Determination of Maximum Adsorption Capacity of Chitosan and Carboxymethyl Chitosan on the Absorption of Metal Ions Cr (VI) Based on the Langmuir Equation

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ABSTRACT

A study has been conducted to investigate the adsorption of chrom (VI) metal ions by hand chitosan and carboxymethyl chitosan. This research aimed to examine the adsorption capacity of chitosan and carboxymethyl chitosan and determine the applicability of the Langmuir isotherm adsorption method for adsorbing Cr (VI) metal ions utilizing these materials. Chitosan was chemically treated with a 40% NaOH solution and monochloroacetic acid, dispersed in 2-propanol at room temperature for 10 h. This reaction resulted in the formation of carboxymethyl chitosan. FT-IR analyzed the functional group of carboxymethyl chitosan. The adsorption process was conducted using a standard solution with varying concentrations of Cr6+, specifically 5, 10, 15, and 20 mg/L. The concentration of Cr6+ adsorbed was measured using an Atomic Absorption Spectrophotometer. The findings demonstrated that carboxymethyl chitosan exhibited the maximum capacity for adsorbing chrom metal ions, with a mass of 0.9179 mg/g carboxymethyl chitosan at a concentration of 20 ppm. Chrom (VI) metal ion adsorption by carboxymethyl chitosan follows the Langmuir equation with an R^2 value greater than 0.9. The maximum adsorption capacity of carboxymethyl chitosan is 1.16 mg/g, which is higher compared to chitosan's capacity of only 0.60 mg/g.

Keywords: Adsorption, Carboxymethyl Chitosan, Chitosan, Chrom (VI) Metal, Langmuir Equation

ABSTRAK

Telah dilakukan penelitian untuk mengetahui adsorpsi ion logam krom(VI) dengan kitosan tangan dan karboksimetil kitosan. Tujuan penelitian ini adalah untuk mengetahui kapasitas adsorpsi kitosan dan karboksimetil kitosan serta mengetahui penerapan metode adsorpsi isoterm Langmuir untuk mengadsorpsi ion logam Cr(VI) dengan memanfaatkan bahan tersebut. Kitosan diolah secara kimia dengan larutan NaOH 40% dan asam monokloroasetat yang didispersikan dalam 2-propanol pada suhu kamar selama 10 jam. Reaksi ini menghasilkan pembentukan karboksimetil kitosan. Gugus fungsi karboksimetil kitosan dianalisis dengan FT-IR. Proses adsorpsi dilakukan menggunakan larutan standar dengan konsentrasi Cr6+ yang bervariasi yaitu 5, 10, 15, dan 20 mg/L. Konsentrasi Cr6+ yang teradsorpsi diukur menggunakan Spektrofotometer Serapan Atom. Temuan menunjukkan bahwa karboksimetil kitosan menunjukkan kapasitas maksimum dalam mengadsorpsi ion logam krom, dengan massa 0,9179 mg/g karboksimetil kitosan, pada konsentrasi 20 ppm. Adsorpsi ion logam Krom(VI) oleh karboksimetil kitosan mengikuti persamaan Langmuir, dengan nilai R2 lebih besar dari 0,9. Kapasitas adsorpsi maksimum karboksimetil kitosan adalah 1,16 mg/g, lebih tinggi dibandingkan kapasitas adsorpsi kitosan yang hanya 0,60 mg/g.

Kata Kunci: Adsorpsi, Karboksimetil Kitosan, Kitosan, Logam Krom (VI), Persamaan Langmuir

1. Introduction

Heavy metals are metals with a high density or density and are pollutants commonly found in terrestrial and aquatic environments. Heavy metals affect the lives of organisms in the environment (including humans) because they are toxic and can cause death if the amount exceeds the established threshold [1].

Chromium is a white metal, not so clayey (hard but brittle and not malleable). Chromium comes from leather dyeing activities, textile manufacturing, or chrom plating [2]. These activities can directly or indirectly affect all ecosystems and human health through the food chain. Chromium is found in oxide states ranging from Cr(II) to Cr(VI), but only three- and six-valence chromium have similar biological properties. Some types of chromium have different effects on organisms. Three-valence chromium is an essential material with low toxic properties compared to six-valence chromium, which is a high oxide [3].

Chromium enters the human body through food (plants and animals) and skin. Plants are polluted with chromium through soil and air, while animals, such as fish, are contaminated with chromium through water. The body will immediately excrete chromium salts that enter the human body. However, if the chromium level is large enough, it will cause damage to the digestive system. Chromium toxicity is influenced by chromium oxidation, temperature and pH [4].

Many methods are used to remove heavy metals, such as chemical precipitation, ion exchange, mechanical filtration, electrodeposition, oxidation-reduction, membrane systems and physical adsorption [5]. Adsorption is one of the physicochemical treatment methods proven effective in removing heavy metals from aqueous solutions. According to Bailey et al. (1978), adsorbents can be defined as materials that are abundant in nature and low in value, require little processing and are waste by-products [6]. Adsorption methods are generally based on the interaction of heavy metal ions with functional groups found on the adsorbent surface through interactions and complex formation, which usually occurs on solid surfaces that have many functional groups such as -OH, -NH, -SH and -COOH [7].

Chitosan is a poly-(β-(1,4)2-amino-2-deoxy-D-glucopyranose) produced from chitin, a natural biopolymer extracted from crustacean shells by producing as acetamido groups present on the chitin chain, generally more than 60% by using a strong base solution [8]. Chitosan is one of the effective biopolymers used as a heavy metal adsorbent because of its non-toxicity, high mechanical strength, biocompatibility, biodegradability and biofunctionality [9]. Due to the limited application of chitosan, it is insoluble in solutions with neutral or alkaline pH because of its highly stable crystalline structure due to strong hydrogen bonding. Its solubility is observed only in acidic solutions below pH 6.5. The solubility of chitosan can be improved by depolymerization and chemical modification [10]. Several studies have been conducted to increase the solubility of chitosan, one of which is by performing an esterification reaction to produce carboxymethyl chitosan.

Carboxymethyl chitosan is a chitosan derivative obtained by adding a carboxymethyl group to the glucosamine group of the chitosan chain. The addition of the carboxymethyl group is known to improve the solubility of chitosan as well as its functional properties [11]. Sun et al. (2007) have examined the adsorption capacity of CMC derivatized with glutaraldehyde for Pb^{2+} ions. The results showed that the adsorption capacity of uncrosslinked CMC was still higher, but crosslinked CMC was much more selective in a single Pb solution and a mixture of Cu^{2+}, Zn^{2+} and Pb^{2+} [12]

Lasindrang et al. (2014) examined the adsorption power of chitosan-coated with activated charcoal on Cr (total), BOD and COD metals. The results showed that the adsorbent can adsorb the highest percentage of adsorbate, namely Cr metal adsorbed as much as 91.9%, BOD (99.5%) and COD (98.47%) [13]. Ananda, F. (2015) has made carboxymethyl chitosan from belangkas shell as an adsorbent to reduce the concentration of Pb (II) metal. The results showed that the optimum pH for Pb metal absorption was at pH 5, with an absorption percentage of 92.61% [14].

Based on the description above, the author is interested in researching a comparative study of the adsorption capacity of chitosan and carboxymethyl chitosan as adsorbents on Cr (VI) metal ions along with the Langmuir isotherm equation.

2. Materials and Methods

2.1. Equipment

This study used glassware, balance analytics, oven, hot plate, thermometer, magnetic stirrers, SSA Test Instrument, and FT-IR.

2.2. Materials

Materials used in this study were chitosan, 2-propanol, $K_2Cr_2O_7$, NaOH pellet, monochloroacetic acid, absolute ethanol, glacial acetic acid, methanol, and aquadest.

2.3. Research Procedure

2.3.1 Preparation of Reagent Solution

a. Preparation of 40% NaOH Solution

A total of 20 g NaOH pellets were dissolved with distilled water in a 50 mL measuring flask to the limit line homogenized. The obtained banana stems were dried in the oven, cut into small pieces, and then crushed with a blender until they became powder.

b. Preparation of 80% Ethanol Solution

An 80 mL of absolute ethanol was put into a 100 mL volumetric flask, then diluted to the limit line of the flask, and then homogenized.

c. Preparation of 2-propanol/Monochloroacetic acid Solution (1:1 w/w)

A total of 14.4 g of monochloroacetic acid was put into a beaker glass and then dissolved with 18.32 mL of 2-propanol.

2.3.2 Preparation of Carboxymethyl Chitosan

Carboxymethyl chitosan was synthesized in the following manner: 3 grams of chitosan was dispersed in 65 mL of 2-propanol and then stirred using a magnetic stirrer for 20 minutes at room temperature. Add 40% NaOH solution and monochloroacetic acid/2-propanol solution (1:1 w/w) to the chitosan solution. Repeat the solution using a magnetic stirrer for 10 hours at room temperature. Afterwards, the solution was filtered. The solid formed was then suspended in 150 mL of methanol and then neutralized with glacial acetic acid to pH 7. The solution was filtered, and the residue was washed using 80% ethanol. The carboxymethyl-modified chitosan product obtained was then dried at room temperature. Furthermore, the products obtained were characterized using FT-IR.

2.3.3 Preparation of Cr^{6+} Standard Solution

A total of 2.828 g of $K_2Cr_2O_7$ crystals were put into a 250 mL beaker containing distilled water, stirred until all the crystals dissolved, put into a 1000 mL volumetric flask, added distilled water to the limit line and homogenized.

2.3.4 Determination of Optimum Contact Time of Chitosan and Carboxymethyl Chitosan

A total of 50 mL of 5 ppm Cr^{6+} standard solution was put into a 250 mL glass beaker. Then 0.5 g carboxymethyl chitosan was added. Stirred with a magnetic stirrer for 30 minutes. Then, the mixture was filtered with Whatman filter paper no. 42. The absorbance was measured using an atomic absorption spectrophotometer at a specific λ of 357.9 nm. The above treatment was carried out with variations in contact time of 10 minutes, 20 minutes, 40 minutes, and 50 minutes. The optimum contact time for chitosan on chromium metal absorption is 20 minutes.

2.3.5 Chitosan and Carboxymethyl Chitosan in Standard Solution

0.5 g of chitosan powder was added with 50 mL of a single solution of Cr(VI) metal ions with concentrations of 5, 10, 15, and 20 ppm. Then, stir with a stirrer for 20 minutes at room temperature. Then, the solution was filtered, and SSA measured the filtrate obtained. The adsorption capacity was calculated using the Langmuir adsorption isotherm model. The same was done for carboxymethyl-chitosan adsorbent with a stirring time of 30 minutes.

3. Results and Discussion

3. 1 Research Results

3.1.1 Preparation of Carboxymethyl Chitosan

Carboxymethyl chitosan was synthesized by reacting chitosan with monochloroacetic acid under alkaline conditions. In the experiment, 3 grams of chitosan and 14.4 grams of monochloroacetic acid were used, and at the end of the process, 2.15 grams of carboxymethyl chitosan was produced.

3.1.2 Determination of Optimum Contact Time of Carboxymethyl Chitosan

Table 1. SSA Measurement Results from Optimum Contact Time Carboxymethyl Chitosan

No.	Time (minute)	Concentration Initial (ppm)	Final concentration (ppm)	Concentration adsorbed (ppm)
1	10	5	3.2899	1.7101
2	20	5	3.2681	1.7319
3	30	5	3.1576	1.8424
4	40	5	3.6633	1.3367
5	50	5	3.6425	13575

3.1.3 Adsorption using Atomic Absorption Spectrophotometry

Table 2. Adsorption Using Chitosan at Optimum Contact Time

No	Co Cr(VI) (ppm)	Ce Cr(VI) (ppm)	Contact Time
1	5	3.9317	20
2	10	8.3708	20
3	15	12.3991	20
4	20	17.1590	20

Description :
Co   : Initial concentration of solution
Ce   : Concentration of solution at equilibrium

Table 3. Adsorption Using Carboxymethyl Chitosan at Optimum Contact Time

No	Co Cr(VI) (ppm)	Ce Cr(VI) (ppm)	Contact Time
1	5	3.1958	30
2	10	6.0132	30
3	15	8.4762	30
4	20	10.8210	30

3.2. Discussion

3.2.1. Preparation of Carboxymethyl Chitosan

Carboxymethyl chitosan is one of the chitosan derivative compounds. The carboxymethyl chitosan is synthesised by dissolving chitosan with 2-propanol and then adding NaOH and monochloroacetic acid. The NaOH compound acts as an alkaline atmosphere builder so that chitosan will bind Na^+ ions, and when reacted with monochloroacetic acid, ion exchange will occur. Na^+ ions will be bound to Cl^- ions released by monochloroacetic acid to form a NaCl salt solution. In contrast, chitosan that has released Na+ ions will be reactive to the carboxyl group of monochloroacetic acid to form carboxymethyl chitosan.

The reaction of carboxymethyl chitosan formation can be seen in Figure 1 below :
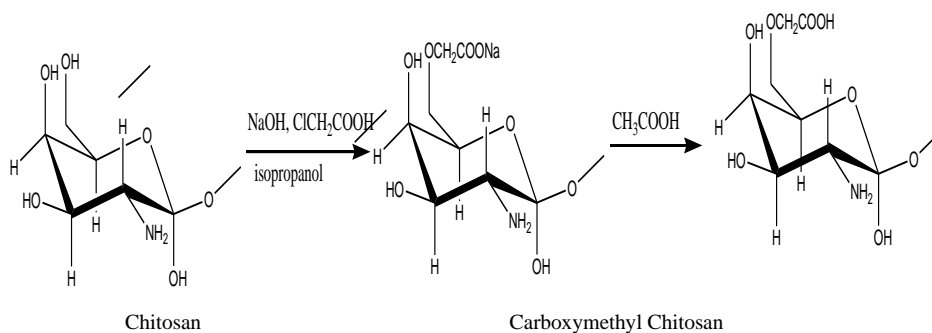
Figure 1. Carboxymethyl chitosan formation reaction
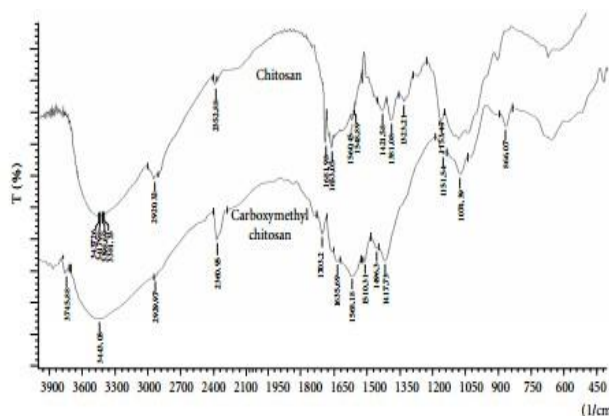
3.2.2. *Functional Group Analysis with FT-IR*

Figure 2. FT-IR spectra of chitosan and carboxymethyl chitosan

The results of functional group analysis with FT-IR showed that carboxymethyl chitosan contains -OH functional group at wave number 3425.58 cm^{-1} and C-H stretching vibration at wave number 2931.80 cm^{-1}. The increase in the intensity of the C=O absorption band that appears at wave number 1604.77 cm^{-1} shows the increase in the C=O group due to the addition of carboxylic groups (-COOH) which indicates the formation of carboxymethyl chitosan. In addition to the evidence of the appearance of -OH and C=O absorption peaks, the formation of carboxymethyl chitosan can be strengthened by the presence of ether absorption regions (C-O stretching vibrations) at wave numbers 1000-1300 cm^{-1} which are sharper than the IR spectra of chitosan.

3.2.3. *Determination of Optimum Contact Time of Cr(VI) Metal Ion Sorption by Carboxymethyl Chitosan*
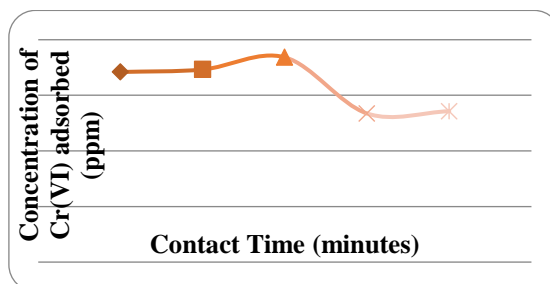

Figure 3. Effect of Contact Time on the Absorbency of Carboxymethyl Chitosan on Metal Cr(VI)

Figure 3 shows that a contact time of 10, 20, and 30 minutes shows that the longer the contact time, the more the concentration of Cr(VI) metal is absorbed. However, at a contact time of 40 minutes, there is a decrease in the absorption capacity of carboxymethyl chitosan on the metal. This is because the number of metal ions in the solution is not proportional to the number of carboxymethyl chitosan particles available, so carboxymethyl chitosan reaches a saturation point, and its absorption capacity decreases. From the picture above, it can be concluded that the optimum contact time for carboxymethyl chitosan was 30 minutes.

3.2.4.   Determination of Maximum Adsorption Capacity of Cr(VI) Sorption by Chitosan and Carboxymethyl Chitosan based on Langmuir Equation

The main objective of this study is to determine the Langmuir adsorption isotherm equation in the absorption process of chromium(VI) metal ions by chitosan and carboxymethyl chitosan. The method used to measure the adsorption process is the Atomic Absorption Spectroscopy method. The measurement results from SSA were then further analyzed based on the empirical formula of the Langmuir equation. The calculation results can be seen in Table 4 below:

Table 4. Amount of Chromium (VI) Ions **Absorbed** by Chitosan at Several Concentration Variations

No	Co Cr(VI) (ppm)	Ce Cr(VI) (ppm)	Cads Cr(VI) (ppm)	*x/m* (mg/g)
1	5	3.9317	1.0683	0.1068
2	10	8.3708	1.6292	0.1629
3	15	12.3991	2.6009	0.2601
4	20	17.1590	2.8410	0.2841

Table 5. Amount of Chromium (VI) Ions Absorbed by Carboxymethyl Chitosan at Several Concentration Variations

No	Co Cr(VI) (ppm)	Ce Cr(VI) (ppm)	Cads Cr(VI) (ppm)	*x/m* (mg/g)
1	5	3.1958	1.8042	0.1804
2	10	6.0132	3.9868	0.3986
3	15	8.4762	6.5238	0.6523
4	20	10.8210	9.1790	0.9179

Tables 4 and 5 show that the amount of Cr (VI) ions adsorbed by carboxymethyl chitosan is more significant in concentration than the amount of Cr (VI) ions adsorbed by chitosan. The relationship between solution concentration and mass of chromium metal ions adsorbed per 0.5 gram of adsorbent is shown in Figure 4 below.
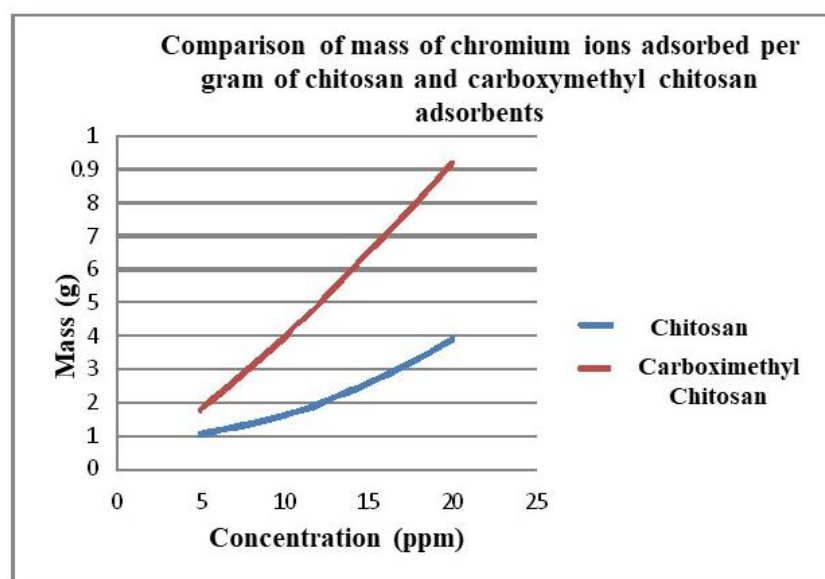

Figure 4. Comparison of mass of chromium ions adsorbed per gram of chitosan and carboxymethyl chitosan adsorbents

Figure 4 shows that the greater the concentration of Chromium (VI) metal ions, the greater the mass of chromium metal ions adsorbed by the adsorbent. Although both figures show an increasing graph, the mass of metal ions adsorbed by carboxymethyl chitosan is greater than metal ions absorbed by chitosan. According to Taboada, et.al (2003), this is due to the abundance of free electron pairs from the Nitrogen amino group in the CMC structure which can bind metal ions. In addition, carboxymethyl chitosan has a flexible and hydrophilic chemical structure. Hydrophile groups are very easily protonated in acidic solutions, generating electrostatic forces that attract the anionic part of the metal complex. While the amino group provides the active side to chelate the metal. (Mourya, et al, 2010).

Testing the adsorption isotherm pattern and maximum adsorption capacity for the absorption process of Cr (VI) metal ions by chitosan and carboxymethyl chitosan was calculated using the Langmuir equation. The Langmuir equation test was carried out using the following equation:

$$\frac{Ce}{\left(\frac{x}{m}\right)} = \frac{1}{ab} + \frac{1}{a}\,Ce$$

The greater the value of a in the Langmuir isotherm equation, the greater the adsorption capacity of the adsorbate by the adsorbent.

To determine the Langmuir isotherm equation, the $Ce/\left(\frac{x}{m}\right)$ price was calculated as shown in Table 36 and Table 7. From the table, graph mapping was then done using *Microsoft Excel* by plotting the price of $Ce/\left(\frac{x}{m}\right)$ versus Ce to obtain the Langmuir equation. The results of mapping with graphs can be seen in Figure 5 and Figure 6 below:

Table 6. Calculation of $Ce\left(\frac{x}{m}\right)$ price by Chitosan adsorbent

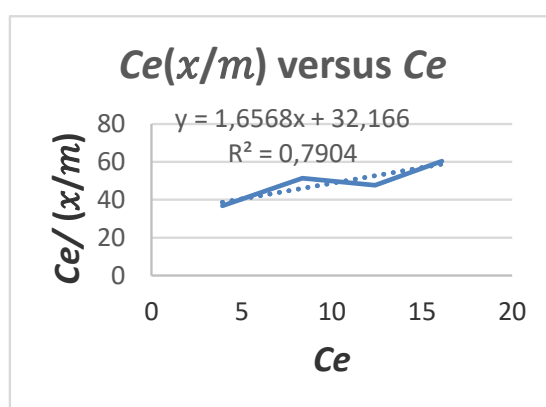| No	Co Cr (VI) (ppm)	CeCr (VI) (ppm)	$\frac{x}{m}$ (mg/g)	$Ce/\left(\frac{x}{m}\right)$
1	5	3.9317	0.1068	36.8136
2	10	8.3708	0.1629	51.3861
3	15	12.3991	0.2601	47.6705
4	20	17.1590	0.2841	60.3977

Figure 5. Langmuir isotherm Adsorption Equation by Chitosan

Table 7. Calculation of $Ce(\frac{x}{m})$ price by Carboxymethyl Chitosan adsorbent

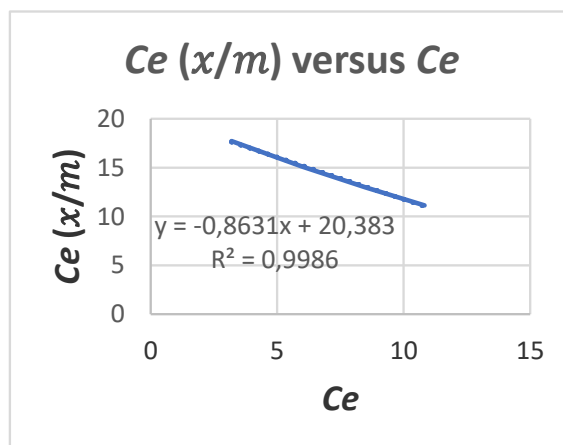| No	Co Cr(VI) (ppm)	CeCr (VI) (ppm)	$\frac{x}{m}$ (mg/g)	$Ce/(\frac{x}{m})$
1	5	3,1958	0,1804	17,7150
2	10	6,0132	0,3986	15,0858
3	15	8,4762	0,6523	12,9943
4	20	10,8210	0,9179	11,1338

Figure 6. Langmuir isotherm Adsorption Equation by Carboxymethyl Chitosan

From Figure 6, it can be seen that carboxymethyl chitosan adsorbent has a good linearization graph and has a coefficient of determination close to 1. This indicates that the Langmuir equation can be applied to the adsorption process of Cr (VI) metal ions using carboxymethyl chitosan. Unlike the case with Figure 6, which shows a non-linear graph with a value of $R^2 = 0.79$, this indicates that the Langmuir equation is unsuitable for the adsorption process of Cr (VI) metal ions by chitosan.

The Langmuir equation obtained in the adsorption process of Cr (VI) metal ions by carboxymethyl chitosan is $\frac{Ce}{(\frac{x}{m})} = -0,8631Ce + 20,383$ while the Langmuir equation obtained in the adsorption process of Cr (VI) metal ions by chitosan is $\frac{ce}{(\frac{x}{m})} = -2,2236Ce + 58,219$, and the constant prices of the two equations are shown in Table 8 below.

Table 8. Langmuir Constant for the Adsorption of Cr (VI) Metal Ions by Chitosan and Carboxymethyl Chitosan

Adsorbent	Constant	Value
Chitosan	a	0,60
	b	0,05
Carboxymethyl Chitosan	a	1,16
	b	0,04

4. Conclusion:

1. The Langmuir isotherm model is more appropriate to use in the adsorption process of Cr (VI) metal ions by carboxymethyl chitosan than in the adsorption process of Cr (VI) metal ions by chitosan. This is evidenced by the excellent linearization in the Langmuir isotherm graph of chromium metal ion adsorption by carboxymethyl chitosan, and has a coefficient of determination close to 1.

2. The greater the concentration of Cr (VI) metal ions, the greater the mass of metal ions adsorbed by chitosan and carboxymethyl chitosan. However, the mass of Cr (VI) metal ions adsorbed by carboxymethyl

chitosan is more than the mass of Cr (VI) metal ions adsorbed by chitosan. The largest mass of Cr (VI) metal ions adsorbed by carboxymethyl chitosan is at a concentration of 20 ppm, which is 0.9179 mg of Cr metal ions absorbed by 0.5 g carboxymethyl chitosan.

3.   The adsorption capacity of carboxymethyl chitosan is greater than the adsorption capacity of chitosan. The maximum adsorption capacity (a) of carboxymethyl chitosan on Cr (VI) metal ions is 1.16 mg/g, while the maximum adsorption capacity of chitosan (a) = 0.60 mg/g.

5. Acknowledgements

6. Conflict of Interest

Authors declare no conflicts of interest

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