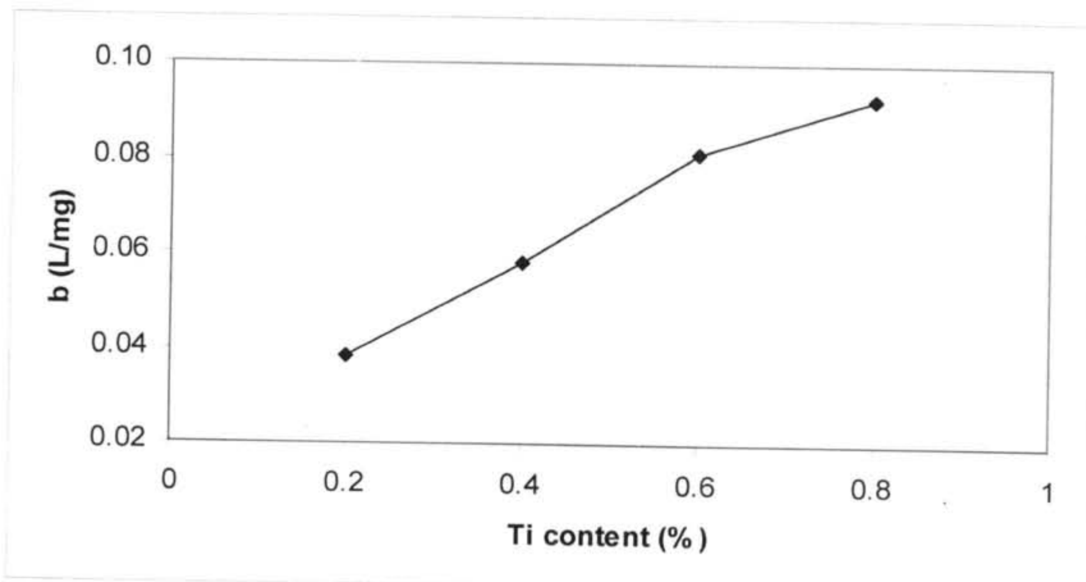
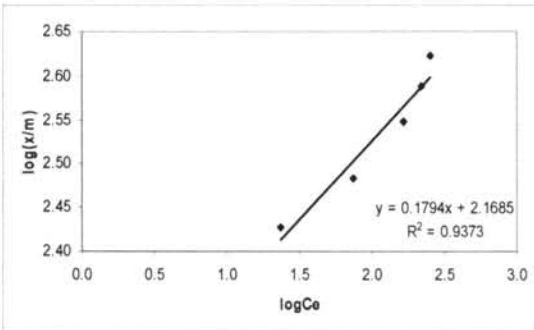
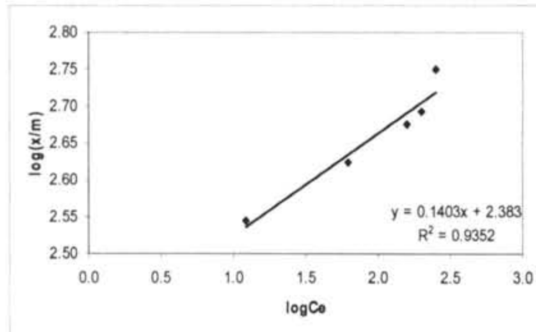


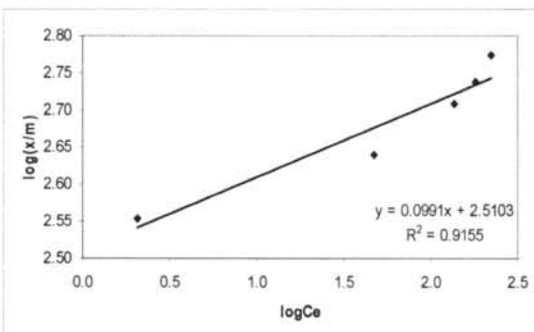

**Figure 4.28** Plotting of relation between *b* and Ti contents



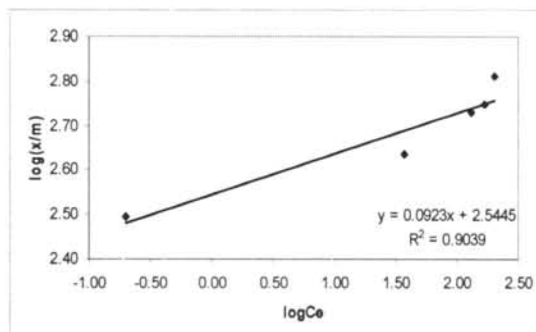

a)1.5% chitosan, 0.2% Ti




b) 1.5% chitosan, 0.4% Ti




c) 1.5% chitosan, 0.6% Ti




d) 1.5% chitosan, 0.8% Ti

**Figure 4.29** Freundlich adsorption isotherm plot for adsorption of chromium(VI) on $TiO_2$ /chitosan film that prepared from a) 1.5% chitosan, 0.2% Ti, b) 1.5% chitosan, 0.4% Ti, c) 1.5% chitosan, 0.6% and d) 1.5% chitosan, 0.8% Ti

Freundlich equation was also applied to adsorption of chromium(VI) onto $TiO_2$/chitosan film surface. The Freundlich equation is basically empirical, and generally agrees with experimental data over a moderate range of adsorbate concentrations. The Freundlich isotherm is represented by the equation (Mckay et al., 1982)

$$Log(x/m) = (1/n)\log C_e + \log k_f \qquad \text{(Eq. 4.15)}$$

Where $C_e$ is the equilibrium concentration of chromium(VI), mg/L, $x/m$ is the amount of adsorbed chromium(VI) at equilibrium per unit mass of $TiO_2$/chitosan film , mg/g, $k_f$, and $n$ are the Freundlich constants. The plotting of log$(x/m)$ versus $logC_e$ based on equation was shown above for the same experimental results in figure. 4.29. The correlation coefficient for the linear regression fit of the Freundlich plot and the expressed equation were presented in table 4.23.

The correlation coefficient for linear regression fit of Langmuir plot in each condition of $TiO_2$/chitosan film (0.2, 0.4, 0.6 and 0.8% Ti with 1.5 % chitosan) was found to be 0.9838, 0.9824, 0.9872 and 0.9792 while the correlation coefficient for the Freundlich plot in each condition of $TiO_2$/chitosan film(0.2, 0.4, 0.6 and 0.8% Ti with 1.5 % chitosan) were found to0.9373, 0.9352, 0.8725 and 0.9039, respectively which were less than that from Langmuir plot. The value of correlation coefficient of chromium(VI) adsorption indicates that adsorption behavior of chromium(VI) onto $TiO_2$/chitosan film tends to be a monolayer adsorption as described by Langmuir isotherm rather than Freundlich isotherms.

#### 4.2.4.2 Determination of kinetic values in photocatalytic reduction of chromium(VI) using $TiO_2$/chitosan films in variation of Ti contents.

The photocatalytic reductions of chromium (VI) with $TiO_2$/chitosan film that prepared from 0.2, 0.4, 0.6 and 0.8% Ti with 1.5% chitosan in variation of initial concentrations of chromium (VI) in the range of 50 – 300 mg/L were conducted. The results of this experimental part were shown about residual fraction of chromium (VI) (Figure 4.31). It was obvious that the efficiency in chromium (VI) removal decrease with increasing of initial concentration of chromium (VI) in solution. To explain the behavior of photocatalytic reduction of chromium (VI) by synthesized $TiO_2$/chitosan film for each condition in term of kinetic study, two patterns of kinetic orders, which were zero-order and pseudo-first order equations which were considered. As seen in chromium (VI) declining pattern, the kinetic order to explain the existed reaction can be either zero order or pseudo first order.

Value of $k_{obs}$ of zero-order pattern was determined from the slope of graph which was plot between $C-C_o$ and reaction time, $t$. The $R^2$ values for linear regression was calculated to exhibit the tendency of the reaction pattern to be describe as a zero-order pattern.

While value of $k_{obs}$ from pseudo-first order was determined from slope of graph which was plot between $-ln(C/C_0)$ and reaction time, $t$ (Figure 4.32). The $R^2$ values for linear regression was calculated to exhibit the tendency of the reaction pattern to be described as pseudo-first order. Values of $k_{obs}$ from pseudo-first order equation were determined as show in table 4.25-4.28.

The photocatalytic reduction of 100 mg/L chromium (VI) concentration under irradiation process for $TiO_2$/chitosan film with different Ti contents and $TiO_2$ powder were compared. The ratio of residual to initial concentration of chromium(VI) in term of $C/C_0$ as a function of irradiation time which illustrate in figure 4.30. It was obvioued that $TiO_2$/chitosan film provided the higher efficiency in chromium(VI) removal than $TiO_2$ powder. This 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 which has superb ability in adsorption pollutants especially metal ions (Ramnani et al.,2005). In consideration of treating efficiency of chromium(VI) using different chitosan contents that prepared from 0.2, 0.4, 0.6 and 0.8% Ti with 1.5% chitosan. The result shown that 0.8 % Ti was the highest efficiency for chromium (VI) removal and lower chromium (VI) efficiency is 0.6, 0.4 and 0.2% Ti, respectively.

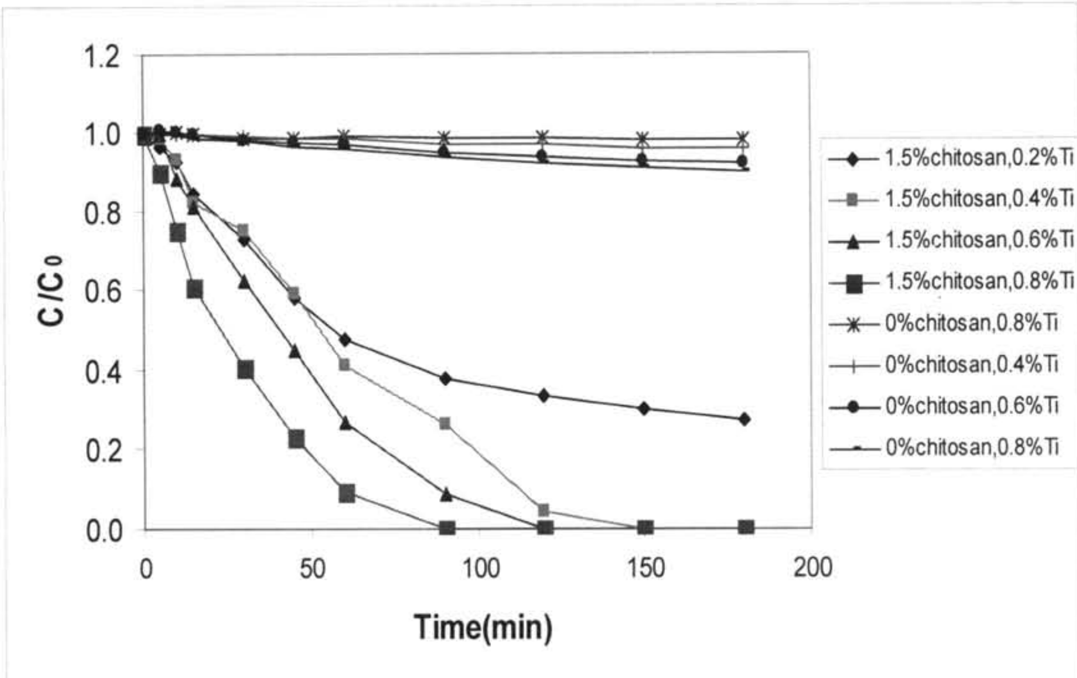
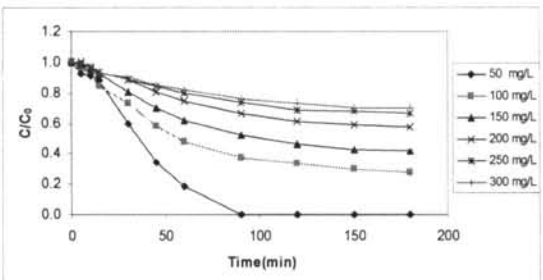


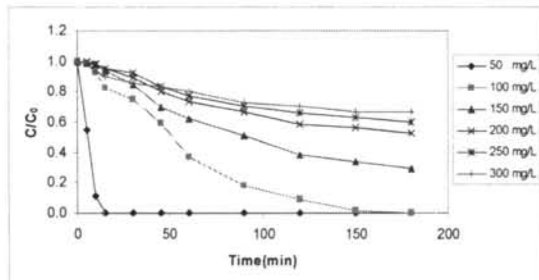

**Figure 4.30** Residual fraction of 100 mg/L chromium (VI) in different Ti contents on $TiO_2$/chitosan film

Considering the pattern of kinetic equation, the photocatalytic reduction reactions of $TiO_2$/chitosan films in different Ti contents could represented by pseudo-first order pattern for initial chromium(VI) concentration in range of 50-300 mg/L because the correlation coefficients ($R^2$) value of zero order less than that correlation coefficients value from pseudo-first order. The rate constant for photocatalytic process in 50 mg/L chromium(VI) concentration that removed by $TiO_2$/chitosan film prepared from 1.5%chitosan with 0.8% Ti could not determine because at the end of adsorption process, residual chromium concentration was equaled to zero.

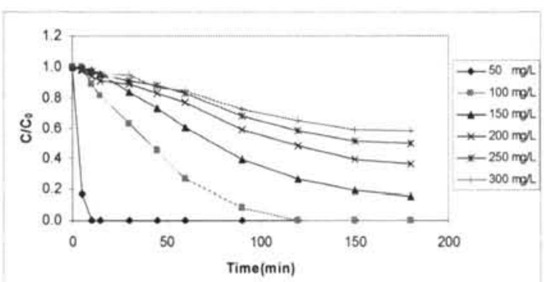
The photocatalytic reduction reactions of $TiO_2$/chitosan films in different Ti contents are the best described by pseudo-first order pattern. As chromium(VI) concentration increased with fixed dosage of $TiO_2$/chitosan film in the system, the reaction become depended on both concentration of chromium(VI) and reaction time.



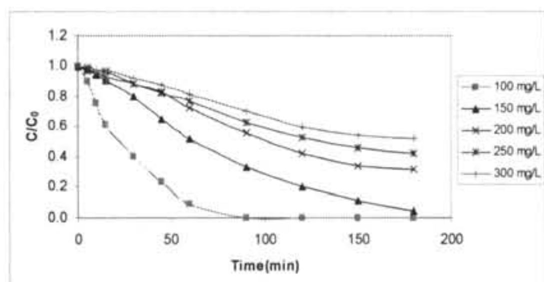

a) 1.5% chitosan, 0.2% Ti,




b) 1.5% chitosan, 0.4% Ti

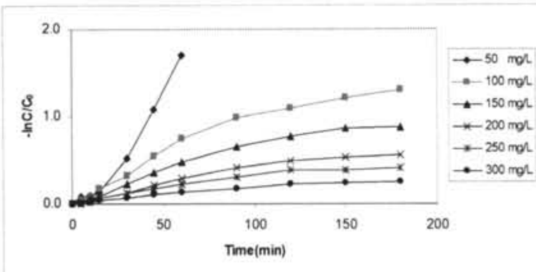



c) 1.5% chitosan, 0.6%

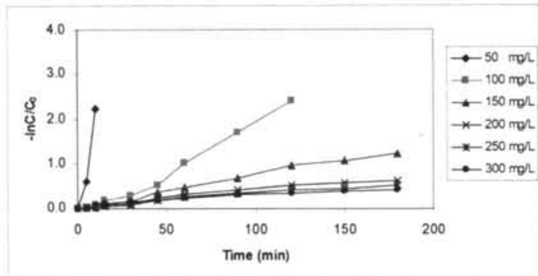



d) 1.5% chitosan, 0.8% Ti

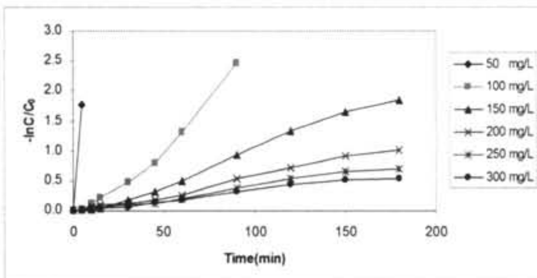
**Figure 4.31** Residual fraction of chromium (VI) in different initial concentrations for $TiO_2$/chitosan film that prepared from a) 1.5% chitosan, 0.2% Ti, b) 1.5% chitosan, 0.4% Ti, c) 1.5% chitosan, 0.6% Ti, d)1.5% chitosan, 0.8% Ti



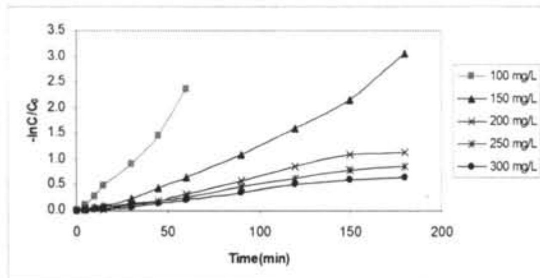

a) 1.5% chitosan, 0.2% Ti,




b) 1.5% chitosan, 0.4% Ti




c) 1.5% chitosan, 0.6%




d) 1.5% chitosan, 0.8% Ti

**Figure 4.32** Relation between $-\ln(C/C_0)$ and time in different of chromium(VI) initial concentrations for $TiO_2$/chitosan film that prepared from a) 1.5% chitosan, 0.2% Ti, b) 1.5% chitosan, 0.4% Ti, c) 1.5% chitosan, 0.6% Ti and d)1.5% chitosan, 0.8% Ti

The plotting of $k_{obs}$ as a function of Ti content on $TiO_2$/chitosan film form each condition and $TiO_2$ powder that used for removed 100 mg/L chromium(VI) concentration which show in figure 4.33. This figure shows that $k_{obs}$ obtained from $TiO_2$/chitosan film provided higher than $k_{obs}$ from $TiO_2$ powder. While the $k_{obs}$ value tendency of $TiO_2$/chitosan film was increased when increased Ti content and $k_{obs}$ from $TiO_2$/chitosan film prepared from 0.8%Ti with 1.5% chitosan was the highest (0.0358 $min^{-1}$) because in this film composed with maximum $TiO_2$ quantity which implied that the film also composed with maximum titanium in anatase phase. In this experiment, $TiO_2$ powder were commercial media which had highly anstase intensity, so this information was related with $TiO_2$ powder XRD pattern that outstanding demonstrated peak of 2- Theta in position 25.3 degree, this position was anatase phase peak. The photocatalytic activity was controlled by anatase proportion in film which was important factor in chromium(VI) removal. Xagas et al.(1999) reported that the media with higher anatase phase could enhance light absorption and pollutant adsorptions conduced to higher photocatalytic activity.

Upon photocatalyic reduction of chromium(VI), $TiO_2$ /chitosan film that prepared from 1.5% chitosan with 0.8% provided the highest efficiency which could remove 100% chromium(VI) in100 mg/L initial concentration with the shortest time. Therefore 1.5% chitosan with 0.8% Ti was the best content for $TiO_2$/chitosan film preparation.

**Table 4.25** Values of $k_{obs}$ from pseudo-first order equation for photocatalytic process using $TiO_2$ /chitosan film that prepared from 1.5%chitosan, 0.2% Ti with 20% acetic acid solution.

| Initial concentrations of chromium(VI) (mg/L) | pseudo-first order | | % Removal |
|---|---|---|---|
| | $k_{obs}$ ($min^{-1}$) | $R^2$ | |
| 50 | 0.0245 | 0.9879 | 100.00 |
| 100 | 0.0085 | 0.9222 | 80.61 |
| 150 | 0.0058 | 0.9348 | 67.53 |
| 200 | 0.0037 | 0.9352 | 52.65 |
| 250 | 0.0028 | 0.9128 | 43.75 |
| 300 | 0.0017 | 0.9400 | 40.39 |

**Table 4.26** Values of $k_{obs}$ from pseudo-first order equation for photocatalytic process using $TiO_2$ /chitosan film that prepared from 1.5%chitosan, 0.4% Ti with 20% acetic acid solution.

| Initial concentrations of chromium(VI) (mg/L) | pseudo-first order | | % Removal |
|---|---|---|---|
| | $k_{obs}$ ($min^{-1}$) | $R^2$ | |
| 50 | 0.2012 | 0.9434 | 100.00 |
| 100 | 0.0183 | 0.9598 | 100.00 |
| 150 | 0.0073 | 0.9892 | 79.92 |
| 200 | 0.0040 | 0.9685 | 60.74 |
| 250 | 0.0032 | 0.961 | 53.05 |
| 300 | 0.0028 | 0.8621 | 46.30 |

**Table 4.27** Values of $k_{obs}$ pseudo-first order equation for photocatalytic process using $TiO_2$ /chitosan film that prepared from 1.5 % chitosan, 0.6% Ti with 20% acetic acid solution.

| Initial concentrations of chromium(VI) (mg/L) | pseudo-first order | | % Removal |
|---|---|---|---|
| | $k_{obs}$ ($min^{-1}$) | $R^2$ | |
| 50 | - | - | 100.00 |
| 100 | 0.0237 | 0.9415 | 100.00 |
| 150 | 0.0103 | 0.9823 | 90.10 |
| 200 | 0.0058 | 0.9862 | 76.01 |
| 250 | 0.0041 | 0.9800 | 64.47 |
| 300 | 0.0033 | 0.9804 | 56.61 |

**Table 4.28** Values of $k_{obs}$ from pseudo-first order equation for photocatalytic process using $TiO_2$ /chitosan film that prepared from 1.5%chitosan, 0.8% Ti with 20% acetic acid solution.

| Initial concentrations of chromium(VI) (mg/L) | pseudo-first order | | % Removal |
|---|---|---|---|
| | $k_{obs}$ ($min^{-1}$) | $R^2$ | |
| 50 | - | - | - |
| 100 | 0.0358 | 0.9745 | 100.00 |
| 150 | 0.0146 | 0.9587 | 97.34 |
| 200 | 0.0066 | 0.9779 | 79.74 |
| 250 | 0.005 | 0.9931 | 71.65 |
| 300 | 0.0039 | 0.9843 | 63.84 |

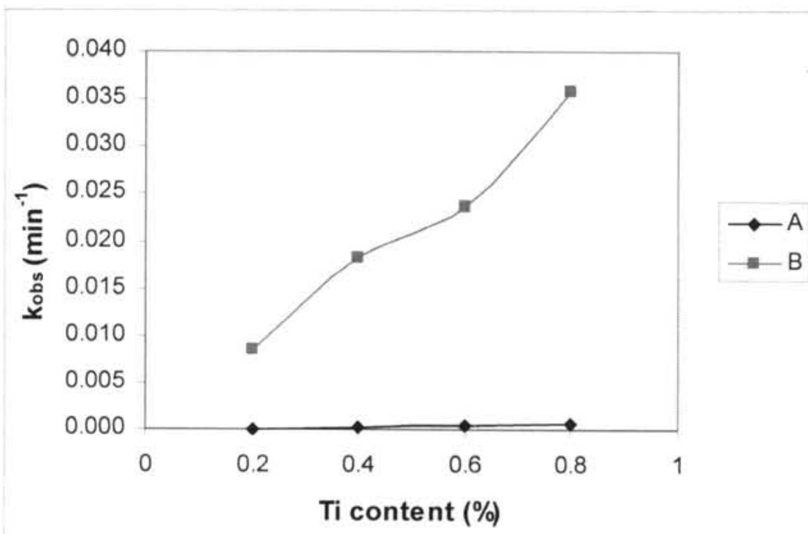
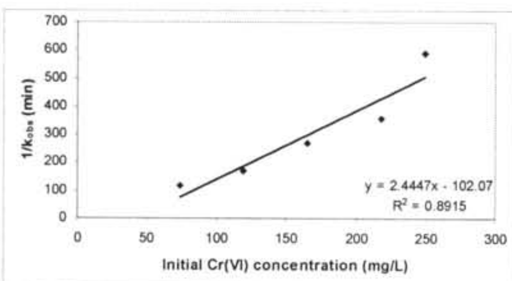



**Figure 4.33** Comparison of photocatalytic decomposition rates using different Ti contents (A is $TiO_2$ powder and B is $TiO_2$/chitosan film) in 100 mg/L chromium(VI) concentration.

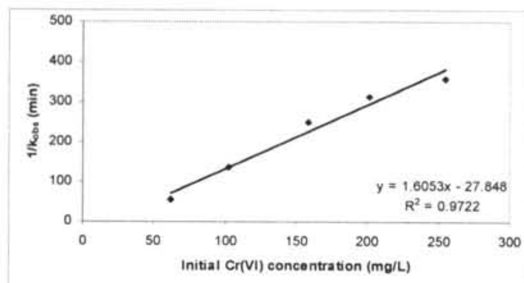
The Langmuir-Hinshelwood rate expression has been successfully used for heterogeneous photocatalytic degradation to determine the relationship between the initial degradation rate and the initial concentration of chromium (VI) (Chen et al., 1998):

$$\frac{1}{k_{obs}} = \frac{1}{k \cdot K_{cr(VI)}} + \frac{[Cr(VI)]_o}{k} \qquad \text{(Eq. 4.16)}$$

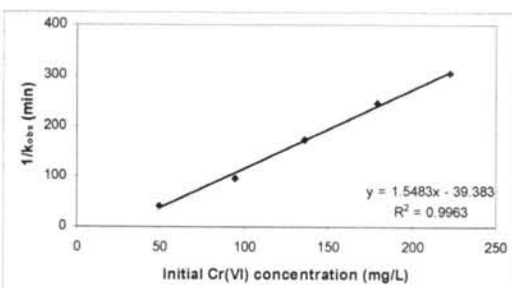
| | |
|---|---|
| Where $[Cr(VI)]_o$ | is the initial concentration of chromium (VI) in the unit of mg/L |
| $K_{cr(VI)}$ | is the Langmuir-Hinshelwood adsorption equilibrium constant in the unit of L/mg |
| $k$ | is the rate constant of surface reaction in the unit of mg/L.min |



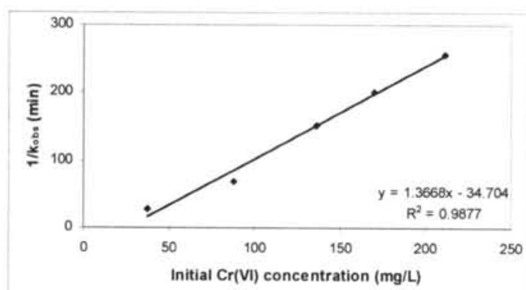

a) 1.5% chitosan, 0.2% Ti




b) 1.5% chitosan, 0.4% Ti




c) 1.5% chitosan, 0.6% Ti




d) 1.5% chitosan, 0.8% Ti

**Figure 4.34** Determination of adsorption equilibrium conseants and degradation rate constants chromium(VI) by using $TiO_2$/chitosan film that prepared from a) 1.5% chitosan, 0.2% Ti,b) 1.5% chitosan, 0.4% Ti, c) 1.5% chitosan, 0.6% Ti and d)1.5% chitosan, 0.8% Ti

Figure 4.34 shows determination of the adsorption equilibrium constant and degradation rate constant for chromium (VI) in the range of initial concentrations 100 to 300 mg/L by plotting between $1/k_{obs}$ and initial chromium(VI) concentration. The Langmuir-Hinshelwood equations for photocatalytic process using $TiO_2$/chitosan films in variation of chitosan contents were followed below equation that show in table 4.29.

**Table 4.29** Langmuir-Hinshelwood equations for photocatalytic process using $TiO_2$/chitosan films in variation of Ti contents

| Chitosan contents (%) | Ti contents (%) | Langmuir-Hinshelwood Equations $\frac{1}{k_{obs}} = \frac{1}{k \cdot K_{cr(VI)}} + \frac{[Cr(VI)]_o}{k}$ |
|---|---|---|
| 1.5 | 0.2 | $\frac{1}{k_{obs}} = \frac{1}{(0.409)(-0.024)} + \frac{[Cr(VI)]_o}{0.409}$ |
| 1.5 | 0.4 | $\frac{1}{k_{obs}} = \frac{1}{(0.623)(-0.058)} + \frac{[Cr(VI)]_o}{0.623}$ |
| 1.5 | 0.6 | $\frac{1}{k_{obs}} = \frac{1}{(0.646)(-0.039)} + \frac{[Cr(VI)]_o}{0.646}$ |
| 1.5 | 0.8 | $\frac{1}{k_{obs}} = \frac{1}{(0.732)(-0.039)} + \frac{[Cr(VI)]_o}{0.732}$ |

## 4.3 The effect of photocatalytic process on mechanical properties of film

From last experiment, it was found that $TiO_2$/chitosan film from 1.5% chitosan with 0.8% Ti was the best condition and provided the highest efficiency for chromium(VI) removal. Therefore in this experiment, the mechanical properties of this films after illumination at each time were investigated. The films in this study consisted of $TiO_2$/chitosan film in best condition (1.5% chitosan with 0.8% Ti ) and chitosan film (1.5% chitosan with 0 % Ti ) which placed in 100 mg/L chromium(VI) concentrated and distilled water for illumination. After photocatalytic process the mechanical properties of film such as its elongation at break and tensile strength were observed.

In term of mechanical properties, tensile strength value of chitosan film (1.5% chitosan with 0 % Ti ) and $TiO_2$/chitosan film(1.5% chitosan with 0.8% Ti ) at time zero or after placed two types of film in distilled water under non-irradiation about 30 min 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 were 61.35% and 46.63%,respectively.

When compared between $TiO_2$/chitosan and chitosan films at time zero, the result shown that tensile strength and elongation at break of $TiO_2$/chitosan film lower than those chitosan film (Figure 4.35 and 4.36). The reason might due to $TiO_2$ particles that mixed into the film which reduce interaction between film molecule. After UV illuminated, tensile strength and elongation at break of two types of film were investigated and it was found that tensile strength and elongation at break of $TiO_2$/chitosan film. In addition, chitosan films in distilled water tended to decrease when increased illumination time because UV radiation might destroy chitosan structure. For $TiO_2$/chitosan and chitosan films in 100 mg/L chromium(VI), those tensile strength and elongation at break tended to decreased when increased illumination time. The explanation might come from the fact that UV radiation can destroy chitosan polymer structure. In addition, at acidic condition chitosan which protonated amino group ($-NH_3^+$) as a functional of chitosan biopolymer might capture negatively charged (chromium(VI) existed as $HCrO_4^-$) causing the destroying intramolecular hydrogen bonding of chitosan polymer.

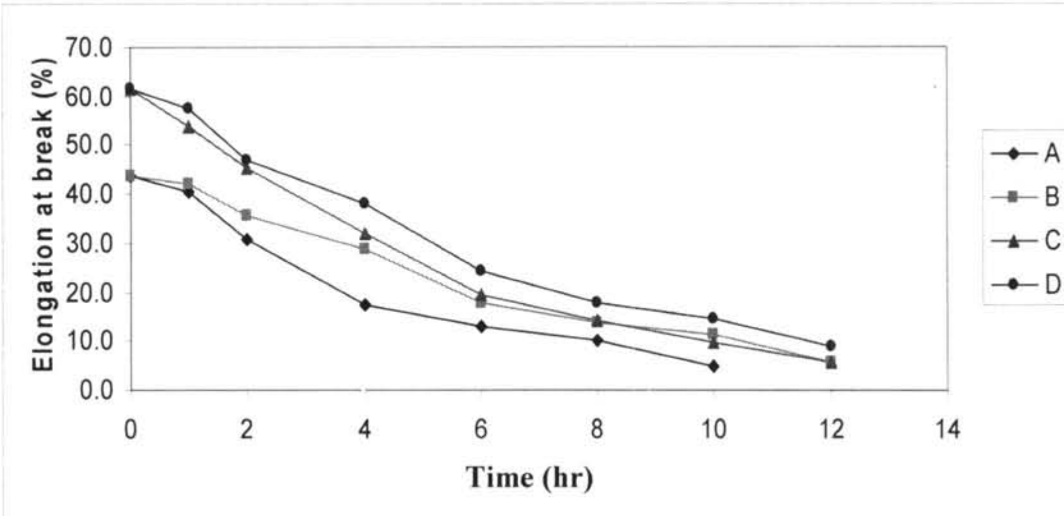



**Figure 4.35** Relationship between elongation at break(%) of film and UV illumination time(hr) (A is $TiO_2$/chitosan film in 100 mg/L chromium(VI), B is $TiO_2$/chitosan film in distilled water, C is chitosan film in 100 mg/L chromium and D is chitosan film in distilled water)

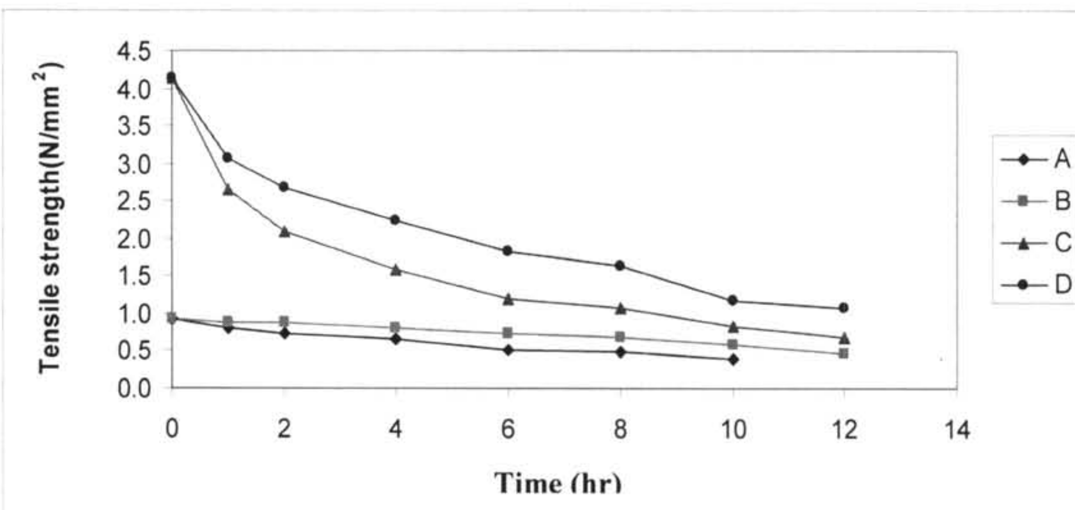



**Figure 4.36** Relationship between tensile strength($N/mm^2$) of film and UV illumination time(hr) (A is $TiO_2$/chitosan film in 100 mg/L chromium(VI), B is $TiO_2$/chitosan film in distilled water, C is chitosan film in 100 mg/L chromium and D is chitosan film in distilled water )