การดูดซับไอออนของเหล็กในน้ำก่อนเข้าสู่กระบวนการผลิตน้ำประปาด้วยไคโตซานจากกระดองปูนา

ชัชญาภา เกตุวงศ์[1] พรพิมล พลคำ[1] สมสุข ไตรศุภกิตติ[1*] วัชรา เสนาจักร์[2]

บทคัดย่อ

ไคโตซานเป็นพอลิเมอร์ธรรมชาติที่ไม่เป็นพิษ ซึ่งเป็นตัวดูดซับชนิดหนึ่งที่ถูกใช้อย่างกว้างขวาง โดยการดูดซับเกิดจากการสร้างพันธะของโลหะหนักกับหมู่อะมิโนในไคโตซาน ในงานวิจัยนี้จึงมีวัตถุประสงค์เพื่อศึกษาการดูดซับไอออนของเหล็กในน้ำก่อนเข้าสู่กระบวนการผลิตน้ำประปาจากหนองน้ำในมหาวิทยาลัยราชภัฏมหาสารคามด้วยไคโตซานที่สกัดจากกระดองปูนา โดยมีการทดลองสองขั้นตอน คือ การสกัดไคโตซานและศึกษาการดูดซับ จากผลการทดลองพบว่าไคโตซานที่สกัดได้สามารถดูดซับเหล็กไอออนได้ร้อยละ 41.51 ปริมาณตัวดูดซับ 0.5 กรัม และเวลาในการดูดซับ 100 นาที ณ สภาวะปกติที่อุณหภูมิห้อง

คำสำคัญ : การดูดซับ เหล็กไอออน ไคโตซาน กระดองปูนา

[1] สาขาวิชาเคมี คณะวิทยาศาสตร์และเทคโนโลยี มหาวิทยาลัยราชภัฏมหาสารคาม
[2] สาขาวิชาชีววิทยา คณะครุศาสตร์ มหาวิทยาลัยราชภัฏมหาสารคาม
** ผู้นิพนธ์หลัก e-mail: somsuk_rmu@yahoo.com*

ADSORPTION OF FERROUS ION IN WATER BEFORE UNDERGOING TAP WATER PROCESS USING CHITOSAN FROM RICEFIELD CRAB SHELL

Chatyapa Ketwong[1] Pornpimol Phonkam[1] Somsuk Trisupakitti[1*] Watchara Senajuk[2]

Abstract

Chitosan is a non-toxic natural polymer and is one of the widely used adsorbents. The adsorption evolved in the instance that bonding in created between heavy metal and groups of amino in chitosan. This study therefore aims at investigating the adsorption of ferrous ions in the water from the swamp inside Rajabhat Maha Sarakham University before undergoing tap water production process by using chitosan extracted from the ricefield crab shell. The experiment was divided into two steps, that is, extracting chitosan and examining the adsorption. The results revealed that the extracted chitosan was able to absorb ferrous ions at 42.51% with the adsorbent amount at 0.5 gram and adsorption time of 100 minutes at the room temperature.

Keywords : Adsorption, Ferrous ions, Chitosan, Ricefield crab shell

[1] Department of Chemistry, Faculty of Science and Technology, Rajabhat Maha Sarakham University

[2] Department of Biology, Faculty of Education, Rajabhat Maha Sarakham University

** Corresponding author, e-mail: somsuk_rmu@yahoo.com*

Introduction

Groundwater is the key water supply in tap water production for consumption and utilization. However, groundwater usually contains metal ions in the form of ferrous bicarbonate ($Fe(HCO_3)_2$) which makes the water transparently clear. But, when left against the air, the water interacts with oxygen and begins to get turbid and precipitate to become Ferric Oxide ($Fe(OH)_3$) in which the color is yellowish red or commonly known as rusty color.

WHO prescribes drinking water should not contain metal ions more than 0.3 milligrams per liter and regulates the life-threatening danger of metal in consumption at 40 milligrams per body weight (World Health Organization, 1996). In addition, metal makes the water unpleasant smell and unfavorable color that results dirty stain on sanitary ware or clothes. Also, this is principal cause for clog up in the filtering system and tap water distribution pipeline. So, before delivering the water into the tap water production process, exceeding standard of metal ions should be eliminated to the amount safe for consumer. The use of adsorption material is one of the method in water purifying system especially the use of chitosan which is natural material and safe for consumer and environment. Chitosan is derivative of chitin and found in crab shell, shrimp shell, squid, fungus, and animals with hard shell. It's attributes are undissolved in the water but dissolved in mild acid, and group of functions sensitive to reaction, that is, amino ($-NH_2$), primary alcohol ($-CH_2OH$), secondary alcohol (-CHOH) which favor chitosan to be utilized in various purposes. Numerous studies used chitosan as adsorbent in adsorbing heavy metal ions in the water, for example, kinetics study of silver ions adsorption (Su-arun, K., and Piyamongkala, K. , 2012) elimination of metal in wastewater by chitosan membrane (Sananmuang *et al*, 2008), or metal ions adsorption (Fe^{2+} and Fe^{3+}) by chitosan and chitosan beads (Ngah *et al*, 2005).

Crab shell is the material that contains high volume of chitosan up to 20% of dried weight [19]. The type of chitosan in crab shell is a α-chitin that has the reversal structure and has high stability by nature. So, this study concentrates on investigating the use of chitosan extracted from ricefield crab shell which is conveniently available material in the local community for use as ferrous ions adsorption in the sample water for tap water production. The outcome of this study would provide the guidelines in ferrous ions treatment of the sample water for use in tap water production, reducing rusty problems and sediments clog up in the water transmission system by using the water sample from natural water source in Rajabhat Maha Sarakham University, Mahasarakham Province, Thailand

Methodology

The experiment was sectioned into three parts, that is, preparation of chitosan extracted from ricefield crab shell, discovering the right condition for batch adsorption, and adsorption of ferrous ions in the sample water before entering the tap water production.

Preparation of chitosan extracted from ricefield crab

Cleaned ricefield crab shell and boiled them at 70-80 degree Celsius for 1 hour. After, grinded them for demineralization process in the reaction with hydrochloric acid (HCl), concentration 1 molar, ratio 1:10, at the room temperature for 1 hour. Later, underwent deprotienation in the reaction with concentrated sodium hydroxide 4% by the weight per volume at ratio 1:10 at 60 degree Celsius for 1 hour under the condition of spinning and filtering process. Next, wash out by distilled water until pH was neutral and proceeded with dehydration. Next, employed deacetylation process to eliminate acetyl group by using concentrated sodium hydroxide 50% by weight per volume at 1:10 ratio and 120 degree Celsius for 1 hour. After, filtered and washed by using distilled water, then performed dehydration at 70-80 degree Celsius.

Investigating ferrous ions adsorptionadsorption

The pH measurement of water sample collected from the pond in Rajabhat Maha Sarakham University was at 5 by the room temperature. To make the experiment concurred with the real condition of water, the researcher controlled the pH value at 5 and used room temperature throughout this experiment on investigating the right conditions for adsorption.

Standard calibration curve graph for ferrous ions, prepared standard ferrous solution (Fe^{2+}) at the concentration of 0, 56, 84, 112, 140 milligram per liter. After, filled in 10% concentrated hydroxylamine hydrochloride solution by weight per volume by using distilled water for 10 minutes. Measured the solution for absorbance by UV-Visible spectrophotometer at the wavelength of 509.73 nanometer, and constructed calibration curve graph for investigating the concentration of metal ions in the next stage.

Investigating adsorption time

Weighed 0.3 gram of chitosan and put into 8 beakers (50-millimeter type). Then, filled in 10 millimeter standard metal solution (Fe^{2+}) at concentration of 5×10^{-4} mol/L. Performed batch adsorption under stirring and spinning condition at the room temperature and pH at 5. Determined adsorption time at 5, 15, 30, 60, 100, 200 and 300 minutes respectively. After, filtered out chitosan and took the solution to analyze for concentration of ferrous ions by using UV-Visible Spectrophotometer technique at the wavelength of 509.73 nanometer. The amounts of Fe^{2+} removed by sorbents q_e and percent extracted %adsorption can be calculated using the following equation (Ngah *et al*, 2005) :

$$\%Adsorption = \frac{\mathrm{C_i} - \mathrm{C_e}}{\mathrm{C_i}} \times 100 \quad (1)$$

$$q_e = \frac{C_i - C_e\, V}{m} \quad (2)$$

Where q_e is the amount of Fe^{2+} adsorbed (mg/g). C_i and C_e are the initial and equilibrium concentration of Fe^{2+} (mg/g), respectively. V is the volume of the solution (L) and m is the weight of the sorbent used (g).

Chitosan concentration appropriate for adsorption

Weighed chitosan at 0.1, 0.2, 0.3, 0.4 and 0.5 grams and put into the 50 millimeter beaker, after filled in 10 millimeter of the standard metal solution (Fe^{2+}) at the concentration of 5×10^{-4} mol/L, pH at 5, at the most appropriate time for adsorption derived from 2.2.1 Then, took the solution to analyze for concentration of ferrous ions by using UV-Visible Spectrophotometry technique at the wavelength of 509.73 nanometer and calculated for adsorption percentage in order to determine chitosan concentration yielding the highest percentage of adsorption.

Adsorption Isotherm

Took the concentration of ferrous ions exceeded from the adsorption by different volumes chitosan for calculation and graph construction based on isotherm adsorption equation of Langmuir and Freundlich as outlined in equation (3) and (4) (Sananmuang *et al*, 2008).

The Langmuir isotherm assumes a surface with homogeneous binding sites equivalent sorption energies, and no interaction between adsorbed species. The equation is written as:

$$\frac{1}{q_e} = \frac{1}{X_m} + \frac{1}{KX_mC_e} \qquad (3)$$

Where q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of the ferrous ions in solution (mg/L), X_m is the constant related to overall solute adsorptivity and K is the Langmuir constant.

The Freundlich isotherm is an empirical equation based on an exponential distribution of adsorption sites and energies. It is represented as :

$$\text{Log } q_e = \text{Log } K_f + \left(\frac{1}{n}\right) \text{Log } C_e \qquad (4)$$

Where q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of ferrous ions in solution (mg/L), K_f is roughly an indicator of the adsorption capacity, and 1/n is the adsorption intensity. A linear plot of Log q_e versus Log C_e confirms the validity of the Freundlich model.

Ferrous ions adsorption in the sample water before entering tap water production process

Calculation of ferrous ions in the water sample before adsorption by chitosan

Took 25 millimeters of the sample water, filled in 2 millimeters of the concentrated hydrochloric acid, boiled for 10 minutes, after cooled down at the room temperature, then filtered out and poured water into a 50-milliliter volumetric flask, washed with 5 milliliter distilled water, filled in with 5 milliliter of 10% concentrated hydroxylamine hydrochloride by weight per volume, filled in 5 milliliter of o-phenanthroline solution, adjusted the volume by using distilled water, left alone for 10 minutes. After, took the solution to measure absorbance by UV-Visible Spectrophotometer at the wavelength at 509.73 nanometer, and substituted the value into the linear equation obtained from standard solution graph in order to calculate for the concentration of ferrous ions.

Calculation of ferrous ions concentration in the sample water after adsorption by chitosan

Took 25 millimeter of sample water that undergone adsorption by chitosan at the room temperature with pH at 5, used chitosan and time yielding the highest adsorption percentage from the experiment item 2.2.1 and 2.2.2 respectively. After, performed the same experiment with the sample water before undergoing adsorption by chitosan.

Results

Analyzing the characteristics of chitosan

Chitosan extracted from ricefield crab is a rough power in light brown color as displayed in Figure 1. Analysis of the characteristics by using Fourier Transformed Infrared Spectroscopy (FT-IR) revealed the spectrum as outlined in Figure 2. Then, appeared the vibrating spectrum of functioning hydroxyl group (OH-stretching, 3448 cm^{-1}), methyl group (CH-stetching, 2815 cm^{-1}), amide group (C=O-stetching, 1651 cm^{-1}), carbonyl group (CO-bending, 1021 cm^{-1}), and amino group (NH-bending, 1458 cm^{-1}) which indicated the characteristics of chitosan (Al Sagheer *et al*, 2009).

Figure 1. The characteristics of chitosan extracted from ricefield crab shell.

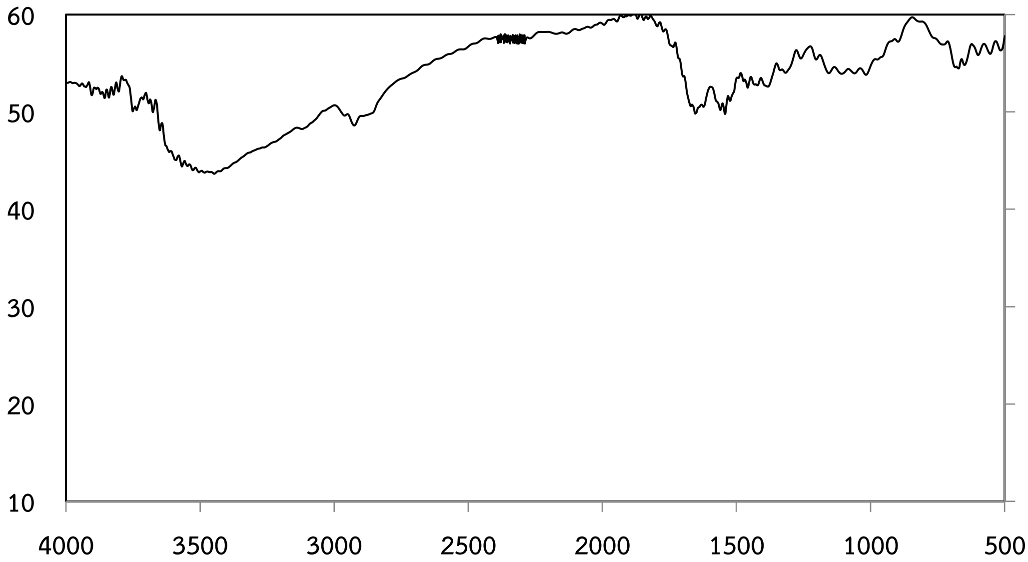

Figure 2. FT-IR spectrum of chitosan extracted from ricefield crab shell.

Taking FT-IR spectrum (-OH) and (-C=O) functional groups of chitin and chitosan to analyze the reaction level in eliminating acetyl group (%DD) from the following equation,

$$\%DD = 100 \times (1-(A_{C=O}/A_{O-H})/1.33)$$

where $A_{C=O}$ refers to absorbance value of function C=O

A_{O-H} refers to absorbance value of function O-H

It was found that chitosan extracted from ricefield crab shell performed the level of eliminating acetyl group (%DD) at 46.26.

Determining the appropriate condition for ferrous ions adsorption

Standard solution graph, took standard solution ferrous ions at the concentration of 0, 56, 84, 112, 140 milligram per liter to measure absorbance at the maximum wavelength of 509.73 nanometer. It was found that when ferrous ions concentration increased, the measured absorbance would increase and was able to plot standard graph between absorbance and concentration of the standard metal ions solution to formulate the linear equation for use in benchmarking the concentration of ferrous ions as outlined in Figure 3.

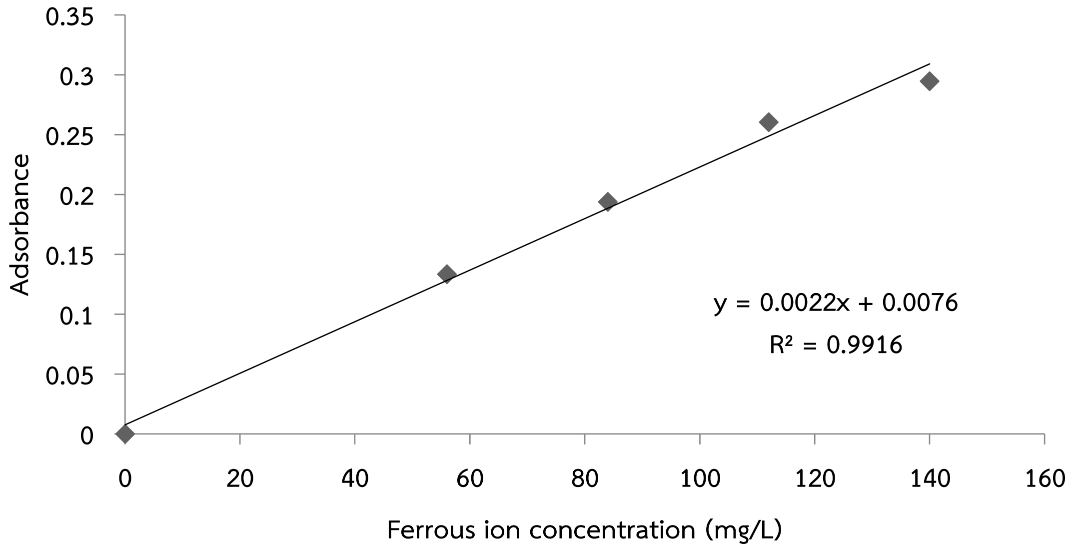

Figure 3. Standard curve of ferrous ions solution.

Adsorption time

Adsorption of ferrous ions with concentration of 5x at 10^{-4} mol/L by chitosan from ricefield crab shell using time 5-300 minutes at room temperature and pH 5, and performed analysis by using UV-Visible Spectrophotometry at the wavelength of 509.73 nanometer, and calculated the adsorption percentage, the time and adsorption percentage was outlined in Figure 4.

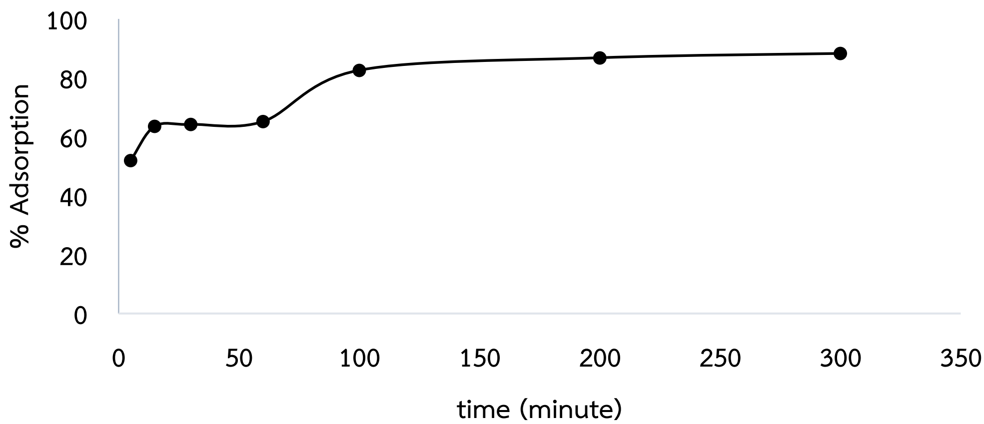

Figure 4. The results of ferrous ions adsorption percentage by using chitosan extracted from ricefield crab shell.

Figure 4 indicated that when time in ferrous ions adsorption increased, the ferrous ions adsorption capacity of chitosan extracted from ricefield crab would also increase and the adsorption would stabilize at the 100 minute. So, this study chose to use the time at the 100 minute in determining the appropriate chitosan concentration in adsorbing ferrous ions and used this formula for ferrous ions adsorption in the sample water before entering the tap water production.

Appropriate concentration of chitosan in adsorption

Used chitosan extracted from ricefield crab at 0.1-0.5 grams in adsorbing ferrous ions with concentration of 5x at 10^{-4} mol/L, at room temperature, pH 5, adsorption time at 100 minute. After, perform analysis by using UV-Visible Spectrophotometry at the wavelength of 509.73 nanometer, calculated for adsorption percentage, and the results were shown in Table 1.

Table 1. Adsorption percentage of ferrous ions by using chitosan extracted from 0.1-0.5 grams of ricefield crab shell, at room temperature, pH 5, and 100 minutes for adsorption time.

Chitosan extracted (gram)	% Adsorption
0.1	65.00
0.2	80.30
0.3	81.44
0.4	82.58
0.5	84.21

From Table 1, it was found that when chitosan extracted from ricefield crab shell was increased, the adsorption percentage of ferrous ions would also increase due to the increment of adsorbent volume was an expansion of adsorbing area. This was similar to the experiment on silver ion adsorption using chitosan by Rakchaiyawan *et al* (2015). And, it was found that, in this study, the use of chitosan at 0.5 gram yielded the highest percentage of ferrous ions adsorption. Therefore, this formula was chosen to use in experimenting ferrous ions adsorption in the sample water before entering the tap water production process.

Adsorption Isotherm

When substituting the concentration following isotherm equation of adsorption proposed by Langmuir and Freundlich, it was found that ferrous ions adsorption by chitosan extracted from ricefield crab shell agreed with Freundlich Equation rather than that of the Langmuir. When reviewing the correlation coefficient (R^2) in Figure 5, this indicated that the adsorption was a continuing pattern which concurred with the study on ferrous ions adsorption using chitosan membrane by Sananmuang *et al* (2008).

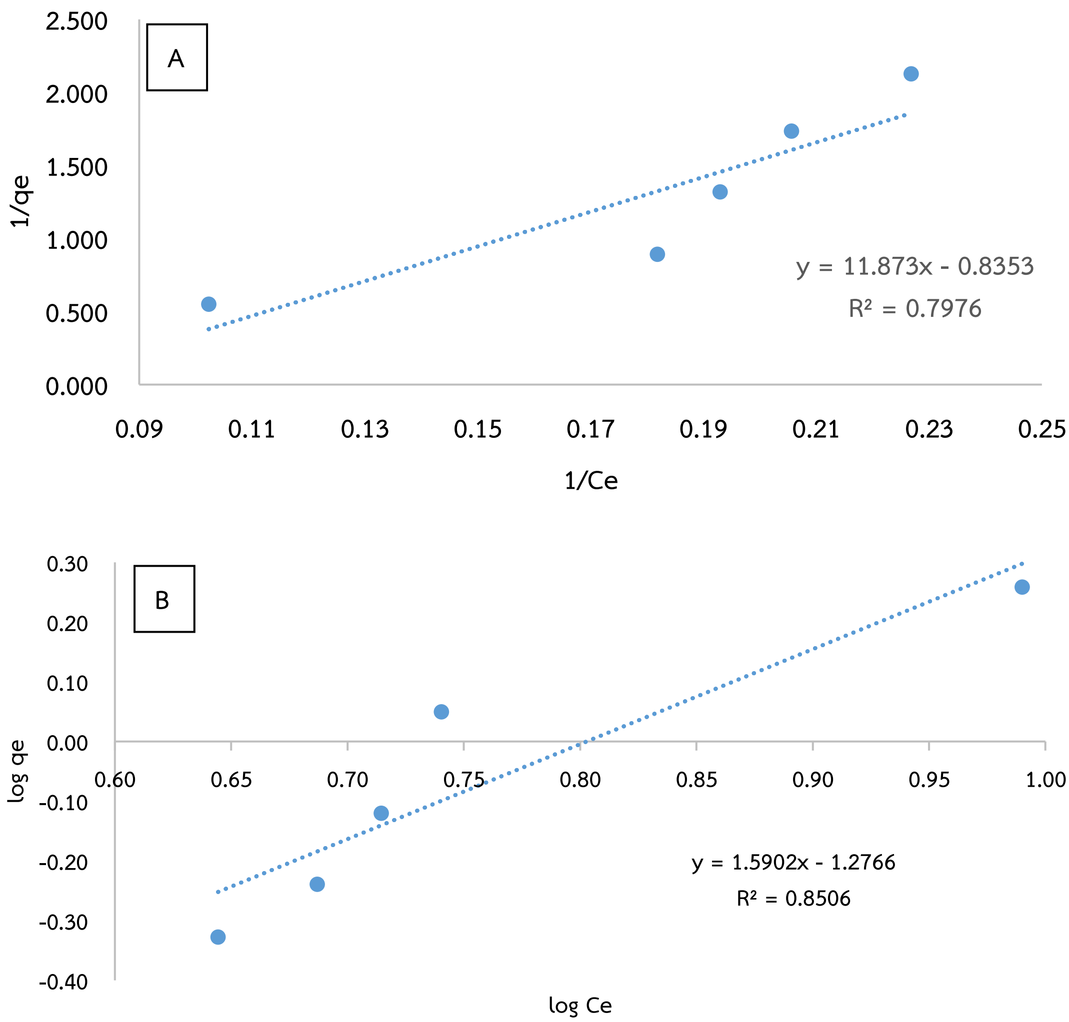

Figure 5. Isotherm adsorption of ferrous ions by chitosan extracted from ricefield crab shell following equations proposed by (A) Langmuir and (B) Freundlich.

Analysis of ferrous ions concentration in sample water

Analysis of ferrous ions concentration in the sample water was conducted by converting all iron ions into ferrous ions (Fe^{2+}) that would evolve the complex solution with 1,10-phenanthroline and then became $Fe(C_{12}H_8N_2)_3^{2+}$ which could absorb the light in the visible range. Then, underwent the analysis by UV-Visible spectrophotometry technique, and revealed the ferrous ions concentration in the sample water before and after being adsorbed by chitosan as outlined in Table 2.

Table 2. Ferrous ions concentration found in the sample water before and after adsorbed by chitosan extracted from ricefield crab shell at room temperature, pH 5, adsorption time at 100 minutes, and 0.5 grams of chitosan.

Water sample	Ferrous ion concentration (mg/L)
Before adsorption	33.36
After adsorption	19.18

From Table 2, it was found that the concentration of ferrous ions in the sample water before and after adsorbed by chitosan extracted from ricefield crab shell was at 33.36 mg/L and 19.18 mg/L respectively. So, chitosan extracted from ricefield crab shell was able to adsorb ferrous ions in the sample water at 14.18 mg/L accounting for 42.51%.

Discussion

Extracting chitosan from ricefield crab shell indicated that the production percentage of chitosan was at 71.82% and the chitosan characteristics were a rough powder with light brown color and rough texture. After, took the extracted chitosan to examine for the ferrous ions adsorption condition at room temperature and pH 5 by using UV-Visible Spectrophotometer technique. It was found that chitosan extracted from ricefield crab shell was able to adsorb ferrous ions. And, when adsorption time was increased, the ferrous ions adsorption capacity of chitosan was also increased, and the adsorption stability began at the 100 minute. Also, when increasing adsorbent concentration, the ferrous ions adsorption capacity was also increased. This could be the fact that increasing the concentration of chitosan adsorbent would also increase amino group which plays the vital role in building the bond with ferrous ions. The concentration of adsorbent at 0.5 grams could yield the maximum adsorption percentage. In addition, adsorption isotherm of ferrous ions by chitosan supported Freundlich isotherm equation which performs the continuing adsorption pattern. This also agreed with the study of Sananmuang[7] on ferrous ions adsorption by chitosan membrane. When applied that adsorption condition for ferrous ions adsorption process with the sample water collected from the pond to produce tap water for consumption and utility at Rajabhat Maha Sarakham, it was found that chitosan extracted from ricefield crab shell was able to adsorb ferrous ions in the sample water. This was determined by examining the concentration of ferrous ions in the sample water before and after being adsorbed with chitosan which were 33.36 mg/L and 19.18 mg/L respectively, and accounted for 42.51% of the adsorption percentage.

Conclusion and Recommendations

Ricefield crab shell is a biological waste, but it could be used as the material in extracting chitosan which is an edible natural polymer and non-toxic for human and environment, and it has the capacity in adsorbing heavy ferrous ions. This experiment used chitosan extracted from ricefield crab shell in adsorbing ferrous ions in the sample water before entering the tap water production. So, to perform the adsorption concurrent with real utilization, the experiment tried to examine the right condition for ferrous ions adsorption by using the condition of the sample water collected from the pond inside Rajabhat Maha Sarakham University at room temperature and pH 5. It was found that the right condition for adsorption was 100 minutes and adsorbent concentration at 0.5 grams. When applying this condition in ferrous ions adsorption with the sample water, it revealed that chitosan was able to adsorb ferrous ions from the sample water. By determining the decrease of ferrous ions concentration in the sample water before and after being adsorbed by chitosan which accounted for adsorption percentage at 42.51%.

The results from this study could be applied in the real situation for tap water production in the precipitating process to decrease the ferrous ions which are the major cause of corrosion and clog up in the tap water transmission system. Or this could be used in experimenting adsorption of other types of heavy metal contaminated in the water such as manganese, lead, and chromium.

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