CHAPTER III

METHODOLOGY

3.1 Materials

3.1.1 Chemicals

All chemical and reagents in this study were analytical grade. TiO_2/chitosan film and chitosan film were prepared by using TiO_2 (Degussa P-25), chitosan flake as chitosan from crab shells which was highly viscosity(Fluka, Sigma-aldrich co., plc.) in acetic acid solution (Merck Chemical). Chromium(VI) prepared by potassium chromate or K_2CrO_4(Merck Chemical) was used to perform the synthetic wastewater of this work. Moreover, the desired pH of the solution was adjusted with NaOH or H_2SO_4 which purchased from Merck Company, and used as received.

3.1.2 Reactor

The adsorption and photocatalytic activities of chitosan and TiO_2/chitosan films were evaluated from reduction of chromium (VI). Chemical reactor (1500 mL) was used as a batch reactor in this study. The UV light source was 10-watt low pressure mercury lamp with wave length 254 nm. The UV lamp was placed over the reactor and film was placed inside screen before put in the reactor. The set-up of reactor is shown in figure 3.1.

3.2 Methodologies

The experiment of this research could be divided into 4 main parts:

Part I Synthesis of TiO_2/chitosan and chitosan films

Part II Characterization of synthesized TiO_2/chitosan and chitosan films

Part III Treating of chromium (VI) using synthesized TiO_2/chitosan and chitosan films

Part IV Determination of film mechanical properties after irradiation process

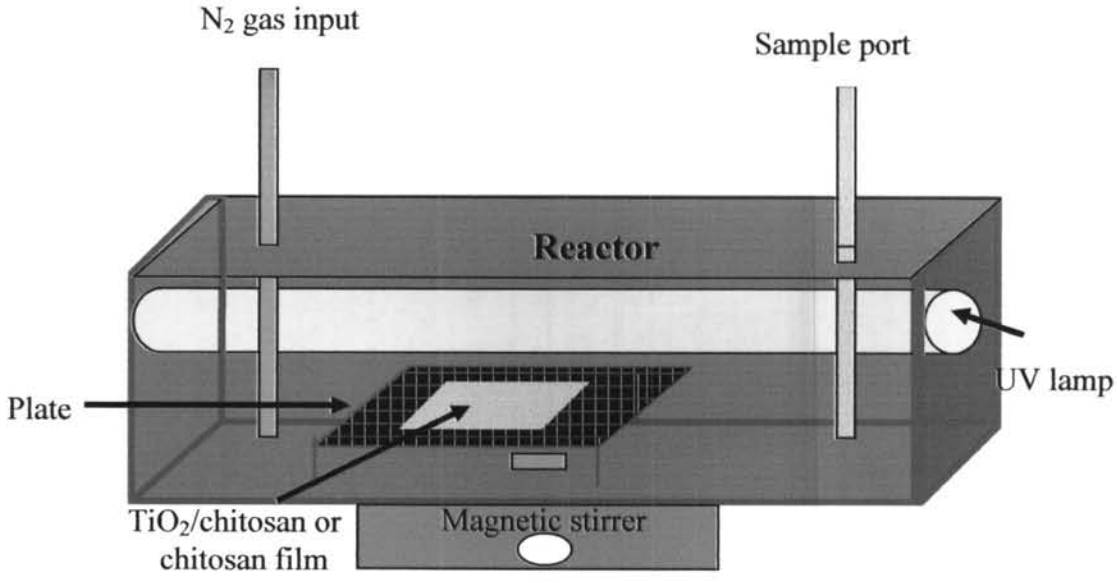

Figure 3.1 Reactor set-up used in this study

3.2.1 Synthesis of TiO_2/chitosan and chitosan films

The films formation were divided into two types which were chitosan film and TiO_2/chitosan films. The first type of film was prepared by mixing variation percentage of chitosan flask without TiO_2 and dissolved in 20% acetic acid solution for 24 hr. After that 5 g of slurry were taken and spread them on 5x6 cm plastic plate. Then the plate was placed in room temperature to dry for 48 hr and peeled the film from glass plates. The film was stored in the confined space. This film was called chitosan film. The second type of film was prepared by mixed varied percentage of chitosan flask with varied percentage of Ti and dissolved in 20% acetic acid solution for 24 hr. After that 5 g of slurry was taken and spread its on 5x6 cm glass plate. Then this plate was placed in room temperature to dry for 48 hr and peeled the film out

from glass plate. The film was stored in the confined space.This film was called TiO_2/chitosan film as described on film formation (Figure 3.2).

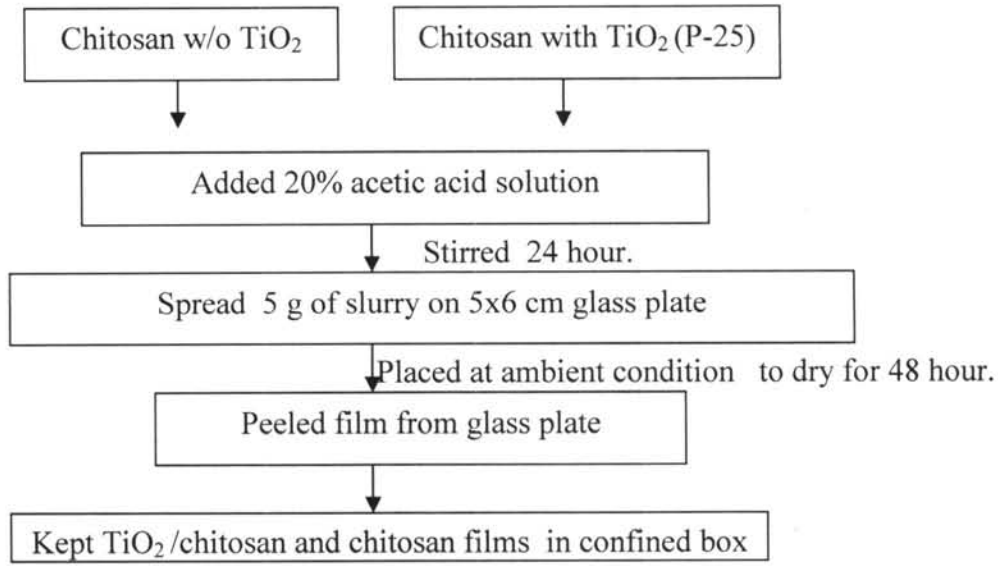

Figure 3.2 Preparation procedure of chitosan and TiO_2 /chitosan films

3.2.1.1 Investigation of effect of chitosan quantity on TiO_2/chitosan and chitosan films preparation

Chitosan films were prepared in variation of chitosan flask 1, 1.5, 2 and 2.5 % w/w without TiO_2 and dissolved in 20% acetic acid solution for 24 hr. For TiO_2/chitosan films were prepared by varied chitosan flask 1, 1.5, 2 and 2.5 % w/w with fixed 0.4 % Ti and dissolved in 20% acetic acid solution for 24 hr. After that 5 gram of slurry were taken and spread them on glass plate size 5x6 cm. Then the plate was placed in room temperature to dry for 48 hr and peeled the film from glass plate. The film was stored in the confined space.

3.2.1.2 Investigation of effect of titanium quantity on TiO_2/chitosan and chitosan films preparation

Chitosan films were prepared by fixed chitosan flask 1.5% w/w without TiO_2 and dissolved in 20% acetic acid solution for 24 hr. For TiO_2/chitosan

films were prepared by fixed chitosan flask 1.5 % w/w with variation of titanium as 0.2, 0.4, 0.6 and 0.8 % Ti dissolved in 20% acetic acid solution for 24 hr. After that 5 g of slurry were taken and spread them on glass plate size 5x6 cm and then this plate was placed in room temperature to dry for 48 hr and peeled the film out from glass plate. The film was stored in the confined space.

3.2.2 Characterization of synthesized TiO_2 /chitosan and chitosan films

The prepared chitosan and TiO_2/chitosan film were characterized by using different techniques. The investigated characteristics of film could describe as follow:

3.2.2.1 Surface morphology of TiO_2/chitosan and chitosan films

To obtain surface morphology of synthesized TiO_2/chitosan and chitosan film were examined by Scanning Electron Microscope (SEM). The difference in morphology of the films in each conditions were identified.

3.2.2.2 Crystal structure of TiO_2/chitosan and chitosan films

To obtain crystal structure of films that obtaining from each condition, the films were characterized by X-Ray Diffaction (XRD). This experiment could explain that the films whether maintained chitosan and TiO_2 properties.

3.2.2.3 Weight of TiO_2/chitosan and chitosan films

Weight of each film that prepared in different condition was measured by weight balance.

3.2.2.4 Thickness of TiO_2/chitosan and chitosan films

Tthickness of each film that prepared in different condition was measured by micrometer. The measurement of film thickness value was measured at 8 point on each film and calculate the average.

3.2.3 Treating of chromium (IV) using synthesized TiO_2/chitosan and chitosan films .

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 were divided in to 2 processes which were adsorption and photocatalytic processes.

3.2.3.1 Investigation of effect of TiO_2/chitosan and chitosan films in different chitosan quantities for chromium(VI) removal by adsorption and photocatalytic processes.

In adsorption process, TiO_2 powder and one piece of TiO_2/chitosan and chitosan films size 5x6 cm was put inside screen and soaked in distilled water for 30 min in order to adjust the film from dry to wet film after that placed its in one liter of synthetic chromium(VI) solution inside the reactor and mixed by magnetic stirrer. The chromium(VI) solution 100 mg/L was equilibrated in the dark (covered by aluminum foil) with the TiO_2/chitosan surface for the adsorption process (Figure3.3). The chromium(VI) solution was agitated thoroughly by magnetic stirrer. In adsorption process each sample was taken at 0, 10, 15, 30, 45, 60, 90, 120 and 150 min for investigated residual chromium(VI) in solution. The sample after illumination was syringed out to analyze the concentration of chromium (VI) with a UV-Vis spectrophotometer. The efficiency for chromium removal of each media was compared and investigated. Only TiO_2/chitosan film in each condition (1, 1.5, 2 and 2.5% chitosan with 0.4%Ti) was depth analyzed fort equilibrium adsorption isotherm. Chromium(VI) 50, 100, 200, 250 and 300 mg/L were equilibrated in dark condition

with the TiO_2/chitosan film surface for adsorption process (Table 3.1). The adsorption isotherms were interpreted by the Langmuir and Freundlich models.

Table 3.1 Experimental conditions for study effect of TiO_2/chitosan and chitosan films in different chitosan quantities for chromium(VI) removal by adsorption process

Types of film	Chitosan contents (%)	Ti contents (%)	Initial concentrations of chromium(VI) (mg/L)
TiO_2/ chitosan film	1	0.4	50,100, 200, 250 and 300
	1.5	0.4	50,100, 200, 250 and 300
	2	0.4	50,100, 200, 250 and 300
	2.5	0.4	50,100, 200, 250 and 300
Chitosan film	1	0	100
	1.5	0	100
	2	0	100
	2.5	0	100
TiO_2 powder	0	0.4	100

In photocatalytic process, prior to irradiation, TiO_2 powder and one piece of TiO_2/chitosan film size 5x6 cm was put inside screen and soaked in distilled water for 30 min to adjust film from dry to wet film and let it reaches the adsorption equilibrium for 150 min and then a UV lamp was turned on to illuminate for 180 min. Chromium(VI) solution was agitated thoroughly by magnetic stirrer. The sample after illumination was syringed out for analyzed residual concentration of chromium(VI) with a UV-Vis spectrophotometer. Each sample was taken at 0, 5, 10, 15, 30, 45, 60, 90, 120, 150 and 180 min for investigated residual chromium(VI) concentration (Figure 3.4). The residual chromium(VI) concentration in the aqueous solution was plotted as a function of time. The observed rate constant , k_{obs} from each experimental condition was calculated.

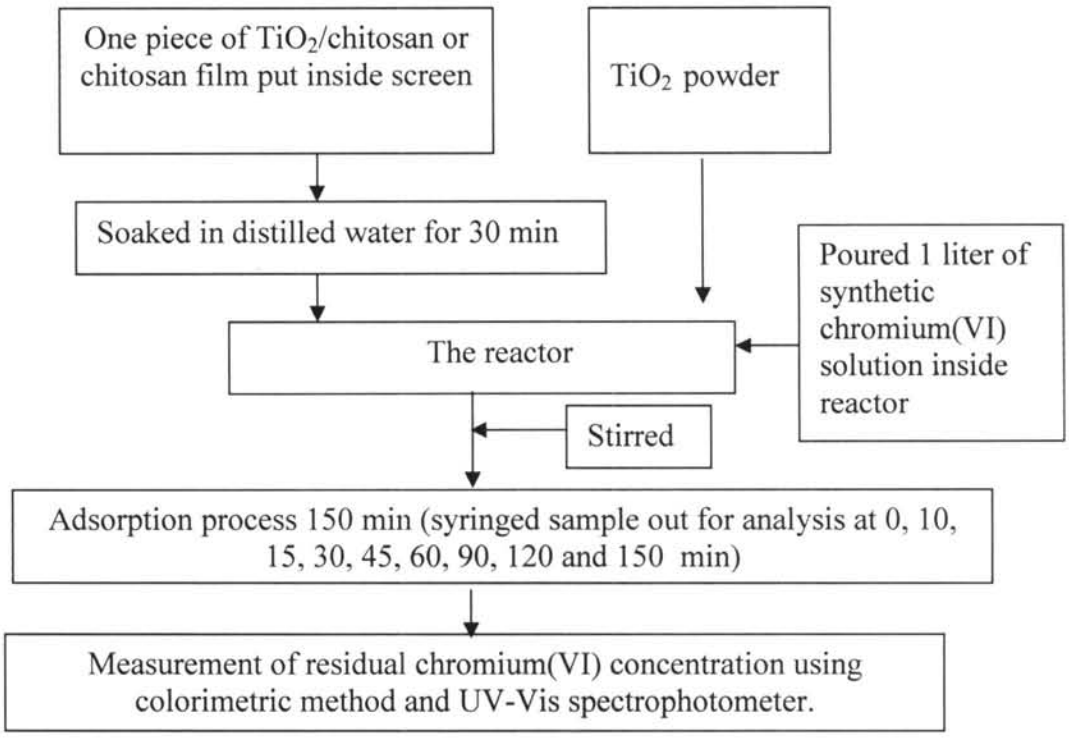

Figure 3.3 Schematic diagram for adsorption process

The observed rate constant, k_{obs} from each experimental condition was calculated and the efficiency for chromium(VI) removal of each media was compared and investigated. Only TiO_2/chitosan film in each condition (1, 1.5, 2 and 2.5% chitosan with 0.4%Ti) was used to remove chromium(VI) in photocatalysis process in different six initial concentrations (50, 100, 150, 200, 250 and 300 mg/L). Results from this part were reported as the plot of observed kinetic rate constant, k_{obs} .

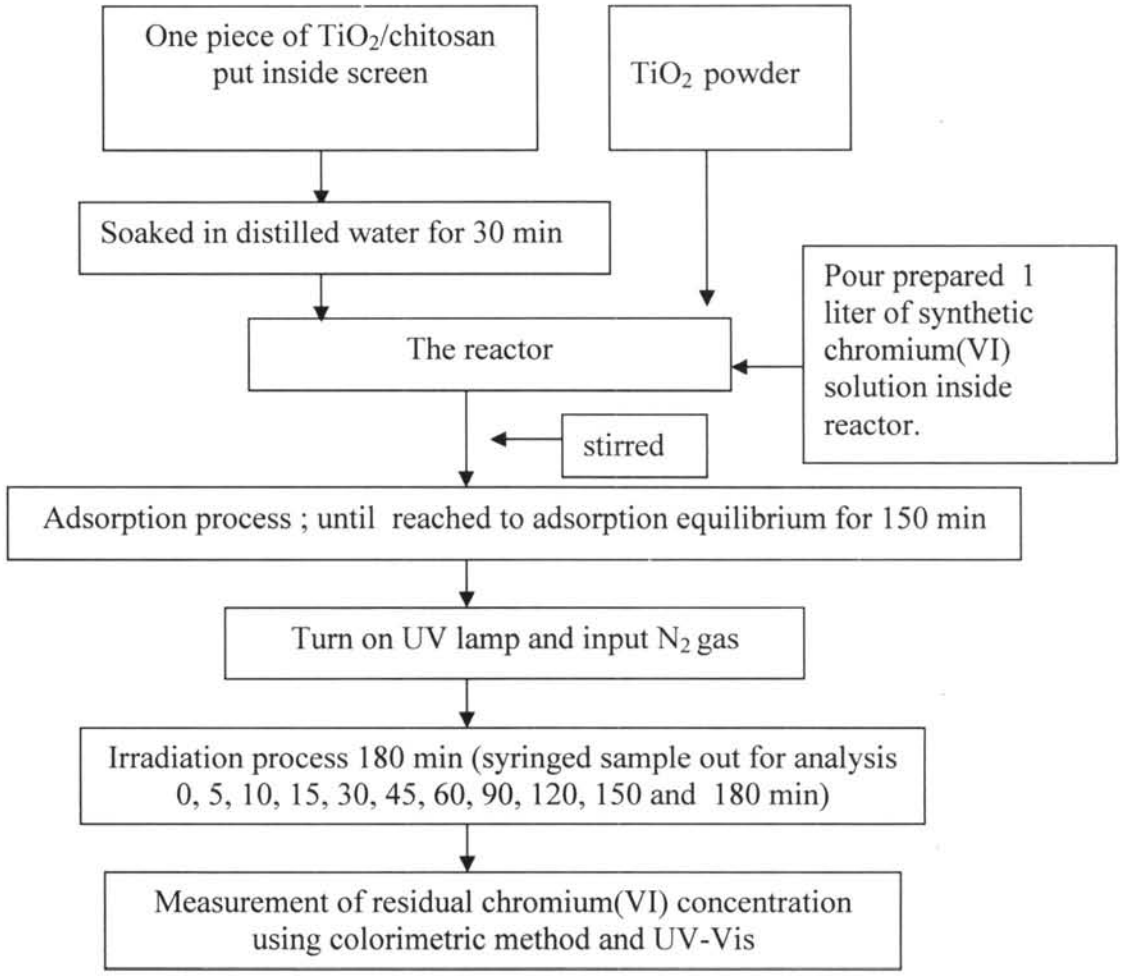

Figure 3.4 Schematic diagram for photocatalytic process

Table 3.2 Experimental conditions for study effect of TiO_2/chitosan and chitosan films in different chitosan quantities for chromium(VI) removal by photocatalytic process

Types of film	Chitosan contents (%)	Ti contents (%)	Initial concentrations of chromium(VI) (mg/L)
TiO_2/ chitosan film	1	0.4	50,100,150, 200, 250 and 300
	1.5	0.4	50,100,150, 200, 250 and 300
	2	0.4	50,100,150, 200, 250 and 300
	2.5	0.4	50,100,150, 200, 250 and 300
TiO_2 powder	0	0.4	100

3.2.3.2 Investigation of effect of TiO_2/chitosan and chitosan films in different titanium quantities for chromium(VI) removal by adsorption and photocatalytic process

In adsorption process, TiO_2 powder and one piece of TiO_2/chitosan and chitosan films size 5x6 cm was put inside screen and soaked in distilled water for 30 min in order to adjust the film from dry to wet film after that placed in one liter of synthetic chromium(VI) solution inside the reactor and mixed by magnetic stirrer. Treating of chromium (VI) solution 100mg/L was equilibrated in dark condition (covered by aluminum foil) with the TiO_2/chitosan surface for the adsorption process. The chromium(VI) solution was agitated thoroughly by magnetic stirrer. In adsorption process each sample was taken at 0, 10, 15, 30, 45, 60, 90, 120 and 150 min for investigated residual chromium(VI) in solution. The efficiency for chromium removal of each media was compared and investigated. Only TiO_2/chitosan film in each condition (0.2, 0.4, 0.6 and 0.8% Ti with 1.5% chitosan) was depth analyzed about equilibrium adsorption isotherm. For investigation adsorption isotherm of chromium(VI) removal by TiO_2/chitosan films. Treating of chromium(VI) solution 50, 100, 200, 250 and 300 mg/L was equilibrated in dark with the TiO_2/chitosan surface for the adsorption process (Table 3.3). The adsorption isotherm were interpreted by the Langmuir and Freundlich models.

In photocatalytic process, prior to irradiation, TiO_2 powder (0.2, 0.4, 0.6 and 0.8%Ti w/o chitosan flask) and one piece of TiO_2/chitosan film (0.2, 0.4, 0.6 and 0.8%Ti with 1.5% chitosan) size 5x6 cm was put inside screen and soaked in distilled water for 30 min in order to adjust film from dry to wet film after that placed its in one liter of synthetic 100 mg/L chromium(VI) inside the reactor as until it reaches to the adsorption equilibrium for 150 min and then a UV lamp was turned on to illuminate for 180 min. The chromium(VI) solution was agitated thoroughly by magnetic stirrer. The sample after illumination was syringed out for analyzed the residual concentration of chromium (VI) with a UV-Vis spectrophotometer. Each sample was taken at 0, 5, 10, 15, 30, 45, 60, 90, 120, 150 and 180 min for investigation residual chromium(VI) concentration. The residual chromium(VI) concentration in aqueous solution was plot as a function of time. The observed rate constant, k_{obs} from each experimental condition was calculated and the efficiency for

chromium removal of each media was compared and investigated. Only TiO_2/chitosan film in each condition (0.2, 0.4, 0.6 and 0.8%Ti with 1.5% chitosan) was used to remove of chromium(VI) in photocatalysis process in different initial concentrations (50,100,150, 200, 250 and 300 mg/L). Results from this part were reported as the plot of observed kinetic rate constant, k_{obs}.

Table 3.3 Experimental conditions For study effect of TiO_2/chitosan and chitosan films in different titanium quantities for chromium(VI) removal by adsorption process

Types of film	Chitosan contents (%)	Ti contents (%)	Initial concentrations of chromium(VI) (mg/L)
TiO_2/ chitosan film	1.5	0.2	50,100, 200, 250 and 300
	1.5	0.4	50,100, 200, 250 and 300
	1.5	0.6	50,100, 200, 250 and 300
	1.5	0.8	50,100, 200, 250 and 300
TiO_2 powder	0	0.2	100
	0	0.4	100
	0	0.6	100
	0	0.8	100
Chitosan film	1.5	0	100

Table 3.4 Experimental conditions to study effect of TiO_2/chitosan and chitosan films in different chitosan quantities for chromium(VI) removal by photocatalytic process

Types of film	Chitosan contents (%)	Ti contents (%)	Initial concentrations of chromium(VI) (mg/L)
TiO_2/ chitosan films	1.5	0.2	50,100, 150,200, 250 and 300
	1.5	0.4	50,100, 150,200, 250 and 300
	1.5	0.6	50,100, 150,200, 250 and 300
	1.5	0.8	50,100, 150,200, 250 and 300
TiO_2 powder	0	0.2	100
	0	0.4	100
	0	0.6	100
	0	0.8	100

3.2.4 Determination of mechanical properties of film after illumination process

TiO_2/chitosan film was prepared by 1.5 %w/w chitosan flask with 0.8% Ti was the best condition chromium(VI) removal by photocatalytic process. Therefore, after irradiation process, the mechanical properties of film such as its elongation at break and tensile strength were observed. One piece of TiO_2/chitosan film that prepared by 1.5 % chitosan flask with 0.8% Ti and chitosan film that prepared by 1.5% chitosan flask without titanium were put inside screen and soaked in distilled water for 30 min in order to adjust film from dry to wet film after that placed into two types of water as distilled water and synthetic 100 mg/L chromium(VI) which were in the reactor. Then, the UV lamp was turned on. After photocatalytic process the films were taken for analysis of mechanical properties as their elongation at break (ASTM D-822(2001)) and tensile strength (ASTM D-822(2001)) by texture analyzer instrument. The mechanical properties of film were analyzed at 0, 1, 2, 4, 6, 8, 10 and 12 hr after illumination.

Table 3.5 Experimental conditions for study effect of illumination process on mechanical properties of film

Types of wet film	Chitosan contents (%)	Ti contents (%)	Initial concentrations of chromium(VI) (mg/L)
TiO_2/ chitosan film	1.5	0.8	0
	1.5	0.8	100
chitosan film	1.5	0	0
	1.5	0	100