Research on the Characteristics of Chitosan and its Adsorption on Common Chlorinated Organics in Wastewater

Abstract

This research explores the characteristics of chitosan and uses it as an adsorbate to adsorb some common chlorinated organics of waste water such as 4-Chlorophenol and tetrachloroethylene. The experiments include the analysis of batch adsorptions and adsorption dynamics of chitosan and the control factors include the concentration and pH value of the targeted contaminant. The results show that the pH value will influence the specific surface area and pore structures of chitosan, and therefore, the lower the pH value, the bigger the specific surface area (the original chitosan and chitosan of pH 4 have specific surface areas 10.3 and 19.7 m^2/g respectively); additionally, according to the FTIR spectrum, different pH values will not explicitly influence functional group species of chitosan; the analyzed results of ^{13}C NMR also show that as pH values go up, the values of aliphatic group and aromatic group respectively decrease from 96.3 and 2.4% (pH 4) to 94.9% and 1.9% (pH 9), which should be the reduction on amino groups and hydroxyl ions under one acidic environment; as a result, carbon proportionally increases. According to adsorption experiments, the chitosan adsorption situation (the values of R^2 are respectively 0.898~0.907 and 0.898~0.940) related to 4-Chlorophenol and tetrachloroethylene may be described by Langmuir isothermal adsorption model. When 4-Chlorophenol and tetrachloroethylene are under different conditions of pH values, the Langmuir b values are respectively about 0.00003~0.00012 and 0.00001~0.00007, and because the b value is a constant related to energy of adsorption bond, it explains that chitosan has a different adsorption mechanism to 4-Chlorophenol and to tetrachloroethylene, and thus, its adsorbed volumes respectively as pH 6＞pH 4＞pH 7＞pH 9 and pH 4＞pH 5＞pH 6＞pH 7＞pH 9. During the experiments of adsorption dynamics, the adsorption reaction order of chitosan to 4-Chlorophenol and tetrachloroethylene may be separated as second order (k is about 1.01×10-6 ~ 3.69×10-5) and first order (k is about 0.044~0.066) under different pH values; the external mass transport coefficients of 4-Chlorophenol and tetrachloroethylene are respectively about 0.081~0.755 and 0.009~0.249; the internal porosity diffusion rate of the 4-Chlorophenol pores is approximately 2.5 times faster than that of tetrachloroethylene. Furthermore, in the experiment of the fixed bed with continuous flow, the breakthrough curve slopes of 4-Chlorophenol have a decreasing order as pH 9＞pH 7＞pH 4＞pH 5＞pH 6, and the adsorption zone saturation time of pH 4 and pH 6 is the same; the curve slopes of tetrachloroethylene have a decreasing order as pH 9＞pH 7＞pH 6＞pH 5＞pH 4 in accordance with the saturation time of the adsorption zone.

Key words: chitosan, adsorption, chlorinated organics, FTIR, and CPMAS ^{13}C NMR.

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1. Preface

The commonly seen Chlorinated Organics in wastewater include 4-Chlorophenol, trichloroethylene and tetrachloroethylene, etc. 4-Chlorophenol is a very important organic compound used in the industry, it has been widely used in the manufacturing purposes of pesticide, bactericide, preservative for woods and agricultural chemicals such as 2,4-D, 2,4,5-T, etc. [1]. For trichloroethylene and tetrachloroethylene, they have special properties such as high dissolving power, low flammability or explosive property, chemical stability, low boiling point and high vapor pressure, etc., therefore, they are widely used in many industry. Typical applications include dry-cleaning and degreasing, cleaning of metal parts and electronic components, cold cleaning, fumigants, stripper, etc., moreover, they are also used as raw materials or intermediate materials [2,3] in the processes of medicine and textile industry. Inappropriate treatment, incomplete treatment technology or accidental leak of Chlorinated Organics will all cause water source to be contaminated by such pollutants, therefore, proper treatment of wastewater of Chlorinated Organics is needed and urgent.

There are many applications of adsorption mechanisms in environmental engineering and analysis, for example, in the wastewater treatment or air pollution treatment procedures, adsorption principles are frequently used to separate the pollutants, therefore, massive amount of adsorbates are used. In recent years, targeting at different purpose and efficiency, new adsorbates are continuously developed and applied, for example: chitosan, fly ash, activated white clay and agricultural waste (rice husk, coconut shell) etc. In addition to the requirement of high adsorption property, the compatibility of adsorbate to the environment is also the development key in the future development of adsorption material.

Chitin, second to cellulose, is the second abundant natural polymer, it exists widely in the shell of crustacean and insects, after deacetylated reaction, the product of Chitin is called chitosan (chitosan) [4], it is a natural polymer, it has characteristics such as abundance, non-toxicity, , bio-compatibility, bio-decomposability, etc., meanwhile, it is porous and tough, it possesses –OH and -NH_2, its structure is as shown in figure 1, therefore, it can be used as adsorbate [5] in the wastewater treatment procedures. In environmental engineering, chitosan has been used in removing heavy metals in the wastewater [6] and the treatment of dyes, it is pointed out in many researches that chitosan has very high potential in the removing of dye [7,8,9,10], its adsorption amount to acidic negative ion dye is about 1,940~1,945 g kg^{-1}, its chromaticity removing effect can reach an effect as high as 99％ [11], meanwhile, pseudo second order dynamic model is used to describe the adsorption dynamic mechanism [12,13], however, the adsorption on chlorinated organic contaminants is rarely investigated, therefore, adsorption experiment of chitosan on chlorinated organics is preformed in this study.

The adsorbate selected by this study is a commercial chitosan (provided by Cheng-Li Corporation), its characteristics will be investigated and a series of isothermal adsorption equilibrium and adsorption dynamic experiments for 4-Chlorophenol and tetrachloroethylene will be done, finally, the related parameters in adsorption equilibrium and adsorption dynamics will be obtained.

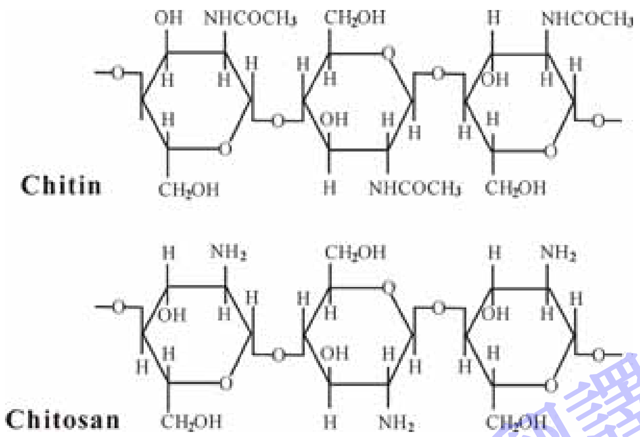

Figure 1 Structural formula of chitin and chitosan

2 Material and method

The adsorbate used in this research is a commercial chitosan (provided by Cheng-Li Corporation), it is extracted from shrimp shell, its specific surface area and deacetylation are 10.3 mg L^{-1} and 90% respectively, powders with diameters in the range 100~120 meshes are selected as adsorbates, the targeted pollutants are 4-Chlorophenol (Fluka, purity ≧98 %) and tetrachloroethylene (J.T Baker, purity ≧99%), 0.05 M sulfuric acid (PEF, purity 97%) and 0.5M sodium hydroxide (RDH, purity 98%) are used to adjuste the pH value of the water solution, normal hexane (J.T Baker, purity 95%) is used as the extracting agent.

2.1 Characteristic analysis of chitosan

This study investigates qualitatively and quantitatively the specific surface area, surface morphology, surface functional group of chitosan, in adsorption aspect, specific surface area is the major factor affecting adsorption performance; SEM, FTIR and ^{13}C NMR, etc. , are the equipments commonly used to observe the surface of adsorbate. Chitosan is highly affected by pH value of the environment, it could easily cause the characteristic change of functional group, therefore, in order to understand the functional group change in detail, the characteristic changes of chitosan under different pH values are investigated in this study.

2.1.1 The measurement of specific surface area

ASAP 2020 analyzer of Micromeritics Instrument Corporation was used to measure the specific surface area and pore size of chitosan under different pH values at 77K (-196℃) by using N_2 as the adsorption and desorption gas.

2.1.2 Scanning Electron Microscope; SEM

SEM uses the electron beam emitted from heated filament and focuses it to an optical spot of about 10 mm in size, under the action of accelerating voltage, point optical source will pass through the electronic optical system formed by electromagnetic lenses, electronic beam of a few nm in size will then be formed. Electron beams are used to scan the surface of chitosan to generate signals, detectors will receive different signals (strong and weak), then have the signals pass through magnifier, the surface morphology of chitosan can then be constructed for observation.

2.1.3 Fourier Transform Infrared spectrum analysis; FTIR

Fourier Transform Infrared spectrum analyzer (Bio-Rad FTS-7) can be used to identify the functional group types on the surface of chitosan. Infrared light is used to excite the molecule and convert it into molecular vibration energy or rotational energy. Through fast Fourier Transform, the absorption band of each molecule can then be distinguished and qualitative analysis can be achieved, moreover, if the quantitative data of NMR spectrum can be used together, functional group change of chitosan under different pH values can then be obtained. For the pre-treatment of the sample, 1 mg chitosan and 300 mg KBr are weighed first and agate grinding bowl is used to grind them into fine powder, then hydraulic machine (9,000 ~ 10,000 kg/m^2) is used to make the tablet, finally, FTIR (Nicolet 3000 NEXUS ESP) is used to analyze the surface functional groups of chitosan under different pH values, the absorption wavelength of this equipment is in the range of 400 cm^{-1} ~ 4,000 cm^{-1}.

2.1.4 CPMAS ^{13}C NMR

Chitosan powder about 0.5~1.0g is added into glass tube with inner diameter of 10 mm and height of 4cm, then put it into the superconducting magnetic field of CPMAS ^{13}C NMR (Bruker MSL-2000 NMR) to measure the functional group types and contents of chitosan under different pH values. The spectrum frequency range of the equipment is 50.33MHz, delay time is 1ms, cycle time is 1 s, Magic-Angle spinning speed is about 3.5kHz.

2.2 Isothermal adsorption equilibrium test

Test factors include concentration and pH values, 4-Chlorophenol has concentrations of 0.04 Cs, 0.06 Cs, 0.08 Cs, 0.1 Cs, 0.2 Cs, 0.3 Cs, 0.4 Cs, 0.5 Cs, respectively, wherein Cs is the saturated solubility of 4-Chlorophenol in water solution (Cs=27,000mg L^{-1}), tetrachloroethylene has concentrations of 0.05 Cs, 0.1 Cs, 0.2 Cs, 0.3 Cs, 0.4 Cs, 0.5 Cs, 0.6 Cs, 0.7 Cs, 0.8 Cs respectively, wherein Cs is the saturated solubility of tetrachloroethylene in water solution (Cs=150mg L^{-1}), the pH values of the solutions are controlled through the adding of sodium hydroxide and sulfuric acid to about 4, 5, 6, 7, 9.

Experiments are performed in batch way, first, chitosan and targeted pollutants solutions are added to glass test tube of 10 ml volume, vibration machine (Deng Yug), at a speed of 175rpm, is used for mixing and vibration for 24 hours; then the centrifugal machine (Hettich Zentrifugen EBA 12), at a rotational speed of 3,000 rpm (2.78g), is used for a centrifugal action of 20 minutes, after the centrifugal action, 1ml of upper clear solution is taken together with normal hexane of 9 ml and added to a test tube of 10 ml. Have it performed with vibration and mixing for about 10 minutes and have it stay quietly to reach a stable status, then take the abstracted normal hexane solution on the upper layer, and use gas chromatography machine/Electronic Detector (GC/ECD; Varian CP3800) to analyze the concentration of targeted pollutants, finally, isothermal adsorption equilibrium curve analysis is performed on it.

2.3 Dynamic experiment of adsorption

In the current study, fully mixing and agitating machine and continuous flow fixed bed equipments are used to perform adsorption dynamic experiments on chitosan, the testing factors include different targeted pollutants and pH values, 4-Chlorophenol and tetrachloroethylene have concentrations of 500 mg L^{-1} and 80 mg L^{-1} respectively, the pH values of the solution are controlled by adding sodium hydroxide and sulfuric acid to about 4, 5, 6, 7, 9, etc.

2.3.1 Batch contact time experiment

The fully mixing and agitating tank has a diameter of 15 ㎝ and height of 15 ㎝, the agitator vane is of Teflon material with a diameter of 8 ㎝. Within the tank body, 8 baffles are installed on the peripherals at an average spacing (as in figure 2), during the running of the experiment, 50g chitosan and prepared 2.7L targeted pollutants of certain concentration are added into the agitator tank, variable speed motor (Ika-Werke) is used to drive the vane, the agitation speed is 300 rpm, inserted layer is placed at the peripheral of the agitator tank, meanwhile, isothermal device (Julabo F30-C) is used to control the solution temperature within the agitation tank, which is remained at about 30℃. In the mean time, a sample of 5ml is taken as the initial concentration, 5ml of sample is taken according to preset time, then use normal hexane for abstraction and use GC/ECD to analyze its concentration.

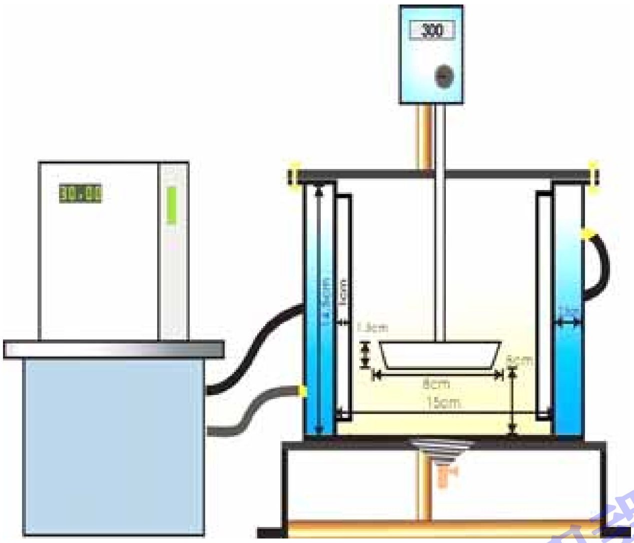

Figure 2 Adsorption dynamic apparatus for chlorinated organic pollutants

2.3.2 Continuous flow fixed bed

Fixed bed is a tube of inner diameter 2 cm (as in Figure 3), on the bottom part of the tube, silicate cotton is used as the support board which can prevent the sinking of chitosan. Fourteen grams of chitosan is added to the tube (the height of the bed is about 13.5 cm) and evenly distributed, then start the quantitative motor (Cole-Parmer 7524-40) at an input flow rate of 2ml per minute and let the targeted pollutants solution to flow upward from the bottom of the tube, in the mean time, 5ml of sample is taken as the initial concentration, then take a sample of 5ml according to a preset time and use normal hexane to abstract and use GC/ECD to analyze the concentration.

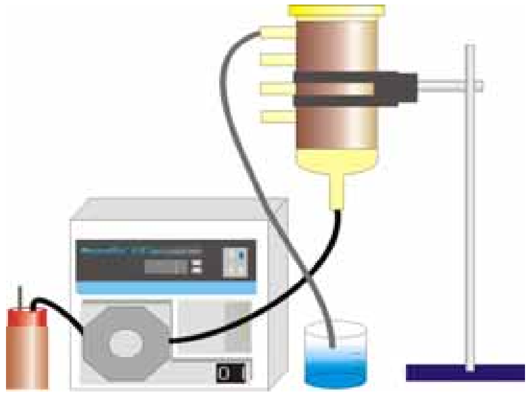

Figure 3 Adsorption dynamic apparatus for chlorinated organic pollutants

3. Results and discussion

3.1 The characteristics of chitosan

Chitosan is highly affected by the pH value of the environment which might lead to characteristic change, therefore, specific surface area, scanning electron microscope, FTIR and CPMAS ^{13}C NMR are used and the adsorption equilibrium and dynamic change are investigated through characteristic analysis.

3.1.1 Specific surface area analysis

Table 1 shows the specific surface area and average pore size distribution of chitosan under the treatment of solutions of different pH values, wherein the one with pH 4 has largest specific surface area and average pore size, they are respectively 19.7m^{2}g^{-1} and 69.1Å, the one with pH 9 has minimum specific surface area and average pore size, they are 10.5m^2 g^{-1} and 69.1Å respectively, from the table we know that the lower the pH value of chitosan, the larger the specific surface area, we think that this might be due to gradual dissolution of chitosan to gel [13] when pH value is smaller than 5.5, which in turn leads to the dissolution of the surface of chitosan and the formation of more small pores and the corresponding increase of specific surface area.

Table 1 The specific surface area and pore size distribution of chitosan under different pH values

	specific surface area (m^2/g)	average pore size (Å)
pH 4	19.7	69.1
pH 5	15.6	68.3
pH 6	10.8	67.8
pH 7	10.3	67.5
pH 9	10.5	69.1

3.1.2 Surface morphology analysis of scanning electron microscope

Scanning electron microscope is highly applicable to the observation of the surface morphology of object, it has capability to display stereo image in three dimensions and the function of depth of focus, in this study, this function is used to observe the pore size change of chitosanat at different pH values. Figure 4 to Figure 7 shows chitosan magnified to 10,000 times at pH 4, we find that under pH 4, new pores appear on chitosan, but there are no apparent pores on the surface of chitosan at pH 7 and pH 9, in the mean time, the number of pores on chitosan at pH 6 is apparently smaller than that at pH 4. From the observation of scanning electron microscope, the data that specific surface area get increased as the lowering of pH values is thus verified.

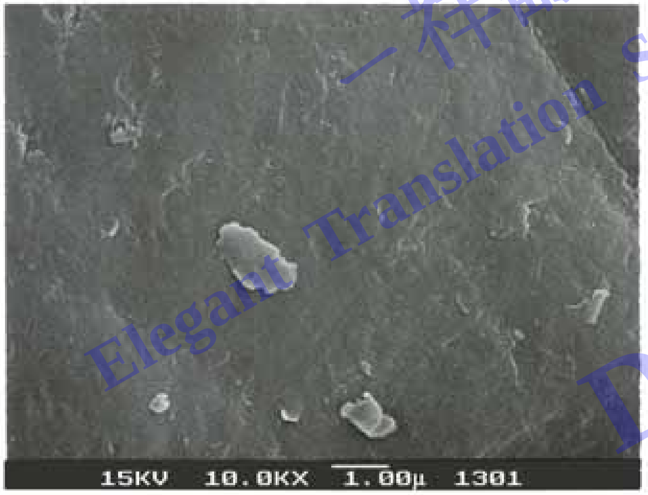

Figure 4 The surface morphology of chitosan with pH value not adjusted (pH 7)

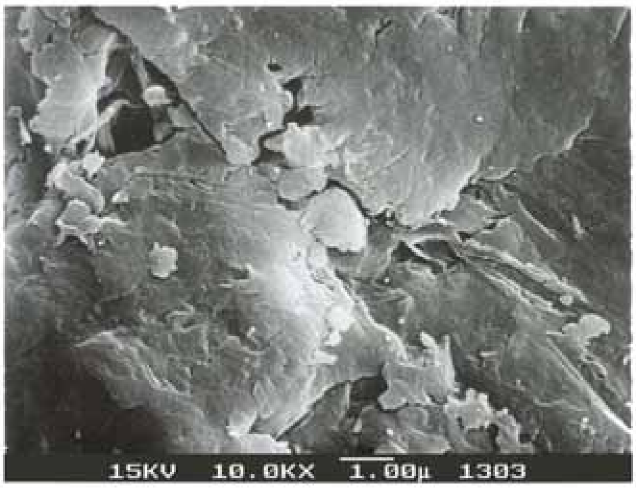

Figure 5 The surface morphology of chitosan at pH 4.

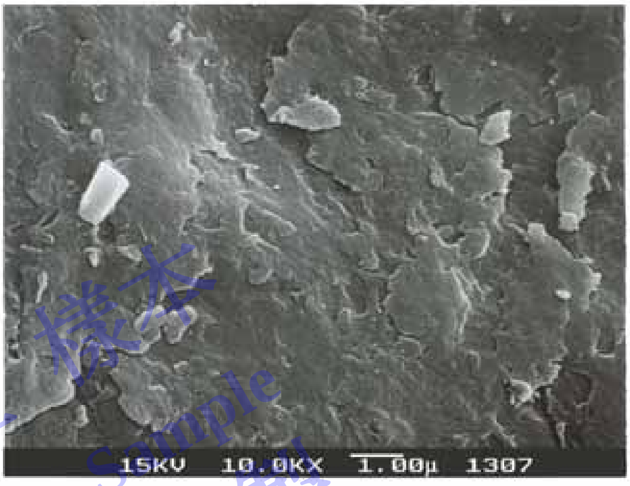

Figure 6 The surface morphology of chitosan at pH 6.

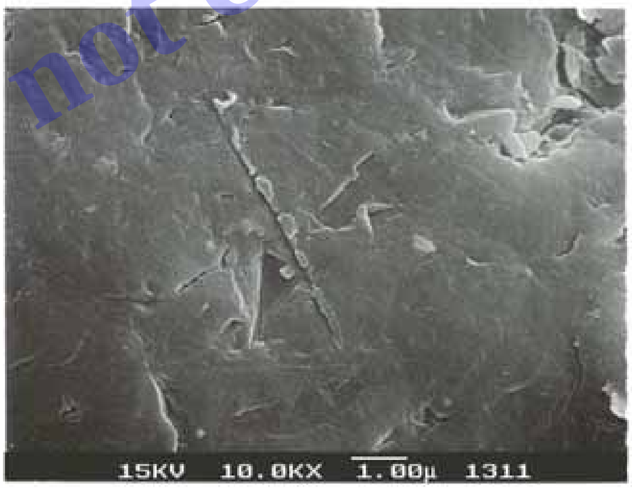

Figure 7 The surface morphology of chitosan with pH 9

3.1.3 FTIR analysis

In order to investigate the effect on chitosan at different pH values, FTIR is used to analyze the functional group change of chitosan at different pH value, this is as shown in figure 8, A, B, C, D, E represent respectively the spectrum of chitosan at original status and at pH 4, pH 5, pH 7 and pH 9, from the spectrum, we know that chitosan possesses OH or N-H (at 3430 and 3433 cm^{-1}), meanwhile,

CH,CH_2,CH_3 branch chains are contained in the aromatic ring (at 2923 and 2924 cm^{-1}), C=C of aromatic compound is also contained too (1659 and 1596 cm^{-1}), functional group of aliphatic group (1424 and 1382 cm^{-1}), functional group of alcohol and hydrocarbon compound (1154 and 1083 cm^{-1}) are all contained. If we compare the FTIR analysis results with the chitosan functional groups mentioned in the literature, we find that the structure of chitosan in this study has a structure very similar to that in the literature, all the OH, NH_2, alcohol and hydrocarbon compound functional groups are contained. Additionally, from figure 8, we know that the strengths of all the absorption bands of chitosan do not have obvious change as the change in pH values, therefore, we know that pH value does not produce change on the chemical structure of chitosan. If CPMAS ^{13}C NMR spectrum is used together, we can observe further more detailed change on the functional group on the surface of chitosan.

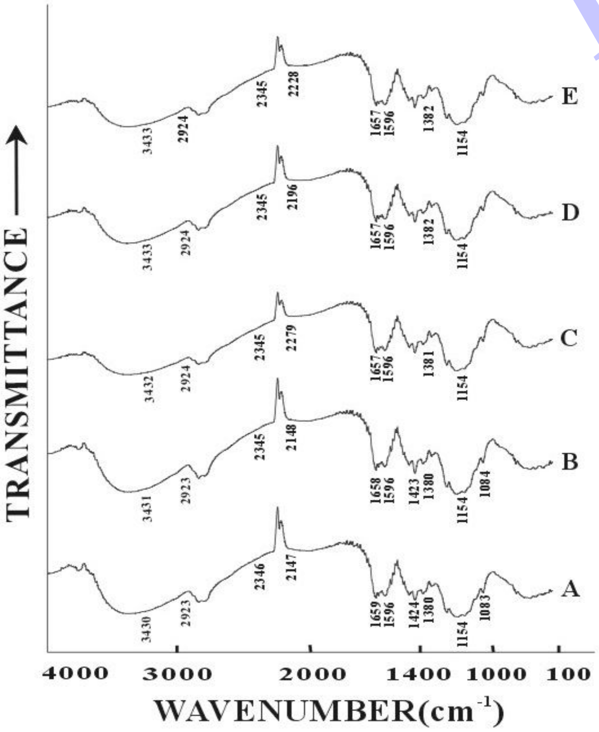

Figure 8 The IR spectra of chitosan at different pH values

3.1.3 CPMAS ^{13}C NMR spectrum analysis

Figure 9 is the CPMAS ^{13}C NMR spectrum of chitosan at different ph values, wherein A, B, C, D, E, F represent respectively the chitosan spectra at original status and at pH 4, pH 5, pH 6, pH 7 and pH 9. Its chemical shift is divided by the models proposed by scholars such as Perminova [18], the divisional scope is as shown in table 2, chemical shift can be divided into 5 zones such as 0~50 (alkyl carbon), 50~90 (hydrocarbon compounds such as alcohol, ether or fat), 90~110 (aldehyde carbon), 110~160 (Aromatic group carbon) and 160~190 (carboxyl group carbon) ppm. Computer is used to perform respective integration on the 5 divided spectrum zones of figure 9, the percentage content of each carbon out of the overall can then be calculated, this is as shown in table 2. From table 2 we know that the carbon content of aliphatic group and aromatic group has only tiny reduction along with the increase in pH value, the data shows that the carbon contents of aliphatic group and aromatic group are reduced from 96.3 and 2.4 (pH 4) respectively to 94.9 and 1.9 (pH 9); this result concludes that pH value has only tiny effect on thefuncitonal group content of chitosan.

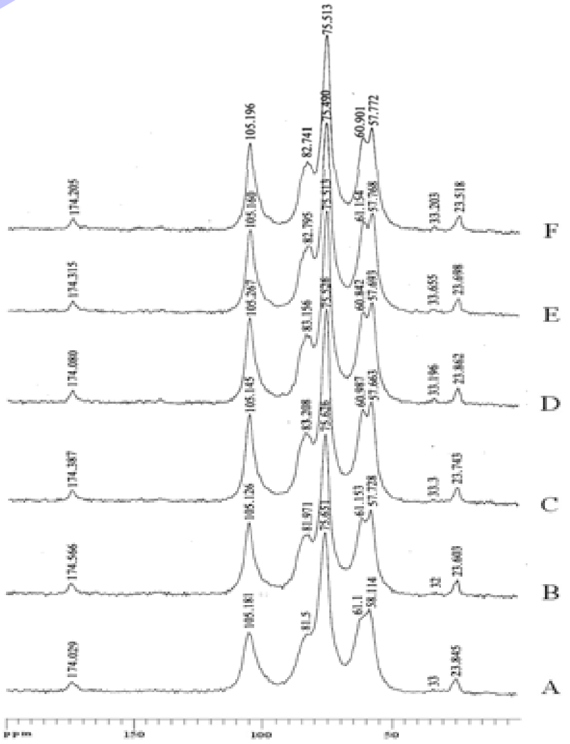

Figure 9 NMR is used to analyze the functional group of chitosan at different pH values.

Table 2 The carbon distribution percentage of chitosan in CPMAS ^{13}C NMR spectrum

Chemical shift	Original	pH 4	pH 5	pH 6	pH 7	pH 9
	%					
ppm						
0~50	5.3	4.0	4.5	4.7	5.1	4.3
50~90	74.2	75.3	73.9	73.9	73.8	73.9
90~110	15.9	17.0	17.0	16.5	16.2	16.7
110~160	2.2	1.9	2.3	2.4	2.3	2.4
160~190	2.4	1.8	2.3	2.5	2.6	2.7
Aliphatic group[a]	95.4	96.3	95.4	95.1	95.1	94.9
Aromatic group[b]	2.2	2.4	2.3	2.2	2.1	1.9
(a/b)	43.3	50.7	41.5	39.6	41.3	39.5
Aromaticity	0.02	0.02	0.02	0.02	0.02	0.02

[a] Aliphatic group is the chemical shift sum of 0~50, 50~90 and 90~110 ppm.

[b] 110~160 ppm is the chemical shift range of aromatic group carbon.

3.2 Isothermal adsorption equilibrium

Chitosan stays in targeted pollutant solution for vibration of 24 hours to reach equilibrium, the equilibrium concentration of targeted pollutant solution is then analyzed C_e(mg/l) and the adsorption capacity q_e(mg/kg) is calculated, this is as shown in equation 1.

$$q_e = \frac{(C_o - C_e) \times V}{W} \qquad (1)$$

q_e : Adsorption amount in equilibrium (mg/kg)

C_o : The initial concentration of targeted pollutant solution (mg/l)

C_e : The equilibrium concentration of targeted pollutant solution (mg/l)

V : The volume of targeted pollutant solution (l)

W : The weight of chitosan (kg)

Figure 10 and figure 11 are the isothermal equilibrium adsorption curves respectively of 4-Chlorophenol and tetrachloroethylene at different pH values; it seems like that the adsorption behavior of 4-Chlorophenol and tetrachloroethylene in the figure by chitosan can be described by isothermal equilibrium adsorption model of Langmuir (R^2 values are 0.898~0.907 and 0.898~0.940 respectively).

$$q_e = \frac{QbC_e}{1 + bC_e} \qquad (2)$$

wherein q_e: is the adsorption amount adsorbed by unit chitosan (mg/kg), Q: is the maximum adsorption amount adsorbed by unit chitosan (mg/kg), C_e: is the equilibrium concentration of targeted pollutant solution (mg/l), b: Langmuir constant.

From the adsorption in figure 10, we know that the adsorption capacity will increase with the increase in equilibrium concentration, the adsorption amount of 4-Chlorophenol are in the order of pH 6＞pH 4＞pH 7＞pH 9; if we take a look at the dissociation constant of 4-Chlorophenol (pk_a=9.2), since 4-Chlorophenol more likely to exist in the molecular state when pH is getting smaller, and since the surface of chitosan are mostly positive charges, therefore, the existence of more molecular states will lead to an adsorption amount by chitosan in the order of pH 9＞pH 7＞pH 6＞pH 4. Moreover, the literature also mentions that different pH values might change the functional groups of chitosan. Under smaller pH values, $-NH_2$ group might obtain more hydrogen ion to form ammonium group of positive charge ($-NH_3^+$)[13], therefore, under pH 4, chitosan will carry more positive charges which might be able to attract more 4-Chlorophenol of negative charges, therefore, the adsorption strength should be in the order of pH 4＞pH 6＞pH 7＞pH 9, from the above descriptions, we know that when pH 9, although 4-Chlorophenol carry more negative charges, chitosan only carries small amount of positive charges, therefore, under the conditions of different pH values, the electrostatic attraction between the positive charge and negative charge of chitosan and 4-Chlorophenol will reach certain degree of equilibrium, therefore, the adsorption amount does not change as the pH changes and show a consistent order of magnitude.

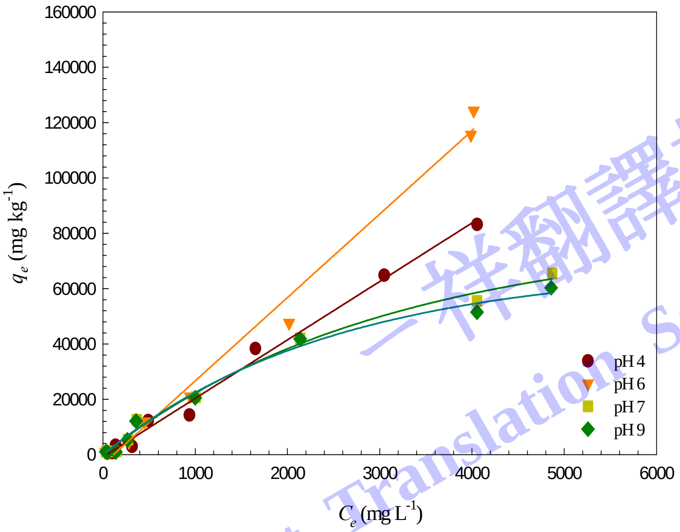

Figure 10 Isothermal adsorption of chitosan on 4-Chlorophenol at different pH values

Figure 11 is the isothermal adsorption equilibrium curve of tetrachloroethylene at different pH values, from the adsorption curve we know that adsorption capacity approaches a fixed value as the increase in equilibrium concentration, the amounts of adsorbing tetrachloroethylene are in the order of pH 4＞pH 5＞pH 6＞pH 7＞pH 9, we estimate that this might be due to larger pore of chitosan at pH 4, tetrachloroethylene can enter the pores more easily and higher adsorption amount is thus obtained. The adsorption behavior of tetrachloroethylene by chitosan can also be described by the isothermal equilibrium model of Langmuir. The simulation parameters of adsorption by chitosan on 4-Chlorophenol and tetrachloroethylene are listed respectively in table 3. Langmuir simulates experimental b values of 4-Chlorophenol and tetrachloroethylene, they are respectively in the range of 0.00003~0.00012 and 0.00001~0.00007, since *b* values are constants related to the bond energies of adsorption, this describes that under different pH values , chitosan will have different bond energies of adsorption on 4-Chlorophenol and tetrachloroethylene.

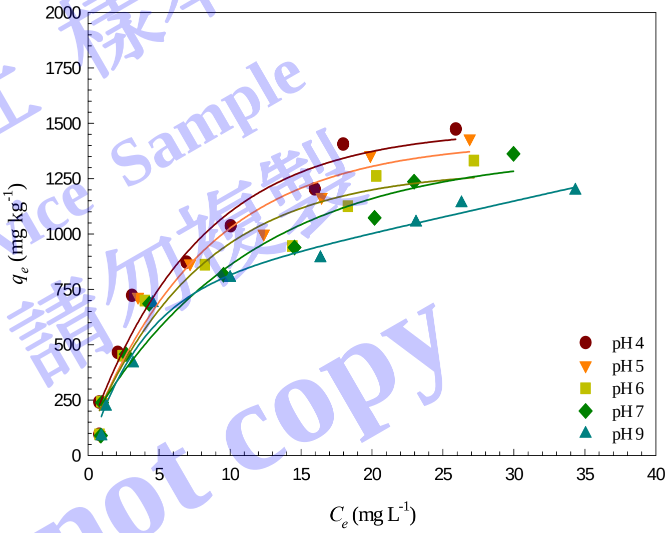

Figure 11 Isothermal adsorption of chitosan on tetrachloroethylene at different pH values.

Table 3 Langmuir parameters of chitosan adsorbing 4-Chlorophenol and tetrachloroethylene at different pH values.

adsorbate	Langmuir		
	Q (mg/kg)	b	R^2
4-Chlorophenol			
pH 4	79,855	0.00007	0.898
pH 6	999,997	0.00012	0.902
pH 7	333,333	0.00004	0.907
pH 9	328,591	0.00003	0.899
tetrachloroethylene			
pH 4	2,700	0.00007	0.898
pH 5	2,500	0.00003	0.905
pH 6	2,000	0.00001	0.902
pH 7	1,666	0.00006	0.907
pH 9	1,428	0.00007	0.940

3.3 Adsorption dynamics

Based on the adsorption dynamic result, we try to investigate the dynamic phenomenon of adsorption of 4-Chlorophenol and tetrachloroethylene by chitosan, these include: the reaction order of adsorption, mass transport coefficients of external surface and diffusion rate within the pores.

3.3.1 Order of reaction

1. First-order reaction

Reaction rate is proportional to the concentration of pollutant within the solution.

$$\ln C_t = \ln C_o - kt \qquad (3)$$

C_t is the pollutant concentration within unit time (mg L^{-1}), C_o is the initial pollutant concentration (mg L^{-1}), k is the reaction rate constant (min^{-1}), t is the time (min). If the data of adsorption test follows first order reaction, a regression straight line will be obtained in a plot of lnC_t versus t, from the slope of this line we can obtain the rate constant k of the first order reaction.

2. Second-order reaction

Reaction rate is proportional to square of concentration of pollutant in the solution.

$$\frac{1}{C_t} = \frac{1}{C_o} + kt \qquad (4)$$

If the adsorption test data follows second order reaction, a regression straight line can be obtained in a plot of 1 / C_t versus t, and the slope of this line can be used to get the rate constant k of the second order reaction.

The relationship of solution concentration change for 4-Chlorophenol and tetrachloroethylene versus time in the agitator tank can be represented respectively in figure 12 and figure 13, the concentration reduction speed of C_t/C_o in the figure has the highest value in the beginning time, however, the speed gets smaller as time gets increased, adsorption of 4-Chlorophenol and tetrachloroethylene reaches saturation at about 90 and 20 minutes respectively. Therefore, the main purpose of this study is to investigate the rate constant before adsorption equilibrium (saturation), from the relationship diagram, we can obtain a regression curve, the rate constants k and R^2 obtained from regression curve are summarized in table 4, which shows the dynamic parameters of the adsorption of 4-Chlorophenol and tetrachloroethylene by chitosan under different pH values. We know from the table that the adsorption of 4-Chlorophenol seems to be a second order reaction, and the k value (3.699×10^{-5}) at pH 6 is larger than the k value (1.011×10^{-6}) at pH 9, this explains that pH 6 has a larger reaction rate; additionally, adsorption of tetrachloroethylene is a first order reaction, its k value is in the order of pH 4 ＝pH 5＞pH 6＞pH 7＞pH 9, from the above we know that pH 4 has the fastest rate constant.

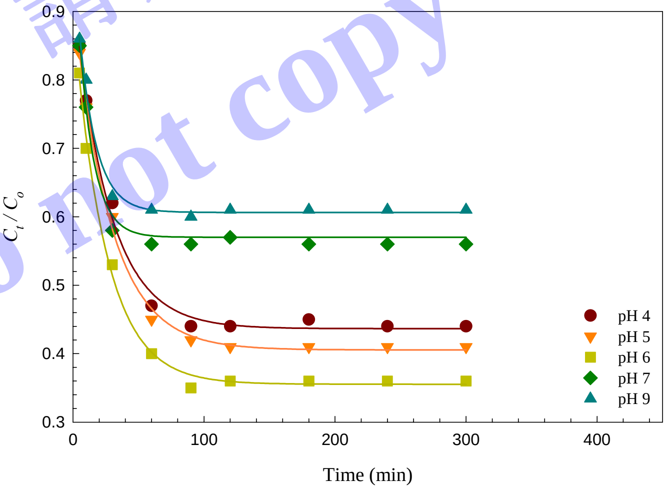

Figure 12 The relationship diagram of the adsorption of 4-Chlorophenol by chitosan versus contact time under different pH values

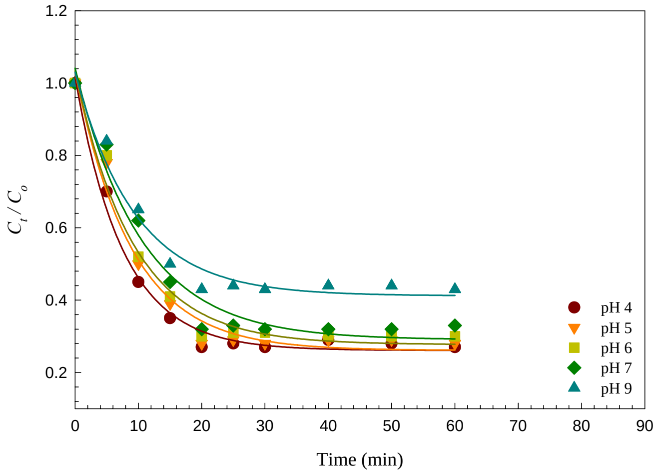

Figure 13 The relationship diagream of the adsorption of tetrachloroethylene by chitosan versus time under different pH values

Table 4 The dynamic parameters of the adsorption of 4-Chlorophenol and tetrachloroethylene by chitosan under different pH values

Parameters	First-order Kinetic		Second-order Kinetic	
	k	R^2	k	R^2
4-Chlorophenol				
pH 4	0.0078	0.930	2.567E-5	0.982
pH 5	0.0083	0.928	2.882E-5	0.969
pH 6	0.0050	0.899	3.699E-5	0.963
pH 7	0.0046	0.831	5.546E-6	0.901
pH 9	0.0047	0.801	1.011E-6	0.909
tetrachloroethylene				
pH 4	0.066	0.986	0.002	0.979
pH 5	0.065	0.993	0.002	0.981
pH 6	0.061	0.991	0.002	0.967
pH 7	0.058	0.989	0.002	0.987
pH 9	0.044	0.991	0.001	0.983

3.3.2 External mass transport coefficient

The mass transport of adsorption material on the external surface of adsorbate is as shown in equation 5 [14]:

$$\left[\frac{d\left(C_t/C_o\right)}{dt}\right]_{t=0} = -k_s S_m \qquad (5)$$

C_t is the solution concentration of unit time (mg L^{-1}), C_o is the initial concentration of unit time (mg L^{-1}), k_s is the mass transport coefficient of external surface (m s^{-1}), s_m is the particulate external surface area of adsorbate of unit solution volume (m^{-1}). Plot C_t/C_o versus t (time), then read C_t/C_o values at each different time points from the linear regression line, then use forward differential to calculate first order derivative value at $t = 0$, we can then obtain k_sS_m value; S_m can be obtained from equation 6 (the particulate external surface area of adsorbate in the solution), substitute the S_m value into equation 2-4, we can then calculate k_s (mass transport coefficient of external surface).

$$S_m = \frac{6M_m}{d_p \rho_p} \qquad (6)$$

M_m is the mass of adsorbate of unit solution (kg m^{-3}), d_p is the average particulate size (μm), ρ_p is the volume density of adsorbate (kg m^{-3}).

In figure 12 and 13 where C_t/C_o is plotted versus t, the mass transport coefficient of external surface is listed in table 5. When this result is compared to the literature of dye adsorption by chitosan [14], we find that the external surface mass transport coefficient k_s in this test is much larger than the literature value (1.374×10^{-5} m s^{-1}), we guess that the molecular weights of 4-Chlorophenol and tetrachloroethylene used in this test are of 128.56 and 165.9 g moL^{-1} respectively, they are obviously smaller as compared to that of dye (350.3~622.6 g moL^{-1})[19], therefore, the external surface mass transport coefficient k_s obtained in this study is larger than the literature value.

We know from the above that the molecular weight of chlorinated organics is smaller and lighter than that of dye, therefore, the external mass transport speed will be faster than that of dye, if we compare 4-Chlorophenol and tetrachloroethylene, since 4-Chlorophenol has a smaller molecular weight than that of tetrachloroethylene, therefore, it has a faster external mass transport speed than that of tetrachloroethylene.

Table 5 The external mass transport coefficient of the adsorption of 4-Chlorophenol and tetrachloroethylene by chitosan under different pH values.

pH	4-chlorophenol	tetrachloroethylene
	k_s(m/s)	k_s(m/s)
pH 4	0.579	0.009
pH 5	0.755	0.249
pH 6	0.196	0.285
pH 7	0.559	0.018

pH 9	0.081	0.081

3.3.3 Diffusion rate parameter within the pore

When concentration gradient diffuses only in single direction along x axis, we can then use the basic differential equation of Fick`s second law to set individual boundary conditions and to solve this diffusion equation, however, the process is very complicated, therefore, some scholars take the square root of time ($t^{1/2}$) to describe the pore diffusion behavior inside the particulate and to obtain rate constant k_p,, the diffusion behavior can then be judged by k_p value [16], this is as shown in figure 7:

$$q_t = k_d t^{1/2} \qquad (7)$$

q_e is the adsorption amount of unit time (mg kg^{-1}), k_d is diffusion constant within the particulate (mg/kg min$^{1/2}$), t is time (min). Take a plot of q_t versus $t^{1/2}$, we can obtain a regression straight line, the diffusion constant k_d within the particulate can be obtained from the slope, from k_d value, we can judge the internal diffusion behavior of adsorption material within adsorbate.

As shown in figure 14 and figure 15, three steps can be divided in the figure, the first step is called momentary adsorption step, the adsorption in this step mainly comes from the external surface of adsorbate and some of the surfaces of macropore, since the diffusion rate in this step is very fast, therefore, its diffusion rate in this step can not be accurately calculated, based on the above reasons, this study does not investigate the diffusion rate in the first step; the second step (k_p, 2) is called asymptotic adsorption step, in this step, adsorption material undergoes internal diffusion within the macropore of adsorbate. The third step (k_p, 3) is called the last equilibrium step, it is mainly based on the internal diffusion within micropore.

For 4-Chlorophenol, its first step occurs within 5 minutes (that is, $t^{1/2}$ is 2.24); the second step is from 5 minutes to 60 minutes ($t^{1/2}$ is from 2.24 to 7.75), the third step is from 60 minutes to 300 minutes ($t^{1/2}$ is from 7.75 to 17.32); for tetrachloroethylene, its first step occurs within 5 minutes (that is, $t^{1/2}$ is 2.24); the second step is from 5 minutes to 20 minutes ($t^{1/2}$ is from 2.24 to 4.47), the third step is from 20 minutes to 60 minutes ($t^{1/2}$ if from 4.47 to 7.75), in this step, the relationship between adsorption amount and time is listed in table 6, it is the internal pore diffusion rate parameters of 4-Chlorophenol and tetrachloroethylene in chitosan under different pH values, from the table we know that, in the second step (k_p, 2), 4-Chlorophenol has a diffusion rate 2.5 times faster than that of tetrachloroethylene, the major reason is that 4-Chlorophenol has a smaller molecular weight than that of tetrachloroethylene, it also has higher probability and faster speed to enter the pore.

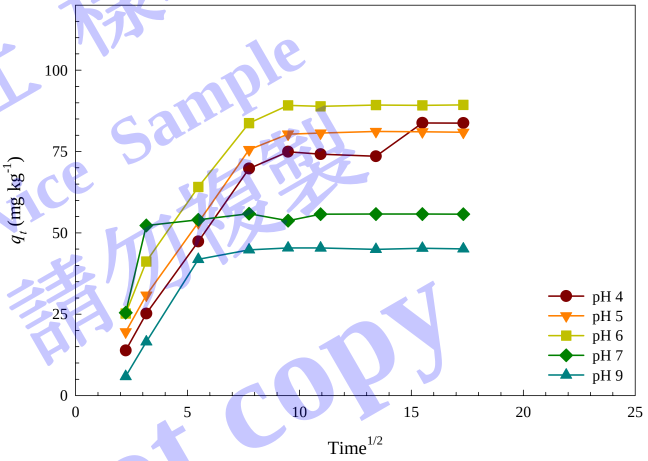

Figure 14 The relationship between internal pore diffusion speed and time for the adsorption of 4-Chlorophenol by chitosan under different pH values

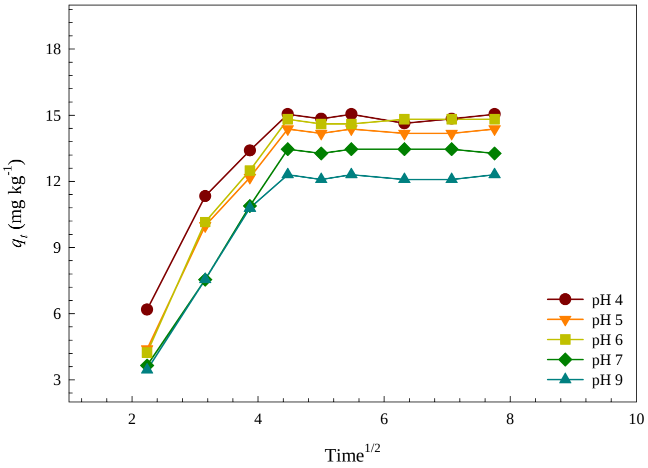

Figure 15 The relationship between internal pore diffusion speed and time for the adsorption of tetrachloroethylene by chitosan under different pH values

Table 6 The internal pore diffusion speed for the adsorption of 4-Chlorophenol and tetrachloroethylene by chitosan under different pH values

pH	4-chlorophenol		tetrachloroethylene	
	k_p,2 (mg/kg min $^{1/2}$)	k_p,3	k_p,2 (mg/kg min $^{1/2}$)	k_p,3
pH 4	10.0129	1.568	3.942	1.4100
pH 5	10.0377	1.777	4.406	0.4149
pH 6	10.3245	1.909	4.672	0.3968
pH 7	4.2210	1.747	4.427	0.0816
pH 9	7.3140	1.573	4.406	0.0094

4 Continuous flow fixed bed

Figure 16 and figure 17 represent respectively the relationship between concentration change and time for 4-Chlorophenol and tetrachloroethylene. From figure 16 and figure 17 we know that the penetration curve of 4-Chlorophenol takes 100 minutes to reach saturation and the saturation time of tetrachloroethylene is shorter than that of 4-Chlorophenol, it is about 30 minutes, moreover, the slope of the curve changes along the change in pH values, the slope of curve in figure 16 has the order of pH 9>pH 7>pH 4>pH 5>pH 6; and the curve of slope in figure 17 has the order of pH 9>pH 7>pH 6>pH 5>pH 4. Based on the view point of adsorption, we know that chitosan of pH 9 has lower equilibrium adsorption amount than that at pH 7, pH 6, pH 5 and pH 4, this means that chitosan at pH 9 has lower adsorption amount for unit weight of gram on 4-Chlorophenol and tetrachloroethylene than those at other pH values, therefore, under the same bed height, the slopes of the penetration curves of 4-Chlorophenol and tetrachloroethylene thus increase. The reason for the larger slope might be because that the pore size of chitosan becomes smaller as the pH value gets higher, 4-Chlorophenol thus can not be fully adsorbed in the pore and reach saturation in very short time, therefore, the rising part of the penetration curve becomes sharper along with the rising in the pH values.

Michaels proposes adsorption amount equation in fixed bed, to calculate the adsorption capacity of fixed bed, the equation is represented as in 3-21 [20]:

$$S_{\max} = C_o \left(V_E - V_B \right)$$

$S_{\max}$: The maximum adsorption amount of fixed bed (mg g^{-1}), C_o: the initial concentration of adsorption material (mg L^{-1}), $V_E - V_B$: The processed wastewater volume (ml) between penetration and saturation.

Table 7 The adsorption amount of chitosan fixed bed on 4-Chlorophenol and tetrachloroethylene under different pH values, from the table we know that 4-Chlorophenol has the maximum adsorption at pH of 6 (1,415 mg kg^{-1}), we guess the reason might be because that at pH 6, chitosan has positive charge and negative charge equilibrium between amino group and chlorine ion, this leads to higher adsorption amount than those at different pH values; tetrachloroethylene has the maximum adsorption amount at pH 4 (524 mg kg^{-1}), we guess that this might be because that chitosan at pH4, has higher specific surface area, which leads to obvious increase in the adsorption amount.

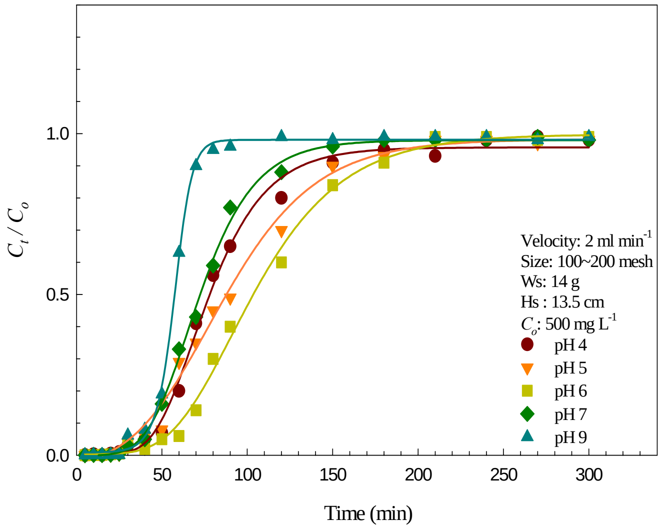

Figure 16 The penetration of chitosan on 4-Chlorophenol at different pH values.

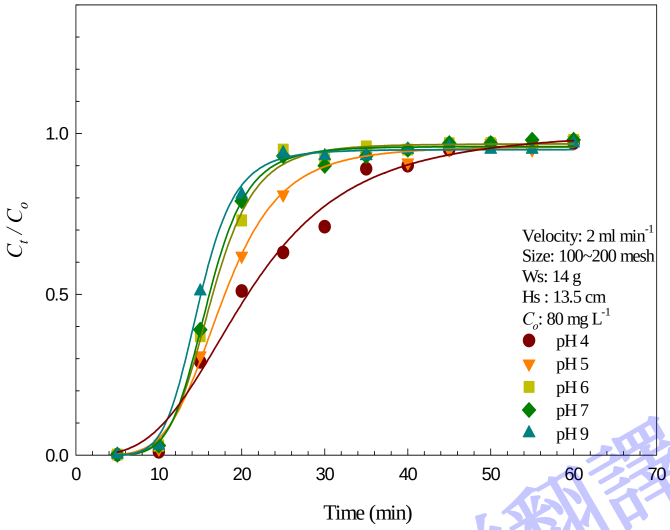

Figure 17 The penetration curve of chitosan on tetrachloroethylene at different pH values.

Table 7 The adsorption amount of chitosan fixed bed at different pH values.

pH	4-chlorophenol	tetrachloroethylene
	$S_{\max}$(mg kg^{-1})	$S_{\max}$(mg kg^{-1})
pH 4	1,415	524
pH 5	1,229	502
pH 6	1,481	457
pH 7	1,088	436
pH 9	1,073	414

4. Conclusion

This article focuses on the study of characteristics and adsorption of chitosan under the treatment of solutions of different pH values, we obtain the following four conclusions:

1. For the characteristics of chitosan at different pH values, we know that pH value will affect the specific surface area and pore structure of chitosan, the smaller the pH value, the larger the specific surface area. Additionally, after the analysis of FTIR and ^{13}C NMR, we know that different pH values do not have obvious change to the functional group of chitosan.
2. The adsorption amount of 4-Chlorophenol by chitosan at different pH values are in the order of pH 6＞pH 4＞pH 7＞pH 9, we guess that this might be because that the electrostatic attraction force between positive and negative charge of chitosan at pH 4 and pH 9 is smaller than that at pH 6.
3. The adsorption amount of tetrachloroethylene by chitosan at different pH values are in the order of pH 4＞pH 5＞pH 6＞pH 7＞pH 9, we think this might be because chitosan has larger specific surface area at pH 4, which in turn leads to higher adsorption amount.
4. The adsorption of 4-Chlorophenol and tetrachloroethylene by chitosan seems to be able to be represented by Langmuir isothermal adsorption model. The Langmuir constant *b* values of 4-Chlorophenol and tetrachloroethylene under different pH values, are 0.00003~0.00012 and 0.00001~0.00007 respectively, this means that the adsorption bond energies of 4-Chlorophenol and tetrachloroethylene by chitosan are different.
5. In the full mixing and agitating tank experiment, we find that the reaction order of the adsorption of 4-Chlorophenol and tetrachloroethylene by chitosan are respectively of second order (R^2 value 0.901~0.982) and first order (R^2 value 0.811~0.944); the external mass transport coefficient of 4-Chlorophenol and tetrachloroethylene are respectively of 0.081~0.755 and 0.009~0.249, we guess that this might be due to the smaller molecular weight of 4-Chlorophenol, which leads to a faster external mass transport, the internal pore diffusion rate of 4-Chlorophenol is about 2.5 times that of tetrachloroethylene.
6. In the continuous fixed bed experiment, the slopes of penetration curves of 4-Chlorophenol have the order of pH 9＞pH 7＞pH 4＞pH 5＞pH 6; the slope of the curve of tetrachloroethylene has the order of pH 9＞pH 7＞pH 6＞pH 5＞pH 4; this is consistent with the

saturation time in the adsorption zone.

5. Acknowledgment

This study is supported by the project research fund of National Science Council, we world like to express our acknowledgment.

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