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Original Research Article

Removal Efficiency of Total Chrome (Cr-T) from Textile Industry Wastewater PT. X with Sodium Bentonite Using the Adsorption Method

Etih Hartati[1]*, Raisa Nur Azizah[1], Dyah Marganingrum[2]
[1]Environmental Engineering Department, Faculty of Civil Engineering and Planning, Institut Teknologi Nasional, Jalan P. H. H. Mustofa No. 23, Bandung, Indonesia 40124
[2]National Research and Innovation Agency, Jalan Cisitu Lama No. 12, Bandung, Indonesia 40135
*Corresponding Author, email: etih@itenas.ac.id

Abstract
As much as 10-50% of dye wastewater from the dyeing process is discharged directly into the environment. Chromium is the metal most often found in textile industry wastewater, one of which comes from dyes of the Congo Red type, so processing is required. One of the treatments to remove total chromium from textile industry wastewater is adsorption, with sodium bentonite as an adsorbent. This study aimed to determine the optimum efficiency and processing of total chromium using sodium bentonite as an adsorbent with a batch system and to determine the appropriate type of isotherm. The method used to test total chromium was the standard addition method which was then measured using an AAS (Atomic Absorption Spectrophotometry). The variables studied were the effect of wastewater pH, sodium bentonite and grain size of wastewater on the efficiency of total chromium removal. The types of isotherms tested are Langmuir and Freundlich isotherms. In removing total chromium with sodium bentonite, optimum conditions were obtained at pH 8 with a grain size of 80 mesh and a volume of 50% wastewater with a removal efficiency of 98.08%. The appropriate isotherm model for sodium bentonite is the Freundlich isotherm.

Keywords: Adsorption; atomic absorption spectophotometry; sodium bentonite; total chrome

1. Introduction

Environmental problems caused by the textile industry can be divided into four classes: air, water, solid pollution, and noise (Körlü, 2019). The dyeing process in the textile industry is a process that produces large amounts of waste every day. The waste is in the form of mud, solids, and liquids consisting of heavy metals such as iron, tin, nickel, copper, zinc and chromium (Islam & Mostafa, 2018). 10-50% of the dyestuff wastewater from the dyeing process is discharged directly into the environment (Sarwar & Khan, 2022). These textile industry effluents, will end up in nearby waterways, agricultural fields, irrigation channels, and finally will enter water bodies such as rivers, seas, etc. (Islam and Mostafa, 2018). Industrial effluents cause variations in the physical, chemical, and biological properties of waters with continuous changes in turbidity, odour, noise, temperature, pH and other parameters that will adversely affect public health, livestock, wildlife, fish and biodiversity (Islam and Mostafa, 2018).

The textile industry is one of the industries whose production process uses a very large amount of water. The technology of this production process is generally carried out by dry process or wet process. Dry process in the textile industry, when the process does not require water as a medium, but only as an auxiliary material. Examples of this process are the process of making yarn (spinning), making fabric (weaving), knitting and making finished fabric (garment). As for the wet process, that is when the textile industry uses water as the main medium in the process, in other words, this process cannot take place without water. The textile refinement process is included in the wet process which will cause the most environmental pollution. The textile industry that carries out wet processes includes the textile industry of bleaching, dyeing, stamping and others (Moertinah, 2008).

Heavy metals are hazardous, non-biodegradable substances that have existed in the environment for a long time and which, in large concentrations is a toxic pollutant carcinogenic to the environment (Bharti & Sharma, 2021). Chromium is one of the most common heavy metals in the textile industry (Nurventi, 2019). Chrome metal (Cr) is a heavy metal that is toxic in the body. Chrome metal usually exists as Cr^{3+} and Cr^{6+} ions. Stable at +3 oxidation, while +6 oxidation is a strong oxidant (Hasyyati, Hartati, & Djaenudin, 2020). Chromium compounds in the textile industry are used in dyeing fabrics with direct dyes in the form of dichromates such as Congo red (C.I Direct Red 28).

The adsorption method is one of the most effective and efficient methods for removing heavy metals contained in wastewater (Prathiksha & Prabhu, 2018). Bentonite is one type of adsorbent that can be used for the adsorption process (Prathiksha & Prabhu, 2018). The adsorption capacity depends on the presence of micro and mesopores, besides that bentonite is easily available worldwide (Prathiksha & Prabhu, 2018). Bentonite expands to 15 times its dry volume when wetted (Fang & Chaney, 2016). There are several types of bentonite that exist in nature, one of which is Sodium Bentonite. This type of bentonite has a higher expanding power than other types (Mukarrom, 2017).

Bentonite is a layered aluminium silicate clay consisting of montmorillonite and clay minerals. Bentonite is characterized by its adsorption properties due to its high surface area and ability to exchange (Amutenya et al., 2022). Bentonite has advantages such as a high surface area for adsorption, high porosity, and high cation exchange capacity and low cost. Modifying the clay structure helps increase the surface area and absorption sites, thereby increasing the adsorption capacity (Prathiksha & Prabhu, 2018). One of the fundamental physical properties of bentonite is ion exchange capacity, surface area power, rheological binding and releasing properties, and plasticity (Putri, 2013).

There are several types of bentonite that exist in nature, one of which is Sodium Bentonite. Sodium Bentonite is a type of monmorillonite that has single water layer particles containing exchangeable Na + cations. This type of bentonite has the ability to expand when dipped in water and can be dispersed for some time in water. The Na2O content in this type of bentonite is generally greater than 2% (Mukarrom, 2017). Sodium bentonite has the power to expand up to eight times when dipped in water, and remains dispersed for some time in water. Colloidal suspensions have a pH: 8.5-9.8 (Putri, 2013).

The most commonly used adsorption isotherm models are the Freundlich isotherm and the Langmuir isotherm. The adsorption isotherm is the equilibrium relationship between the concentration and the fluid phase in the adsorbent particles at a specific temperature (Lestari, Mahatmanti, & Haryani, 2016). According to Freundlich, every porous solid object has the potential as an adsorbent, and the adsorbent physically adsorbs it (Zein, Wardana, Refilda, & Aziz, 2018). The Langmuir isotherm assumes adsorption occurs in a monolayer on a uniform surface with a set number of sites or allowances, once a site is filled, no further allowance occurs on that site (Zein et al., 2018).

The pH point of zero (pHpzc) charges is the pH of the adsorbent suspension, which does not affect the adsorbent's acidic or basic functional groups (Fadilla, 2021). pH point of zero charges is when the initial pH value is equal to the final pH (the pH value at the intersection of a straight line from the initial pH curve to the final pH). At this pH value, the adsorbent no longer contributes to pH.

The effect of pH on the adsorption process is when pH lower than pzc then the solution is acidic encourages protons (H^+) more than OH^- ions so that the adsorbent surface is positively charged and attracts anions, whereas when the pH greater than pzc then the adsorbent surface is negatively charged so it attracts cations but rejects anions (S. H. Dewi and Ridwan, 2018).

Atomic Absorption Spectrometry (AAS) is a quantitative method of metal analysis by measuring the concentration of an element by passing light at a specific wavelength emitted by the element's radiation source through the particular element of the sample (Abrham and Gholap, 2021).

The novelty of this research is that there are many variations used, where in other studies usually only compare one of the existing research variations, which include pH variation, variation of % volume of wastewater, and variation of sodium bentonite grain size. Besides that the use of adsorbents in this study is specifically mentioned, while in other studies only bentonite is mentioned in general.

This study aimed to determine the optimum efficiency and processing of total chromium using sodium bentonite as an adsorbent with a batch system and to determine the appropriate type of isotherm.

2. Methods

The raw wastewater material comes from the textile industry's inlet Waterwater PT. X. and the picture can be seen at **Figure 2.** The steps of this research consisted of preparing wastewater samples with variations in pH and volume concentration of wastewater, followed by absorption of total chromium (Cr-T) using sodium bentonite using various mesh sizes.

Figure 2. Inlet of wastewater PT. X

The wastewater samples came from the inlet of PT. X with sampling using the grab sampling method refers to Indonesian National Standard (SNI) 6989.59:2008. The sample is then put into a jerry can with a capacity of 20 L.

Table 1. Wastewater quality parameter measurement method

No	Parameter	Unit	Used Method	Sources
1	pH	-	Potentiometric	SNI 6989: 2019 About how to test the degree of acidity (pH) using a pH Meter
2	Total Chromium (Cr-T)	mg/L	Absorption Atomic Spectroscopy (AAS) as a Flame	APHA. 2017. Standard Methods for The Examination of Water and Wastewater 23th Edition. America Public Health Association Section 3030 A

The bentonite is separated using a sieve analysis method where the bentonite that has been chopped is then sieved. The sizes of bentonite used are 40, 60, 80, and 100 mesh. This refers to previous research conducted by (Handayani & Elvi, 2013). The determination of the value of pHpzc on Na-bentonite aims to determine the surface charge of the adsorbent more clearly. The principle is to describe the surface condition of the adsorbent when the charge density is equal to zero. This study was carried out by adjusting the wastewater at pH 2, 4, 6, 8, 10, and 12 which were then added to 0.15 grams of bentonite per the research conducted by Fadilla (2021).

In this study, the first wastewater was varied into three pH variations, namely pH 6, 8 and 10. The determination of the pH variation was regulated based on the pH value of the point of zero charges (pHpzc) of the sodium bentonite used. The average pHpzc value of sodium bentonite is 8, so a value of 6 represents an acidic pH or pH below the pHpzc value, while a pH value of 10 represents an alkaline pH or a pH above the pHpzc value.

After varying the pH, each sample varied the persen of the volume of wastewater. The variations used are 25%, 50%, 75%, and 100%. The total volume used is 200 ml. In all variations, 1 gram of bentonite was added, followed by a stirring process using a stirrer for 30 minutes at a speed of 30 rpm. The duration of stirring and speed refers to a study conducted by Fadilla (2021), where the industrial wastewater used has an optimum contact and stirring time at a speed of 30 rpm with a time of 30 minutes. After that, the sample was measured using Atomic absorption spectroscopy (AAS) with the calibration method, where the wastewater sample was added to a standard solution whose concentration was known to disguise the matrix between the sample and the standard. Calibration method is a method that is often used in determining heavy metal concentrations (Setiawan, 2022). Heavy metal series made on heavy metal parameters using 1 blank that is free of heavy metals and at least 3 concentration series of each metal (APHA, 2017). Making a series of standards in this study amounted to 5 with reference to the optimum concentration of total chromium. The standard solution series used can be seen in **Table 2**.

Table 2. Standardised series for heavy metal measurement

No.	Test Parameters	Optimum Concentration (mg/L)[1]	Standardised Series Used
1	Total Chromium (Cr-T)	0.2 - 10	0.2; 0.5; 1; 5; 10

(Source: [1] Astm E 663-86, 1991 About Standard Practice for Flame Atomic Absorption Analysis)

The efficiency of Removal as represented in Eq. 1

$$\%RE = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

With the description of the formula:

RE : Removal efficiency
C_o : Concentration before adsorption
C_e : Concentration after adsorption

The Langmuir's isotherm as represented in Eq. 2, where, q_{max} represent the maximum adsorption capacity (mg/g) and KL (L/mg) is the Langmuir's isotherm constant

$$\frac{Ce}{qe} = \frac{1}{q_{max}} Ce + \frac{1}{K_L \cdot q_{max}} \quad (2)$$

Based on Equation (2), a linear graph is then made with the value of 1/qe as the y-axis and 1/ce as the X-axis. So then the slope and intercept values can be obtained (Zein et al., 2018). The description of the formula above is as follows:

C_e : concentration of metal ions in solution after removal
q_e : adsorbat absorbed (mg/g)
KL : Langmuir constant (L/mg), where the value is 1
q_{max} : optimum removal capacity (mg/g)
Co : initial concentration of metal ions in solution
KL : Langmuir constant (L/mg)
RL : separation factor or equilibrium parameter
If the value of RL = 0, the adsorption is unfavourable or irreversible,
If 0 < RL < 1, it indicates favourable adsorption,
If RL = 1 adsorption is linear or unfavourable, and

If RL > 1, then adsorption is unfavourable.

The Freundlich's isotherm as represented in Eq. 3, Where, K_f is the Freundlich's conctant and used to measure the adsorption capacity, and 1/n is the adsorption intensity.

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (3)$$

Based on Equation (3), a linear graph is then made with the log qe value as the y-axis and log Ce as the X-axis. So then the slope and intercept values can be obtained (Zein et al., 2018). The description of the formula above is as follows:

Where:

Kf : Freundlich constant, obtained by making the antilog of the intercept value
n : adsorption intensity, obtained from 1/slope
q_e : adsorbed adsorbate (mg/g)
C_e : metal ion concentration in solution after removal

3. Result and Discussion

The initial characteristics of the textile industry wastewater can be seen in **Table 3.**

Table 3. Initial characteristics of textile industry wastewater PT. X

Parameter	Quality Standard	Results
Total Chromium (Cr-T) (mg/L)	1[1]	1.41
pH	6.0 – 9.0[1]	6.5

Based on the results in **Table 3**, the parameters were tested and then compared with Regulation No 16 of the Minister for the Environment, Annex II of 2019 and Government Regulation No 22 Annex VI of 2021. Sampling was carried out three times at different times, so a characteristic test was carried out on each sample. Some parameters exceed the quality standards, so there is a need for processing so that the liquid waste is produced by PT. X can meet the quality standards.

pHpzc is the intersection point between the initial and final pH curves (S. H. Dewi and Ridwan, 2018). In this condition, the pH of the suspension of the adsorbent does not contribute to the presence of acidic and basic functional groups (Fadilla, 2021). The measurement results of pHpzc that the surface of sodium bentonite has a neutral charge at pH 8. According to the literature from Dewi and Ridwan (2018), if the pH value is less than pHpzc then the surface of the adsorbent will be positively charged and attract anions. In contrast, if the pH value is more than pHpzc then the surface of the adsorbent will be negatively charged and attract cations. The illustration of the equation that occurs at pHpzc, can be seen in **Figure 3**.

$$\text{Surface}^{+}{}_{(n+1)} \underset{+H^{+}}{\overset{+OH^{-}}{\rightleftharpoons}} \underset{pH_{pzc}}{\text{Surface}^{o}{}_{n}(p)} \underset{+H^{+}}{\overset{+OH^{-}}{\rightleftharpoons}} \text{Surface-}_{(n+1)}$$

Figure 3. Graphic of pH_{pzc}
(Source: Fadilla, 2021)

Several variations of pH are used in the adsorption process, namely pH 6, 8, and 10. The total chromium-reducing efficiency data can be seen in **Figure 3**.

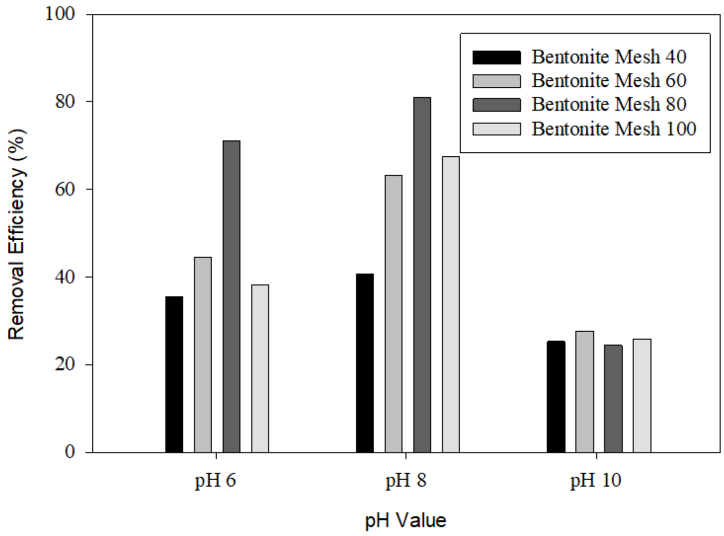

Figure 4. Effect of pH on the average absorption efficiency of total chromium

Based on **Figure 4**, it can be seen that the bentonite adsorbent has the highest average efficiency at pH 8 with a bentonite size of 80 mesh, which is 80.94%. So it can be concluded that the optimum pH is when bentonite is at the same pH as the pH point of zero charges. Based on the research title Study of Reduction of Chromium Metal (Cr) Levels in Electroplating Artificial Waste using the Precipitation and Adsorption Method conducted by Madalena (2019), the Cr metal adsorption process is getting better under acidic conditions. This is because, at alkaline pH, the cr ions tend to form hydroxide complexes. So it will be challenging to carry out the adsorption process. This is supported by the results of research conducted where the optimum efficiency is achieved when the pH of the wastewater is 3. The pH value will affect the ability of Cr-T absorption by bentonite, where when the pH value of acid chromium < 3, then the ion chromium is an anion, whereas when the pH of chromium is >3, the chromium ion is a cation (D. S. Dewi and Dewi, 2019). In the adsorbent (bentonite), when the pH value is < pHpzc, the bentonite is positively charged or attracts and attracts anions. So the lower pH value will cause more Cr-T metal to be absorbed, which is by the results of research conducted by (Dewi & Dewi, 2019) entitled The Effect of Contact Time and pH on Cr (Vi) Ions in Textile Waste Using Bioadsorbents Guava Leaves and Tea Leaves. In the experiment, the most significant average absorption efficiency value was not in the most acidic variation but in conditions when the bentonite pH was the same as the pHpzc. The thing that affects is that the bentonite charge above or below the pHpzc value will interfere with the absorption of Cr-T due to the presence of protons which will then affect the ability of sodium bentonite to absorb Cr-T. Another thing which is the effect of pH on the efficiency of Cr-T metal removal, according to Benefield's (1992) theory, is that Cr can precipitate well in the pH range of 8 to 9.5 because its solubility is minimal (close to 0).

According to Checinel and de Souza (2014), one factor that influences the adsorption process is the pore size and surface area of the adsorbent, where the smaller the pore size, the higher the surface area. In this study, the adsorbent used was sodium bentonite. The grain size of sodium bentonite used consists of 4 variations, sizes 40, 60, 80, and 100 mesh. Theoretically, the removal efficiency using adsorbents will increase with the smaller the particle size of the adsorbent, this is because the smaller the particle size, the surface area will increase, so that more ions will be absorbed by the adsorbent surface (Wijayanti et al., 2019).

Table 3. Cr-T removal efficiency at optimum pH

pH	% volume of wastewater	Bentonite Separation (Mesh)			
		40	60	80	100
		Removal Efficiency (RE) %			
8	25%	39.62	78.91	97.75	97.47
	50%	33.51	96.90	98.08	92,71
	75%	54.71	21.85	79.69	88.00
	100%	35.21	55.57	48.25	54.79

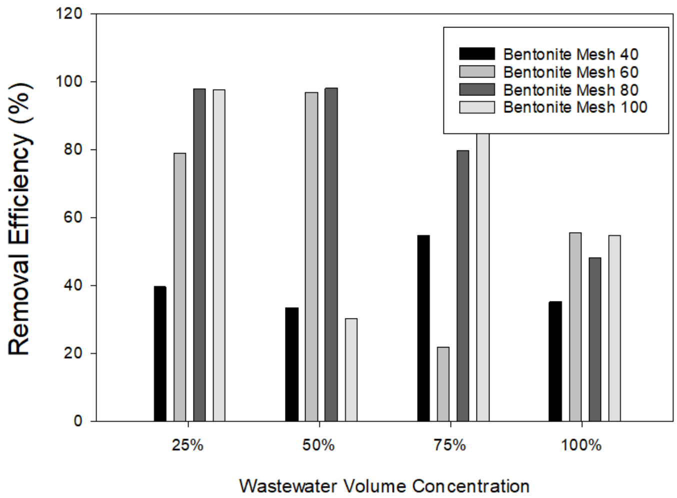

Figure 5. Effect of mesh size on total chromium absorption efficiency at optimum pH

Based on **Table 3** and **Figure 5**, it can be seen that the largest Cr-T removal efficiency is in the variation of the size of bentonite 80 mesh with a volume concentration of 50% wastewater, which is 98.08%, then on the size of bentonite 100 mesh with a volume concentration of 25% wastewater which is 97.47%. The processing efficiency value of total chromium at each concentration and variation of bentonite grain size fluctuates. Still, the average value of removal efficiency increases with the smaller grain size of bentonite. This is by the results of research conducted by Handayani (2013), which states that the finer the particle size, the higher the adsorption capacity. This statement is corroborated by the results of his research, where the efficiency of absorption of methylene blue colour by bentonite with a size of 100 mesh is greater than that of 40, 60, and 80 mesh.

Based on **Table 3** at the most optimum grain size (100 mesh), it can be seen that the relationship between % volume of wastewater and removal efficiency is that the greater the % volume of wastewater, the removal efficiency will decrease. As mentioned by Jakfar (2020), one of the influencing factors is the concentration of adsorbate. Where, the more the volume of wastewater, the concentration of adsorbate will increase. According to the literature (Charazińska et al., 2021), the higher the concentration value of the adsorbate, the smaller the efficiency value of its absorption, where the heavy metal removal efficiency of the 5 health facilities tested decreased along with the increase in the concentration of wastewater used. So it can be concluded that with the increasing volume of wastewater added, the removal efficiency of total chrome decreases.

Based on the Lestari literature (2016), the adsorption isotherm is the equilibrium relationship between the concentration and the fluid phase in the adsorbent particles at a specific temperature. The isotherm model that is often used is the Langmuir and Freundlich isotherm. Langmuir isotherm assumes that adsorption occurs only in one layer (monolayer), while the Freundlich isotherm adsorption occurs in several layers (multilayer) or physical heterogeneity. Langmuir and Freundlich's isotherm data can be seen in **Table 4** until **Table 5** and **Figure 6** until **Figure 7**.

Table 4. Langmuir isotherm

a	b	q_{max}	1/KL	R_L	R^2
2.313	0.372	0.432	6.210	0.217	0.822

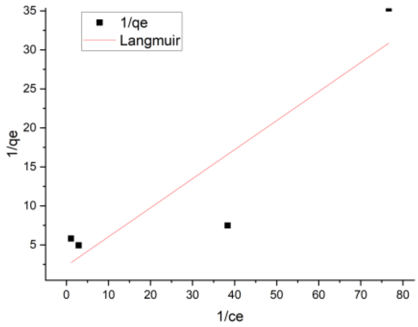

Figure 6. Linear relationship graph of langmuir's isotherm

Table 5. Freunlich isotherm

a	b	1/n	K_f	R^2
-1.132	0.747	1.339	0.074	0.985

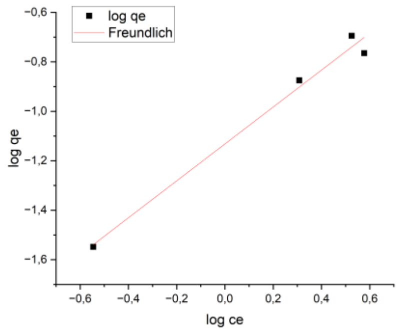

Figure 7. Linear relationship graph of freundlich's isotherm

The graph of the linear relationship between the Langmuir isotherm and the Freundlich isotherm was used to determine the adsorption pattern on the adsorbent surface of sodium bentonite. **Figure 5** shows a graph of the Langmuir and Freundlich isotherms. Based on the results of research and analysis, the R^2 value of the Langmuir isotherm is 0.822, and the Freundlich isotherm is 0.985. The R^2 value for the Freundlich isotherm is greater than the Langmuir isotherm, which means that the adsorption of Cr-T using sodium bentonite tends to follow the Freundlich equation where the absorption occurs in several layers of the adsorbent (multilayer) or is physically heterogeneous (Physisorption). According to Apriyanti (2018), physisorption is an adsorption event that occurs due to physical forces characterized by a little heat of adsorption. The Kf value obtained from the Cr-T adsorption test results using sodium bentonite is 0.074, and the n value is 0.747. The n and Kf values are parameters that indicate the adsorption capacity of an adsorbent. The greater the value of Kf, the adsorption power of the adsorbent being tested will increase (Fadilla, 2021).

The application for the function of knowing the isotherm model on Sodium Bentonite in industry is to determine the bonds that occur in Sodium Bentonite so that it can be known how to break the bond more precisely. The disconnection serves to reuse sodium bentonite that has been used as an adsorbent. So that based on the isotherm model, bond breaking on Sodium Bentonite is sufficient to do with the heating process, because the bond formed is heterogeneous physics in multilayer.

4. Conclusion

Based on the results of the research and analysis related to the absorption of total chromium from the waste water of the textile industry, PT. X, it can be concluded that the optimum efficiency and treatment of total chromium using sodium bentonite as adsorbent was achieved at pH 8 with a grain size of 80 mesh sodium bentonite at 50% volume of wastewater and the adsorption model tends to follow the Freundlich with R2 value of 0.985. The weakness of this research was some characteristics of the adsorbent not studied, so it cannot be concluded with certainty the elements contained, functional groups, pore size and surface area of the variations in the adsorbent.

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