Removal of Cu (II) ion from Aqueous Solution by Chitosan (Shrimp Shell)

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Abstract

This research is concerned with adsorption of Cu (II) ion by chitosan. Chitosan is one of the most studied polysaccharides and abundant after cellulose. It is also a fine chemical used to absorb fat from body, heavy metal adsorbent, medicine, cosmetic and agriculture. Chitosan was prepared from the shrimp shell waste. Shrimp shells were collected from the Taung Goke Market, Rakhine State. These shell wastes were potential to be used as raw material for chitosan source. The chitin contained in these shells could be isolated through the deproteination and demineralization processes. These chitins were converted into the chitosan through the deacetylation process. The obtained chitosan was characterized by degree of deacetylation, FT-IR technique and SEM technique. These were used where the adsorption of Cu (II) ion successively. In the case of adsorption, the different amount of samples and various time effect were used. The two isotherms (Langmuir and Freundlich) are used to find the dose and contact time effects in this research. From the determined results, it is found out that the DD% of chitosan was found to be 99.4 %. The value of dimensionless constant separation factor (R_L) between the range of 0 and 1.

Keywords; adsorption, DD%, chitin, chitosan, isotherms

INTRODUCTION

In environment science, the electropositive metals with a density greater than 5 gcm^{-3} are termed as "Heavy Metals" (Nevel,1980). Heavy metals such as copper, cadmium, mercury and lead are found in wastewater from mining, smelting, manufacturing agriculture or waste disposal technologies (Ayranci and Conway,2001). These heavy metals are not biodegradable and their presence in streams and lakes to ions in living organisms and causing health problems in animals, plants and human beings (Srlnlvas, et.al.,2013).

Copper and its compounds are widely distributed in nature, and this element is found frequently in surface water and in some ground water. Its density is 8.92 gcm^{-3}. Copper is an essential and beneficial element in human metabolism and is generally considered non-toxic expect at high doses. Copper contributes to corrosion of aluminum and zinc and also imparts an undesirable bitter taste to water. Excessive human intake of Cu leads to severe mucosal irritation and corrosion widespread capillary damage, hepatic and renal damage, central nervous system irritation followed by depression. The aesthetic objective for copper in drinking water is set data maximum of 1.0 mg/L (Srlnlvas,et.al.,2013). The World Health Organization (WHO) recommended that the maximum acceptable concentration of Cu (II) in drinking water is 1.5 mg/L. For this reason, the discharge of industrial effluents containing Cu (II) must be stringently regulated in order to reduce environmental pollution. In this research, the Cu (II) ion is removed by adsorption techniques with chitosan.

Chitosan is one of the most studied polysaccharide nowadays. It is the most abundant after cellulose. It is the component of the crustacean. It contains 20-40 % protein, 20-50 % calcium carbonate and 15-40 % chitin. It is also a fine chemical used to absorb fat from body, heavy metal adsorbent, medicine, cosmetic and agriculture. A white hard polysaccharide

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chitin, which known as 2-acetamido-2-deoxy-D-gluco-pyranose units through (1-4) linkage, is extracted from crustacean's exoskeleton (Mike and Blackwell,1987), (Austin et.al.,1989).

Chitosan is obtained from the chitin through the alkaline deacetylation process. Since, it is non-toxic and presents excellent biological properties such as biodegradation in the human body, immunological, antibacterial, and wound-healing activity (Synoweicki and Al-Khateeb, 2003), (JayaKumar et.al.,2005), as shown in Scheme 1. Chitin can be also formed in the skeleton of crab, shrimp, and lobster, as well as in the exoskeleton of marine zooplankton spp., including coral and jellyfishes (Shahidi and Abuzaytoun, 2005). And also, it can be extracted from various sources to be converted through deacetylation process by using sodium hydroxide (NaOH). The obtained chitosan from the chitin through the deacetylation process which is formed by repeating units of beta (1-4) 2-amino-2-deoxy-D-glucose or D-gulcosamine.

Adsorption on solid- solution interface is an important means for controlling the extent of pollution due to heavy metal ions. Among these heavy metal ions, studied included Cu.

Adsorption is usually described through isotherms, that is, functions which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid). One can find in literature several models describing process of adsorption, namely Freundlich isotherm, Langmuir isotherm, BET isotherm, etc. (Kopecky, et.al.,1996).

The aim of the present study is the preparation of chitosan by using shrimp shell waste from Taung Goke Township to use it as a key material for the application such as the removal of heavy metal (Cu (II) ion).
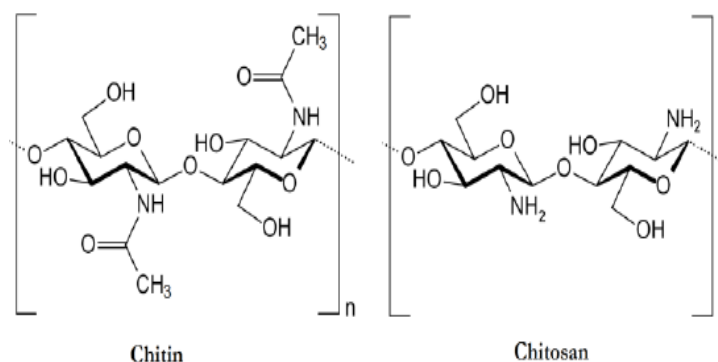
Scheme 1. Chemical structures of chitin and chitosan

MATERIALS AND METHODS

Materials

Raw shrimps with large size were purchased from Taung Goke market, Taung GokeTownship, Rakhine State. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were then diluted to the concentration required for the methodology with distilled water. All chemicals were used without further purification. All specific chemicals used are described in detail in each experimental section.

A stock solution of 0. 1 % for copper (II) sulphate was prepared 1g of copper (II) sulphate by dissolving in 1 L of distilled water.

Instruments employed in this work consists of lab ware, glassware and other supporting facilities. The following are some of the instruments used in this research.

-Balance (SHIMADZU ATX 224)

-Magnetic stirrer (JISCO)

- UV-Vis Spectrophotometer (Spectro UV-2550)

Methods (Extraction of Chitosan)

The extraction of chitosan can be carried out by the following processes after removing the loose tissue from the shrimp shells then washed, dried and grind to obtain dry powder. The main procedure for obtaining chitosan is based on the alkaline deacetylation of chitin with strong alkaline solution with different concentrations. The investigation was conducted in three steps are illustrated in Figure 1, as follows;
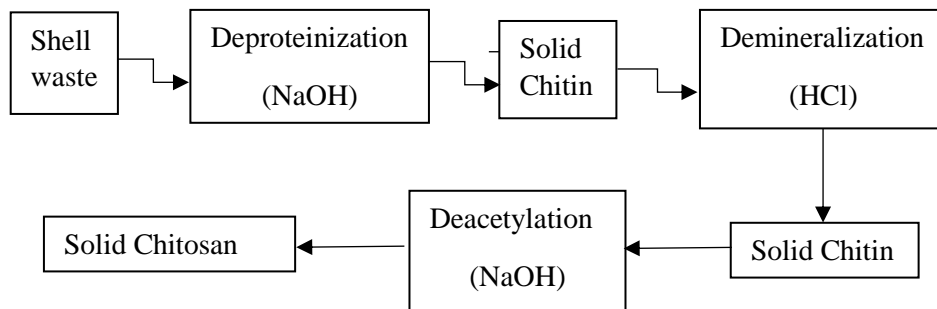
Figure 1. Schematic Diagram of Chitosan Production

Deproteinization process

The deproteinization was carried by heating 2 gm of shrimp shells powder after adding 28 mL of 2 N NaOH at 70 °C for 1 hr with stirring. The product was neutralized by washing under running tap water. The solid was collected and washed with distilled water. And then the solid product was dried in vacuum.

Demineralization process

The dry solid 1 gm was treated with 14 mL of 10 % HCl (3.25 N) at 70 °C and kept for 2 hr. The solid product was collected and washed with distilled water and dried.

Deacetylation process

Then the demineralized product (1 g) was treated with 14 mL of 35 % 8.75 N NaOH at room temperature for 75 hr with stirring. The acetylated solid was filtered and then washed with distilled water to reach pH 7. The deacetylated product was dried in a vacuum.

Characterization of chitosan

For approximate analysis of chitosan, the followings were determined to characterize the prepared chitosan from shrimp shell waste.

(i)   Degree of Deacetylation (DD %)

(ii)   FT-IR analysis

(iii)   SEM analysis

Degree of Deacetylation (DD %) was determined by acid-base titration method (Domard & Rinaudo, 1983) with modification. Chitosan (0.1 g) was dissolved in 30 mL HCl aqueous solution (0.1 M) at room temperature. After adding 5-6 drops of methyl orange indicator, the red chitosan solution was obtained. And then, this solution was titrated the (0.1

M) NaOH solution until it turned orange. Finally, the percentage of degree of deacetylation was calculated from the following calculated method and the result is shown in Table 1.

$$DD\% = \frac{C_1V_1 - C_2V_2}{Mx0.0994} \, x0.016x100$$

Where, C_1 = The concentration of standard HCl solution (M)

   C_2 = The concentration of standard NaOH solution (M)

   V_1= The volume of the standard HCl aqueous solution used to dissolve chitosan (mL)

   V_2 =The volume of the standard NaOH solution consumed during titration (mL)

   M = The weight of chitosan (g)

The prepared chitosan was characterized by Infrared (IR) spectroscopy (IR-Tracer 100 Shimadzu Japan) and Scanning electron Microscope (SEM) (ZEISS). All analyses were done in Department of Chemistry, Western Yangon University. From the IR spectrum, the functional groups of the prepared chitosan were detected. The morphology of chitosan was examined from SEM image.

Effect of dosage

The accurately weighed different samples varying from 0.002 g to 0.10 g were added to the conical flask. The copper (II) sulphate solution (10 mL) was added into each conical flask and it was shaken by magnetic stirrer for 90 minutes. After shaking, the solution was filtered by funnel and filter paper into each test tube. Analyses were carried out by UV-Vis spectrophotometer. The Langmuir parameters for the metal uptake properties of chitosan was shown in Table 3 and Figure 4.

Effect of contact time

The effect of contact time on removal efficiency of Cu (II) ion was studied by varying time 15-90 min, while keeping the optimum dose of adsorbents (0.1 g) and 250 mgL^{-1} copper (II) sulphate solution (10 mL) as constant. The results were shown in Table 8 and Figure 7.

RESULTS AND DISCUSSION

Degree of Deacetylation of the Prepared Chitosan

Table 1. Percentage of Degree of Deacetylation of the Prepared Chitosan

Sample	Method	DD %
Chitosan (0.1 g)	Acid-bade titration	99.4

FT IR Analysis

The IR spectrum data for the produced chitosan revealed the following peaks: peak at 3485.00 cm^{-1} is assigned to -OH and -NH stretching vibrations, while the peaks at 2891.30 cm^{-1} is assigned to the aliphatic C-H stretching vibration in the -CH and -CH$_2$ groups. The amide frequencies consist of the -C=O bond stretch of the remaining acetamido and the N-H bending vibrations of the -NH$_2$ groups are observed at 1654.92 cm^{-1}. The peak at 1420.00 cm^{-1} is assigned to -NH$_2$ deformation. Further bending vibrations are observed at 1379.10 cm^{-1} for the C-C-H symmetric bending vibration in alcohol. Stretching vibrations are also observed at

1320.00 cm^{-1} for the C-N stretching vibration and 1160.00 cm^{-1} for the C-O stretching vibration of the alcohol groups as shown in Figure 2.
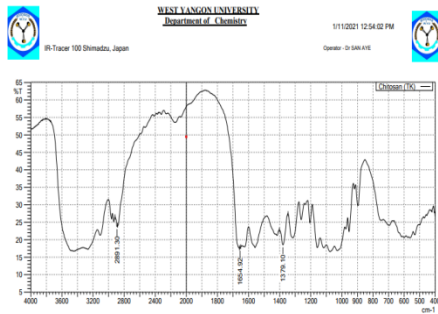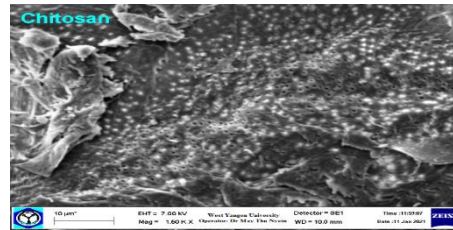

Fig 2. FT IR spectrum of chitosan   Fig 3. SEM photograph of chitosan

Table 2. Interpretation of IR spectrum

No.	Type of functional group	Type of vibration	Observed Wavenumber (cm^{-1})	*Referred Wavenumber (cm^{-1})
1	OH (hydroxyl), NH (amino)	Stretching	3485.00	3200-3550
2	-CH, -CH$_2$	Stretching	2891.30	2850-2960
3	-C=O	Stretching	1654.92	1650-1780
4	-NH$_2$ (deformation)	Bending	1420.00	1400-1600
5	-C-O	Stretching	1160.00	1050-1250

* Paula Bruice Organic Chemistry 4th Edition

SEM Analysis

The SEM photograph shows the morphology of the extracted chitosan as shown in Fig 3 which presented smooth and porous surface with heterogeneous structure on it.

Uptake of Cu (II) ion by Dosage Method

Table 3 shows the data regrading the Langmuir parameters; work out on the basis of dosage method by using chitosan. Figure 4 shows that the Langmuir linear isotherm plotted for each sorbent towards the uptake of Cu (II) ion. The linear plot shows correlation factor (R^2) nearly equal to 1. This means to point out the uptake of Cu (II) ion by chitosan was probably satisfactory.

The Langmuir equation to be used in the evaluation of the Langmuir constant can be represented by: $C_{ads} = \dfrac{K_L C_e}{1 + a_L C_e}$

Where, C_{ads} =   monolayer coverage
        C_e =   the solution phase metal ion concentration
        K_L =   the Langmuir equilibrium constant
        a_L =   the Langmuir constant

From it, the linear Langmuir equation can be deduced as $\dfrac{C_e}{C_{ads}} = \dfrac{1}{K_L} + \dfrac{a_L}{K_L} C_e$.

Regrading the above, Figure 4 gave the linear plot. From the linear plot, Langmuir constant K_L, a_L and K_L/a_L were evaluated. The resulting data are shown in Table 4 for chitosan.

Table 3. Langmuir Isotherm: Adsorption of Cu (II) ion by adsorbent

Chitosan C_0= 250 mgL^{-1}, Solution volume =10 mL, Time =90 min

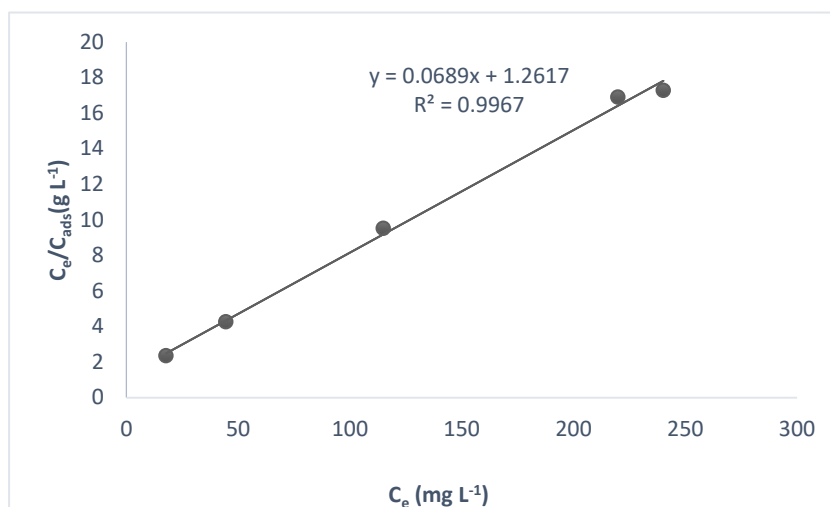| No.	Dose (g)	C_e(mgL^{-1})	x(mg)	x/m (mgg^{-1})	C_e/C_{ads} (gL^{-1})
1	0.02	240.21	0.2781	13.9065	17.273
2	0.04	220.00	0.521	13.025	16.891
3	0.06	115.00	0.726	12.100	9.504
4	0.08	44.50	0.839	10.488	4.243
5	0.10	17.79	0.75	7.500	2.345

Figure 4. Langmuir Isotherm: Adsorption of Cu (II) ion on Chitosan

Table 4. Langmuir Isotherm model constants and correlation coefficients for adsorption of Cu (II) ion from aqueous solution using Chitosan

Type of Adsorbent	Langmuir Parameter			
	K_L (Lg^{-1})	a_L(Lmg^{-1})	K_L/a_L(mgg^{-1})	R^2
Chitosan	0.7926	0.0546	14.516	0.9967

Table 5 indicates the sorption parameter according to the Freundlich empirical equation (i.e., $C_{ads} = a\, C_e^b$), where 'a' and 'b' are Freundlich constants. These constants depend on the nature of the solution used the sorption capacity, temperature and sorption intensity. In the logarithm form, the linear equation is log C_{ads} = b log C_e + log a. Freundlich linear plot is shown in Figure 5. The evaluated empirical constants 'a' and 'b' are presented in Table 6. The

correlation factor (R^2) are nearly equal to 1 which means that the sorption of Cu (II) ion by chitosan was also favorable.

The effect of dosage on the removal of Cu (II) ion by using chitosan shows that the removal efficiency is increased with the increasing dose of chitosan as shown in Table 7. According to this result, the optimal dose (0.1 g) of removal efficiency with 92.880 % was found as shown in Figure 6.

Table 5. Freundlich Isotherm: Adsorption of Cu (II) ion by adsorbent
Chitosan C_0 = 250 mgL^{-1}, Solution volume = 10 mL

No.	Log C_e (mgL^{-1})	Log C_{ads} (gL^{-1})
1	2.381	1.505
2	2.342	1.228
3	2.061	0.987
4	1.658	0.628
5	1.250	0.370

Table 6. Freundlich Isotherm model constants and correlation coefficient for adsorption of Cu (II) ion from aqueous solution using Chitosan

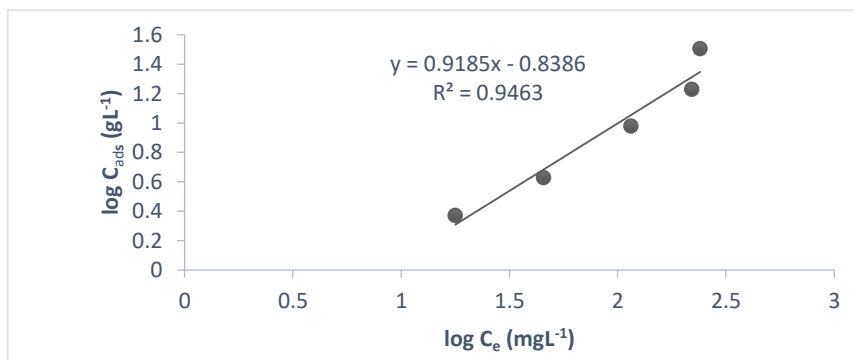| Type of Adsorbent	Freundlich parameter		
	a (gL^{-1})	b (mgg^{-1})	R^2
Chitosan	0.1450	0.9185	0.9463

Figure 5. Freundlich Isotherm: sorption of Cu (II) ion on Chitosan

Table 7. Effect of Dosage between Cu (II) ion with Chitosan
C_o= 250 mgL^{-1}, Solution volume= 10 mL, Time= 90 min

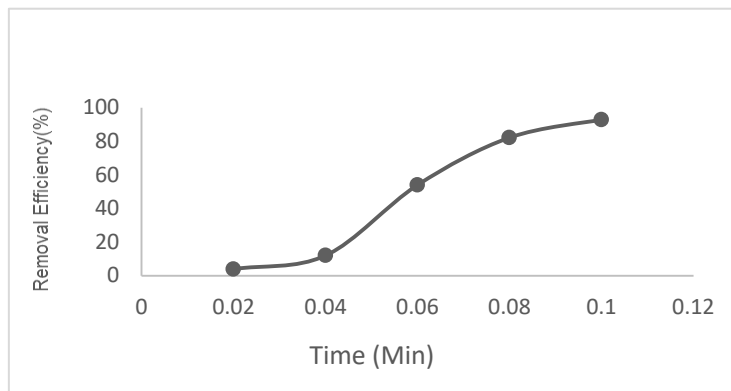| No.	Dose (g)	Ce (mg L^{-1})	Removal Efficiency (%)
1	0.02	240.21	3.92
2	0.04	220.00	12.00
3	0.06	115.00	54.00
4	0.08	44.50	82.20
5	0.10	17.79	92.88

Fig 6. Effect of Dosage on removal of Cu (II) ion using Chitosan

Effect of Contact Time

      The effect of contact time is shown in Table 8 and Figure 7. The effect of contact time on the removal of Cu (II) ion by using chitosan shows that the removal efficiency is increased with the time and the equilibrium state is reached at 75 minutes. It shows that chitosan is the good removal of heavy metal such as Cu (II) ion from the wastewater from the various sources of pollutions.

Table 8. Effect of Contact Time between Cu (II) ion with Chitosan

C_o= 250 mgL^{-1}, Solution volume= 10 mL, Dose= 0.1g

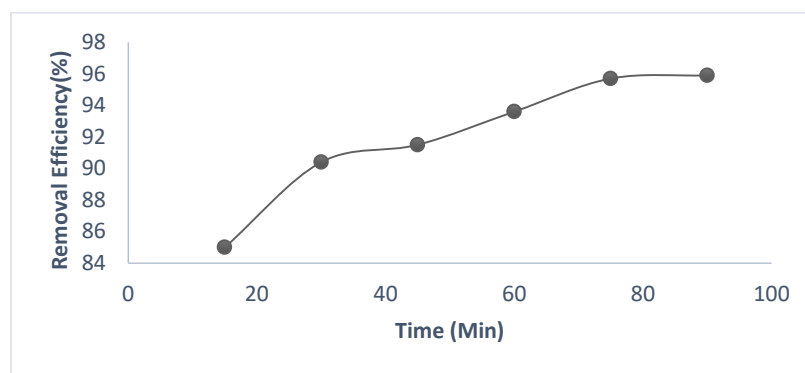| No.	Time (min)	C_e(mgL^{-1})	Removal Efficiency of Cu (II) ion (%)
1	15	0.0150	85.0
2	30	0.0096	90.4
3	45	0.0085	91.5
4	60	0.0064	93.6
5	76	0.0043	95.7
6	90	0.0041	95.9

Figure 7. Effect of Contact Time on Removal of Cu (II) ion using   Chitosan

CONCLUSION

Preparation of chitosan from shrimp shell waste has already solved the environmental problems. Besides, low costs of chitosan production can be used for the various applications such as food, cosmetic, water treatment, paper and so on. The amount of DD% (94.34 %), which showed that the prepared chitosan was the good deacetylation of chitin to chitosan. From the interpretation of IR spectrum, it can be concluded that three main types of functional groups were presented; amino/acetamido group as well as primary and secondary hydroxyl groups. From the SEM photograph, it can be concluded that the porous and smooth surface with heterogeneous structure on it. This research showed that the effect of dose for Langmuir model and Freundlich model (R^2) values are 0.9967 and 0.9463(nearly equal to 1). This means that sorption on Cu (II) ion was favorable. Since the removal efficiency on dosage effect (92.880 %), the optimal dose (0.1 g) was chosen for the contact time effect. The effect of contact time on the removal of Cu (II) ion by using chitosan shows that the removal efficiency is increased with the time. It can be considered that sorption is fast due to ion-ion bond and then diffusion control sorption. It shows that chitosan is the good removal of heavy metal such as Cu (II) ion. And then, it would be reduced water pollution and the waste materials (shrimp shell waste) which can be used the removal of the heavy metals from the waste water in the various sources of pollutions. It can be concluded that the use of chitosan for removal for Cu (II) ion may appear to be eco-friendly efficiency.

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Online Materials

https://preparation and characterization of fully deacetylated chitosan www.sciencedirect.com (7.10.2021)
https://chitin and chitosan: properties and applications onlinelibrary.willey.com (10. 2.2022)

APPENDIX

Calculation of Degree of Deacetylation, Langmuir and Freundlich Parameters

From Degree of Deacetylation,

$$DD\% = \frac{C_1V_1 - C_2V_2}{Mx0.0994} x0.016x100$$

C_1 = The concentration of standard HCl solution (M)

C_2 = The concentration of standard NaOH solution (M)

V_1 = The volume of the standard HCl aqueous solution used to dissolve chitosan (mL)

V_2 = The volume of the standard NaOH solution consumed during titration (mL)

M = The weight of chitosan (g)

From Langmuir linear equation,

$$\frac{1}{C_{ads}} = \frac{1}{K_L C_e} + \frac{a_L}{K_L}$$

$$\frac{1}{C_{ads}} = \frac{1}{K_L C_e} + \frac{a_L}{K_L} C_e$$

We have the Langmuir Isotherm by plotting C_e/C_{ads} vs C_e

Monolayer saturation capacity, K_L/a_L (mgg^{-1}) =1/slope

Langmuir equilibrium constant, K_L (mgL^{-1}) =1/intercept

Langmuir constant, a_L (gL^{-1}) =K_L x slope

From Freundlich linear equation,

log C_{ads}= b log C_e + log a

We can construct an isotherm that is a plot of log C_{ads} vs log C_e

From Freundlich linear equation,

Sorption intensity (b)= slope of the isotherm

Sorption capacity (a)= anti-log (intercept of the isotherm)