Modification and Application Study of Activated Natural Zeolite for the Treatment of Liquid Waste from Chemical Laboratory

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Article Info

Abstract

Natural zeolite from Malang Regency is a raw material that can be used as an adsorbent for heavy metal waste. However, this natural zeolite needs activation and optimization to be utilized maximally as an adsorbent. This study was conducted for both physical and chemical activation of natural zeolite. Characterization results of XRD indicated that the natural zeolite possesses crystalline phases and is of the mordenite type. Based on the XRF results, the Si/Al ratio increased from 5.768 to 6.119 after activation. Based on the characterization results using the BET method with SAA analysis, the surface area of non-activated natural zeolite was determined to be 20.8045 m²/g, while activated natural zeolite had a surface area of 137.8196 m²/g. Results of the adsorption study in treating liquid laboratory waste using simulated Pb and Cr metal wastes demonstrated that activated natural zeolite performed more effectively as an adsorbent than non-activated natural zeolite. The adsorbent's optimum mass was 0.3 grams, resulting in an adsorption percentage of 97.43% for Pb and 97.56% for Cr, with a contact time of 30 minutes at pH 6. The adsorption kinetics of Pb and Cr metals were described using a pseudo-second-order rate equation. The adsorption of Pb and Cr was depicted using the Langmuir equation, indicating the monolayer formation on the homogenous adsorbent surface during the adsorption process. The activated natural zeolite has the potential to be employed as an independent adsorbent in the treatment of heavy metal waste.

1. Introduction

A laboratory is a facility for conducting learning and research experiments. Laboratories are an essential part of enhancing the knowledge and skills of students. The increased number of Chemistry students results in an increased demand for laboratory usage. In 2022, 319 new students joined the Department of Chemistry, Universitas Negeri Malang, Indonesia. The high activity level in laboratories, whether for learning or research, increases the volume of liquid waste. The liquid waste produced from learning and research activities contains heavy metals, including Pb, Co, Cr, Cd, and Fe. Direct disposal of heavy metal ions into the environment can lead to water and soil pollution [1]. These metals are toxic and carcinogenic, so special handling is required before they are disposed of in waste collection.

According to Minister of Health of The Republic of Indonesia Number 32 [2], the maximum permissible limits of certain metals in water for sanitation purposes are as follows: Fe at 1 mg/L, Mn at 0.5 mg/L, Cd at 0.005 mg/L, Zn at 15 mg/L, and Pb at 0.05 mg/L. Meanwhile, based on the criteria set by the US Environmental Protection Agency (US EPA) for drinking water and wastewater quality, the maximum allowable concentrations are as follows: Fe at 300 µg/L, Pb at 15 µg/L, Cr 100 µg/L, Mn at 50 µg/L, Hg at 2 µg/L, Zn at 5,000 µg/L, and Ag at 100 µg/L. Heavy metals cannot naturally degrade and may accumulate in living organisms [3]. If these heavy metals enter the body, they can cause metabolic disturbances and cancer [4]. Therefore, before disposal, treatment should be carried out to reduce the concentration of heavy metals [5].

Among heavy metals, lead is a toxic element. Lead can disrupt the central nervous, kidneys, liver, and

digestive systems [6]. Meanwhile, chromium (VI) in water can cause diarrhea, bladder cancer, liver and kidney damage, and skin issues [7]. Cr (VI) is highly hazardous to humans due to its toxic and carcinogenic properties [8]. Therefore, it is crucial to undertake treatment measures to reduce the concentrations of Pb and Cr metals generated from laboratory activities, considering the extreme toxicity and high usage volume of these metals. However, no wastewater treatment facility is currently available in the Chemistry Laboratory, necessitating research innovation to address the heavy metal wastewater treatment problem using natural materials.

Indonesia has established regulations for handling hazardous waste, including heavy metal waste. One of the regulations governing this matter is the Minister of the Environment and Forestry of the Republic of Indonesia No. 6 of 2021 [9]. This regulation primarily aims to protect the environment and human health from the adverse effects of heavy metal waste. This regulation is crucial in maintaining environmental sustainability by regulating various aspects, including pollution control, waste management, treatment, recovery, and monitoring. Furthermore, Minister of the Environment and Forestry of the Republic of Indonesia No. 6 of 2021 [9] also promotes more sustainable research in handling heavy metal waste. This creates opportunities for developing innovative methods and technologies to reduce the negative impacts of heavy metal waste and safeguard a healthier environment for the community.

Several methods have been employed to reduce the concentration of heavy metals in liquid waste, including ion exchange resin [10], membrane filtration [11], biosorption [12], and adsorption [13]. Among these methods, adsorption is considered the most effective due to its simplicity, low cost, and ease of implementation [14]. Zeolite is one of the materials that can be used for the adsorption of heavy metals. Some advantages of using zeolites as adsorbents include their high adsorption capacity, resistance to saturation, high selectivity, and ease of regeneration [15]. The combination of high adsorption capacity, saturation resistance, selectivity, and ease of renewal makes zeolites a preferred choice in various applications such as water purification, gas processing, and chemical separation industries. Zeolite is abundant in nature, yet its utilization is not fully optimized. The mordenite zeolite, in particular, can serve as an adsorbent for both liquids [16] and gases [17]. The zeolite adsorbs heavy metal ions through an ion exchange mechanism [18], making it possible for regeneration [19]. Consequently, zeolite is widely utilized as an adsorbent in liquid waste treatment.

Based on the statements presented, handling the waste from research using environmentally friendly and efficient natural materials is essential. Activated natural zeolite can be utilized as an adsorbent for heavy metal waste. However, this natural zeolite needs activation and optimization to maximize its use as an adsorbent. This research aims to modify natural zeolite both physically and chemically. Subsequently, an adsorption study of activated natural zeolite was carried out to process liquid waste from a laboratory.

2. Experimental

2.1. Materials and Tools

The materials used in this research included natural zeolite sourced from Malang, East Java, Indonesia, HF 40%, HCl 37% (AR), NH_4Cl (AR), $Pb(NO_3)$ (AR), $CrCl_6 \cdot 3H_2O$ (AR), acetic acid glacial, NH_4OH, distilled water, deionized water, universal pH indicator, fine filter paper, and laboratory liquid waste.

The tools used in this research included mortar and pestle, 100 mesh sieve, chemical glassware, stirring rod, spatula, funnel, evaporating dish, alumina crucible, desiccator, reflux apparatus set, retort stand and clamp, distilled water bottle, measuring glass, volumetric flask, Erlenmeyer flask, dropper pipet, analytical balance, hotplate stirrer, oven (Memmert), furnace (Thermolyne), shaker (Eyela), X-ray Diffraction (Rigaku MiniFlex 600), X-ray Fluorescence Spectrometer (Rigaku NEX DE), Surface Area Analyzer (Micromeritics TriStar II Plus 3.01), and Atomic Absorption Spectroscopy (Thermo Scientific iCE 3000).

2.2. Preparation and Activation of Natural Zeolite

Natural zeolite was powdered using a mortar and pestle until it became a fine powder and then sieved to a 100-mesh size. The natural zeolite powder was washed using distilled water and heated in an oven at 105°C for 4 hours. Next, the zeolite was calcined in a furnace at a temperature of 505°C for 2 hours. The dried zeolite was then treated with a 1% HF solution and refluxed for 30 minutes. It was subsequently washed with deionized water until neutral and then dried in an oven for 2 hours at 105°C. Following this, the zeolite was calcined at a temperature of 505°C for 4 hours in the furnace. The dried zeolite activated with 1% HF was then treated with a 6 M HCl solution and refluxed for 6 hours. It was then washed with deionized water until neutral. Next, it was dried in an oven at 105°C for 4 hours and calcined in a furnace at 505°C for 2 hours.

The zeolite activated with 1% HF and 6 M HCl was further treated with a 1 M NH_4Cl solution and refluxed for 6 hours. After 6 hours, it was washed with deionized water until neutral and dried in an oven at 105°C for 4 hours. Subsequently, it was heated in a furnace at 505°C for 4 hours. The dried activated zeolite was referred to as Activated Natural Zeolite (ANZ).

2.3. Characterization Adsorbents of the Natural Zeolite and the Activated Natural Zeolite

The natural zeolite and the activated natural zeolite were then subjected to characterization using X-ray Diffraction (XRD), X-ray Fluorescence (XRF), and Surface Area Analyzer (SAA). The adsorption of heavy metal waste using the activated natural zeolite as an adsorbent was carried out with variations in mass, contact time, adsorbent concentration, and pH. The concentrations before and after adsorption were analyzed using Atomic Absorption Spectroscopy (AAS).

2.4. Adsorption Study

2.4.1. Determination of Optimum Adsorbent Mass

Forty mL of liquid waste was mixed with 0.1 gram of adsorbent and then agitated using a shaker at 100 rpm for 30 minutes. After 30 minutes, it was filtered, and the filtrate was collected for analysis using AAS. The same procedure was repeated for laboratory waste adsorption with variations in the adsorbent mass of 0.15, 0.2, 0.25, and 0.3 grams.

2.4.2. Determination of Optimal Contact Time

Forty mL of liquid waste was mixed with the adsorbent at the optimum adsorbent mass condition. It was then agitated using a shaker at 100 rpm for 5 minutes. After 5 minutes, it was filtered, and the filtrate was collected for analysis using AAS. The same procedure was repeated for laboratory waste adsorption with variations in contact time of 10, 20, 30, and 45 minutes.

2.4.3. Determination of Optimal Adsorbate Concentration

Forty mL of liquid waste was mixed with the adsorbent. It was then agitated using a shaker at 100 rpm. Adsorption was carried out with the optimum mass and contact time. Then, it was filtered, and the filtrate was collected for analysis using AAS. The same procedure was repeated for laboratory waste adsorption with variations in adsorbate concentration of 2, 4, 6, 8, and 10 ppm.

2.4.4. Determination of Optimal pH

The adsorbent was mixed with 40 mL of liquid waste at varying pH levels of 2, 4, 7, 8, and 10. Glacial acetic acid was added to obtain acidic pH, while NH_4OH was added for basic pH. The mixture was then agitated using a shaker at 100 rpm. Adsorption was performed with the optimum mass, contact time, and adsorbate concentration. Then, it was filtered, and the filtrate was collected for analysis using AAS.

3. Results and Discussion

3.1. Preparation and Activation of Natural Zeolite

The natural zeolite from Malang is a greenish-gray chunk. Before activation, the natural zeolite was initially ground using a mortar and pestle and then sieved to a 100 mesh-size. Subsequently, natural zeolite was washed with deionized water to remove impurities. Activation was carried out through both physical and chemical methods. The physical activation involved heating the zeolite in an oven at 100°C for 2 hours, and followed by calcination at 505°C for 4 hours. The heating process aimed to evaporate water and remove impurities that might block the zeolite pores [20].

Chemical activation, on the other hand, involved immersing the zeolite in solutions of 1% HF, 6 M HCl, and 1 M NH_4Cl. Chemical activation, especially using acids, is a common method for modifying zeolites. The immersion in a 1% HF solution aimed to remove free silica, thus enhancing the mesopore volume [21]. The immersion was carried out for 30 minutes to avoid structural damage.

Silicon reacts with HF to form the volatile gas SiF_4. The reaction that occurs is shown in Equation (1).

$$SiO_2(s) + 4\,HF(aq) \rightarrow SiF_4(g) + 2H_2O(l) \tag{1}$$

The subsequent activation involves the natural zeolite in a 6 M HCl solution for 6 hours. Acid activation is often referred to as the dealumination process. During dealumination, anions in the solution interact with metal ions to form salt compounds. The salts were then removed by deionized water until the pH was neutral [17]. Dealumination was carried out to eliminate inorganic impurities and Al_2O_3 oxides. It leads to an increase in the Si/Al ratio and surface area [22]. Aluminum in the zeolite framework reacts with the HCl solution to form $AlCl_3$ [23].

The final activation step included treating the natural zeolite with NH_4Cl solution. The goal was to remove water and inorganic impurities through an ion exchange mechanism [24]. The reaction between NH_4^+ ions and metal cations in the zeolite results in the formation of NH_4–zeolite [25]. Upon heating, NH_4–zeolite is converted to H–zeolite and releases NH_3 gas. The activation reaction of natural zeolite is illustrated in Figure 1.

Physical activation is achieved through a heating process. The purpose of heating is to release water molecules and entrapped gas impurities within the zeolite pores, thereby increasing the surface area, crystallinity, and pore volume of the zeolite [17, 26]. After the activation process, the activated zeolite is obtained with a bone-white color. Both the natural zeolite and the activated natural zeolite were then characterized using X-ray Diffraction (XRD), X-ray Fluorescence (XRF), and Surface Area Analyzer (SAA). Figure 2(a) was non-activated natural zeolite, and Figure 2(b) was activated natural zeolite.
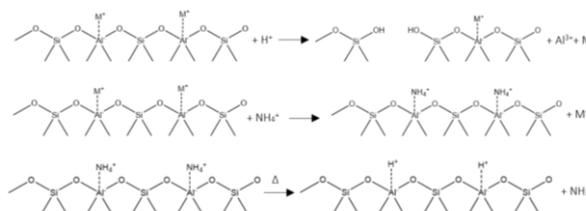

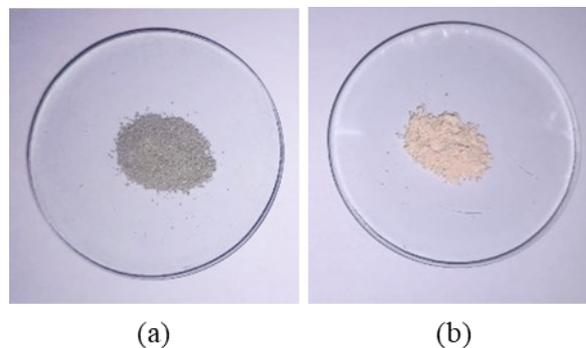**Figure 1.** The activation reaction of natural zeolite

(a)   (b)

Figure 2. (a) Non-activated natural zeolite and (b) activated natural zeolite

3.2. Characterization Adsorbents of the Non-activated Natural Zeolite and the Activated Natural Zeolite

3.2.1. XRD

Characterization using XRD aims to determine the crystallinity phase and types of minerals in the natural zeolite. The crystallinity phases can be observed from the intensity of the diffraction peaks produced. Materials with high crystallinity phases are indicated by high and sharp peak intensities. Figure 3 was the diffractogram of mordenite zeolite, the activated natural zeolite, and the non-activated natural zeolite.

From Figure 3, it can be observed that there is no significant change in the diffraction patterns. This indicates that the activation at 505°C did not cause damage to the zeolite structure [23]. The intensity of the diffraction peaks becomes sharper after the zeolite activation process. Increasing intensity indicates an enhancement in crystallinity due to removing impurity oxides [27]. The type of zeolite mineral can be determined by comparing the diffraction pattern and 2θ angles obtained from the analysis with the Joint Committee on Powder Diffraction Standard (JCPDS) database. Table 1 compares the 2θ angles and interplanar spacings between non-activated natural zeolite, activated natural zeolite, and the mordenite zeolite database.

From the data obtained through XRD characterization, it is evident that there is a shift in the 2θ angles after the activation process. The shift in the 2θ angles indicates the successful activation of the natural zeolite. Based on the similarity of the diffraction patterns between the non-activated natural zeolite and the activated natural zeolite with the mordenite zeolite database (JCPDS No. 6-239), it can be concluded that the main constituent of the natural zeolite from Malang Regency is the mineral mordenite, consistent with a reported previous research finding [18]. This conclusion is drawn from the appearance of peaks at 2θ = 13.585°, 19.706°, 22.387°, 25.734°, 26.404°, 27.740°, and 30.970°, which closely resemble the characteristic peaks of mordenite zeolite at 2θ = 13.45°, 19.61°, 22.2°, 25.63°, 26.25°, 27.67°, and 30.89°.
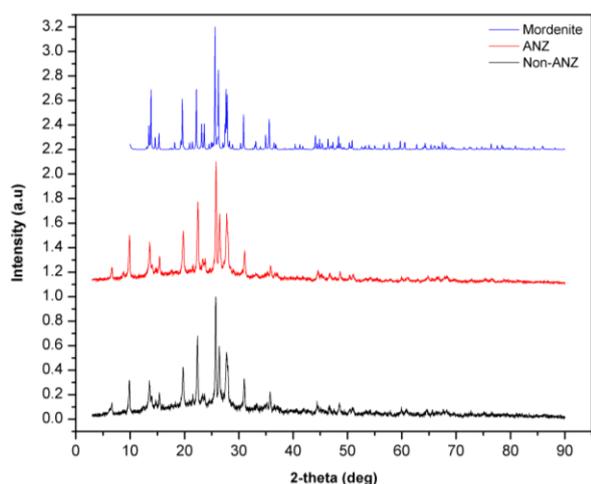

Figure 3. Diffractogram of mordenite zeolite, the activated natural zeolite, and the non-activated natural zeolite

Table 1. Comparison of 2θ angles and interplanar spacings between non-activated natural zeolite, activated natural zeolite, and mordenite zeolite database

Non-activated Natural Zeolite		Activated Natural Zeolite		Mordenite Zeolite	
2θ(°)	d-spacing (Å)	2θ(°)	d-spacing (Å)	2θ(°)	d-spacing (Å)
13.585	6.513	13.585	6.513	13.45	6.584
15.338	5.772	15.410	5.475	15.30	5.791
19.706	4.501	19.798	4.481	19.61	4.527
21.533	4.123	21.610	4.108	21.45	4.142
22.387	3.968	22.490	3.950	22.20	4.004
23.681	3.754	23.760	3.742	23.64	3.764
25.734	3.459	25.784	3.452	25.63	3.476
26.404	3.372	26.454	3.366	26.25	3.395
27.740	3.213	27.774	3.209	27.67	3.223
30.970	2.8851	31.050	2.877	30.89	2.894
35.783	2.5073	35.855	2.502	35.61	2.521

3.2.2. XRF

Analysis is used to determine the components of the non-activated natural zeolite and the activated natural zeolite. Generally, the components of the natural zeolite consist of silica and alumina. Meanwhile, the other constituent components include balancing cations such as Fe^{2+}, Ca^{2+}, Mg^{2+}, K^+, and Na^+. These elements can be exchanged with other metal cations through ion exchange mechanisms [18]. The remaining components are impurities that occupy the pores of the zeolite. Impurities in natural zeolite are removed through activation and calcination [28]. The components of the natural zeolite and the activated natural zeolite can be seen in Table 2.

The characterization results indicate that the activation of zeolite has been successfully achieved, as evidenced by the increase in the percentage of SiO_2 after activation. This increase in SiO_2 is accompanied by a decrease in Al_2O_3, increasing the Si/Al ratio. Zeolites with a higher Si/Al ratio tend to have a larger adsorption capacity. This is because a higher number of Si atoms in the zeolite structure can provide more active sites for the adsorption of target molecules. Thus, these findings indicate that the activation has improved the adsorption capacity of zeolite by increasing the Si/Al ratio.

Table 2. Components of the non-activated natural zeolite and the activated natural zeolite

Component	Non-activated Natural Zeolite	Activated Natural Zeolite
Al_2O_3	13.2	12.6
SiO_2	86.2	87.3
Si/Al ratio	5.768	6.119

3.2.3. SAA

Characterization using SAA was carried out to determine the surface area, diameter, and pore volume of zeolite. The analysis results in Table 3 indicate that the surface area and pores of the activated natural zeolite have increased. This increase in characteristics is due to replacing metal cations with H^+ and the removal of impurities present in the natural zeolite [29]. This enhancement of characteristics demonstrates the successful activation of the natural zeolite. The surface area data obtained from the characterization, utilizing the SAA instrument with the BET method, is detailed in Table 3.

From the results of surface area analysis using the BET method, it is evident that activated natural zeolite has a surface area of 137.8196 m^2/g. In a previous study involving the activation of natural zeolite from Malang Regency, which only included physical activation, the surface area reached only 99.096 m^2/g [26]. These findings indicate that physical activation alone is less effective in increasing the zeolite surface area, necessitating chemical activation.

The reduction in the pore diameter of natural zeolite after activation is due to the involvement of cation replacement during the activation process, where cations present in natural zeolite are replaced by H^+ ions. H^+ ions are smaller than cations like Na^+ and K^+, allowing them to enter the zeolite pores and replace larger cations. This can result in a shrinkage of the zeolite pore diameter after activation. Additionally, impurities in natural zeolite can be removed during activation. These impurities usually occupy small or micropores. When these impurities are removed, previously blocked pores can open up, leading to an increase in pore volume and a reduction in pore diameter.

The International Union of Pure and Applied Chemistry (IUPAC) categorizes materials based on their pore diameter into three groups: micropores (pore diameter less than 2 nm), mesopores (pore diameter between 2 and 50 nm), and macropores (pore diameter greater than 50 nm) [30]. Based on the obtained data, it can be concluded that natural zeolite from Malang Regency falls into the mesoporous material category.

Table 3. The surface area of non-activated natural zeolite and activated natural zeolite

Characteristics	Non-activated Natural Zeolite	Activated Natural Zeolite
Surface Area (m^2/g)	20.8045	137.8196
Pore Volume (cm^3/g)	0.074127	0.145245
Pore Diameter (nm)	14.2520	4.2155

Based on the analysis using the Barret-Joyner-Halenda (BJH) method, the average pore diameter of natural zeolite is recorded at 30.5598 nm, with a pore volume reaching 0.074127 cm^3/g. The presence of these pore diameters and volumes in zeolite has the potential to be utilized as an adsorbent for heavy metals in wastewater, given that these pores can provide a large surface area for interaction with adsorbates.

3.3. Adsorption Study

The adsorption process is classified into physisorption, chemisorption, and ion exchange mechanisms. Zeolite adsorbs heavy metal ions through the ion exchange mechanism [19]. In this case, heavy metal ions in the solution, such as Pb^{2+}, Cr^{3+}, and Cr^{6+}, replace the cations present in the zeolite. This ion exchange process results in heavy metals being bound to the adsorbent's surface. Heavy metal cations can replace cations in the zeolite's crystal structure and form zeolite-heavy metal complexes bound to the zeolite framework. The heavy metal ions that have replaced zeolite cations migrate into the zeolite, leaving the adsorbate solution with a lower concentration of heavy metals. The ion exchange reaction can be represented in Equation (2), with S being either Si or Al.

$$[S\text{-}OM]_z + H^+_{(aq)} \leftrightarrow [S\text{-}OH]_z + M_{(aq)} \qquad (2)$$
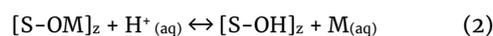
The adsorption of heavy metals is influenced by several factors, including the adsorbent mass, solution concentration, pH, stirring rate, and adsorbent size [31, 32]. This study observed several parameters, including the adsorbent mass, pH, contact time, and adsorbate concentration. Variations in these parameters were performed to determine the optimum conditions for the adsorbent to adsorb heavy metals in the waste samples. This research also identified the type of adsorption isotherm, focusing on Freundlich and Langmuir isotherms. Moreover, the adsorption kinetics were determined by examining the pseudo-first-order and pseudo-second-order kinetics. The results of this study are expected to provide insights into the mechanism and optimum conditions for heavy metal adsorption, which can be valuable in developing effective and sustainable waste treatment methods.

3.3.1. Determination of Optimum Adsorbent Mass

The addition of various adsorbent masses aims to determine the optimal mass of adsorbent required to adsorb the heavy metals in the sample. The optimum mass is determined by adding different amounts of adsorbent to the waste sample and allowing it to contact for 30 minutes with an agitation speed of 100 rpm. The determination of the optimum mass of the adsorbent for metal adsorption is illustrated in Figure 4a and b.
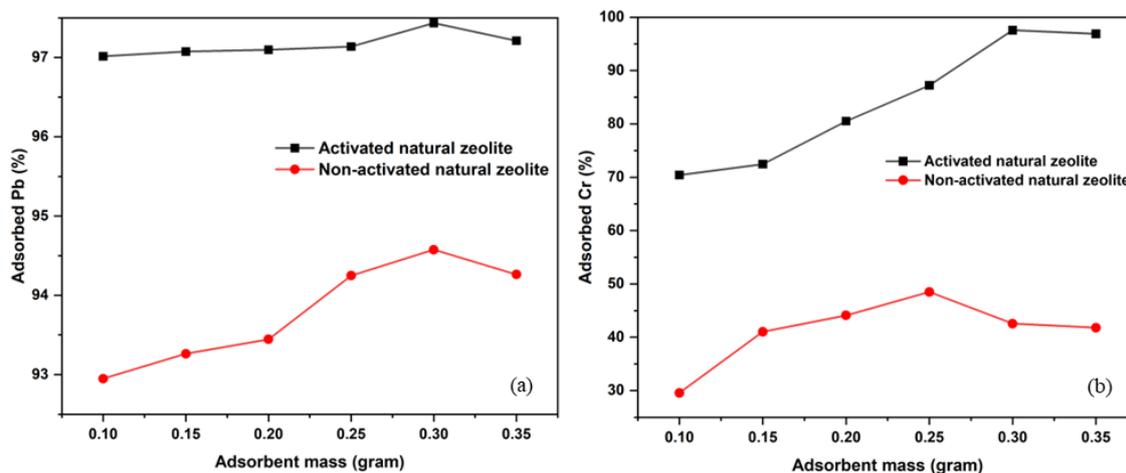
Figure 4. Determination of the optimum mass of the adsorbent for (a) Pb adsorption, (b) Cr adsorption

Figure 4a and b show that activated natural zeolite is a more effective adsorbent for adsorbing Pb and Cr metals. Pb and Cr metals adsorbed concentrations increase with the increasing adsorbent mass. This occurs because the increase in adsorbent mass results in a greater available surface area for adsorption. Therefore, the more mass of adsorbent used, the more metals can be adsorbed [31]. Thus, the optimum mass of the adsorbent for adsorbing Pb(II) and Cr(VI) metals is 0.3 grams. Under these conditions, the percentage of adsorbed Pb(II) metal reaches 97.43%, while Cr(III) and Cr(VI) metals are adsorbed at a rate of 97.56%. Therefore, in subsequent research, 0.3 grams of activated natural zeolite was used as the adsorbent for the adsorption of these heavy metals.

The decrease in adsorption percentage after reaching the optimum adsorbent mass can indeed occur. After reaching the optimum adsorbent mass, all available adsorption sites on the surface of the adsorbent may have already been occupied by metal ions from the solution. Consequently, the introduction of additional adsorbent mass does not lead to an increase in adsorption percentage, as there are no vacant sites left to adsorb additional heavy metals.

3.3.2. Determination of Optimal Contact Time

The optimal contact time is determined by adding the adsorbent to the waste sample with varying contact times. The temperature used is 25°C with an agitation speed of 100 rpm. The determination of the optimal time is illustrated in Figure 5.

During the initial contact time, the adsorption rate of heavy metals is notably rapid. This is attributed to the abundance of active sites available on the surface of activated natural zeolite, facilitating swift adsorption processes [31]. Heavy metals quickly move to the available adsorption sites. As time progresses, the adsorption efficiency increases and reaches its peak for 30 minutes. This suggests that a significant amount of heavy metals has been adsorbed during this period, indicating that active sites on the surface of the adsorbent remain available for adsorption. The optimum contact time is achieved for 30 minutes.
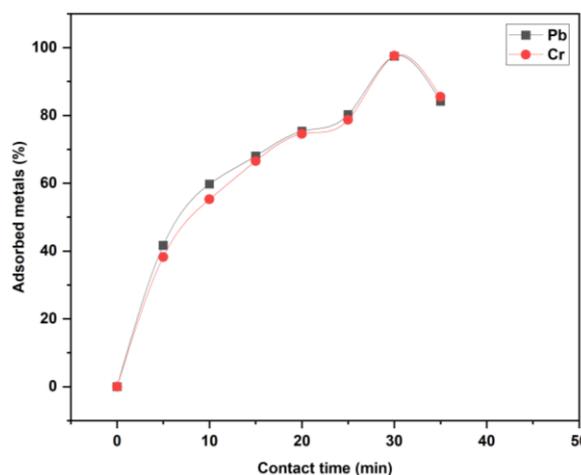

Figure 5. Determination of the optimal contact time

The adsorption sites on activated natural zeolite have reached their maximum capacity, and the adsorption process has reached equilibrium conditions. After passing the optimum contact time, there is a decrease in the rate and efficiency of heavy metal adsorption. This is due to the adsorbent's surface and pores becoming saturated with heavy metals, and the adsorption sites have been depleted, leading to desorption [9]. Desorption is the release of heavy metal ions that have been adsorbed back into the adsorbate solution.

3.3.3. Determination of Optimal Concentration of the Adsorbate

Determining the optimum adsorbate concentration in this study aims to find the ideal concentration of heavy metal ions to be adsorbed by the activated natural zeolite. In this experiment, various concentrations of heavy metal ions ranging from 2 to 10 ppm were added to the adsorbent, and then the adsorption rate by the activated natural zeolite was measured. The primary goal was to identify the concentration that yields the highest adsorption efficiency. The determination of the optimal concentration of the adsorbate is illustrated in Figure 6.
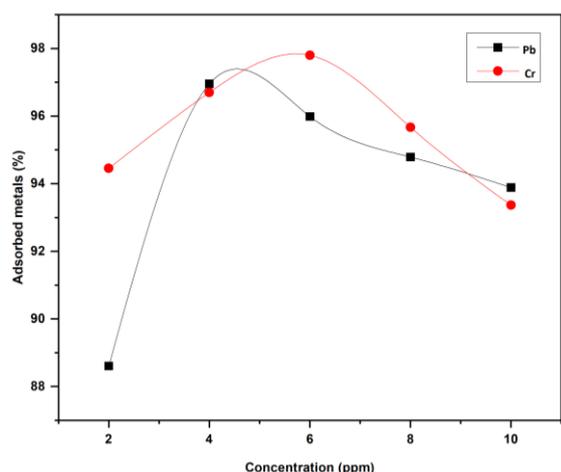
Figure 6. Determination of optimal concentration of the adsorbate

The adsorption of metal ions by the adsorbent tends to increase with the increasing concentration of the adsorbate in the solution [33]. However, after reaching equilibrium conditions, there is a decrease in the amount of metal ions adsorbed by the adsorbent. This occurs because more heavy metal ions can enter the adsorbent through the ion exchange. When the active sites on the adsorbent become saturated, the adsorption process does not continue, and the amount of adsorbed metal decreases. Thus, the optimum concentration is reached when the active sites on the adsorbent have reached their maximum capacity. Beyond this point, increasing the adsorbate concentration does not increase the amount of metal adsorbed by the adsorbent.

3.3.4. Determination of Optimal pH

pH is one of the parameters that can influence the process of heavy metal adsorption in liquid waste. This study performs adsorption with pH variations ranging from 2 to 10. The maximum adsorption of Pb^{2+} and Cr^{6+} ions occurs at pH 6, with adsorption efficiencies of 97.211% and 98.561%, respectively. The determination of the optimal pH is illustrated in Figure 7.
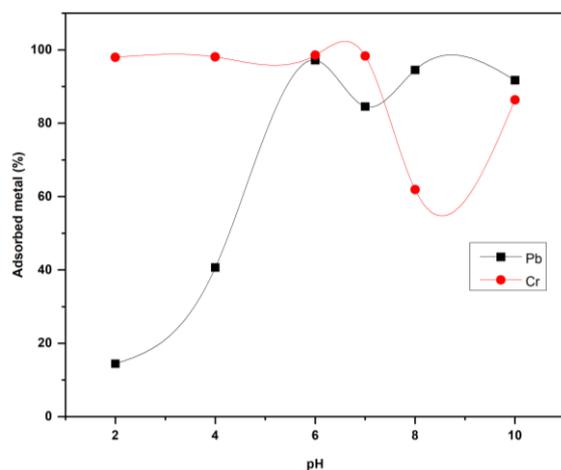

Figure 7. Determination of the optimal pH

The effectiveness of metal adsorption increases at a pH of 4. An increase in pH can enhance the efficiency of heavy metal adsorption. In highly acidic conditions, the concentration of H^+ increases, leading to competition between H^+ ions and metal ions to bond with the adsorbent [31, 32]. Under very acidic pH conditions, metal ions in the solution undergo hydrolysis. This leads to the adsorption of Pb and Cr metals becoming less effective. The hydrolysis reaction is presented in Equation (3).

$$M^{2+} + nH_2O \rightarrow [M(OH)_n{}^{2-n}]^+ + nH^+ \qquad (3)$$
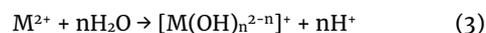
The hydroxo complexes resulting from the hydrolysis reaction are more easily adsorbed than heavy metal cations. At pH 6, the adsorption of Pb^{2+} ions increases. Electrostatic forces occur between Pb^{2+} ions and the negatively charged surface of the adsorbent, resulting in attractive forces that enhance adsorption efficiency [33]. At alkaline pH, there is a decrease in adsorption efficiency as it surpasses the solubility product constant, and precipitation occurs [14, 32]. In alkaline solutions, the electrostatic attractive forces between the adsorbent and the adsorbate decrease, reducing adsorption capacity [32].

3.3.5. Adsorption Kinetics Model

The comparison of contact time against the adsorption capacity of the activated natural zeolite adsorbent can be used to determine the adsorption kinetics. Adsorption kinetics is used to understand the rate of heavy metal adsorption, specifically Pb and Cr, using activated natural zeolite as the adsorbent. Various equations can be used to determine the adsorption kinetics model. The kinetics observed in this study include pseudo-first-order kinetics and pseudo-second-order kinetics. The linear equation for pseudo-first-order kinetics is obtained from the time graph on the x-axis and $\log(q_e-q_t)$ on the y-axis. The linear equation for pseudo-second-order kinetics is obtained from the time graph on the x-axis and t/q_t on the y-axis.

The determination of the adsorption kinetics model is based on the value of the coefficient of determination (R^2), which is larger or closer to 1. In addition to the coefficient of determination, adsorption kinetics can be determined by comparing the calculated adsorption capacity (q_{cal}) with the measured adsorption capacity (q_e) from the experiment data. If q_{cal} approaches or aligns with q_e, it indicates that the chosen kinetics model effectively models the kinetics of adsorption. The time profile of (a) Pb (II) and (b) Cr (VI) adsorption on activated natural zeolite at various initial concentrations at pH 6 and room temperature is illustrated in Figure 8 (a) and (b). The adsorption kinetics curves are depicted in Figures 9 to 12. Table 4 compares two possible adsorption kinetics models, pseudo-first-order and pseudo-second-order. The following table shows a comparison of adsorption kinetic parameters.
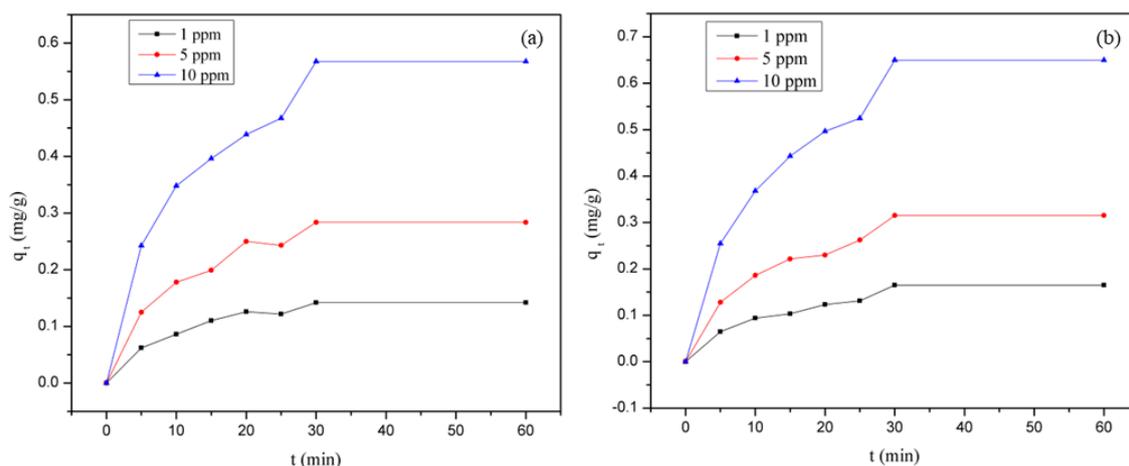
Figure 8. (a) Time profile of Pb (II) adsorption, (b) time profile of Cr (VI) adsorption
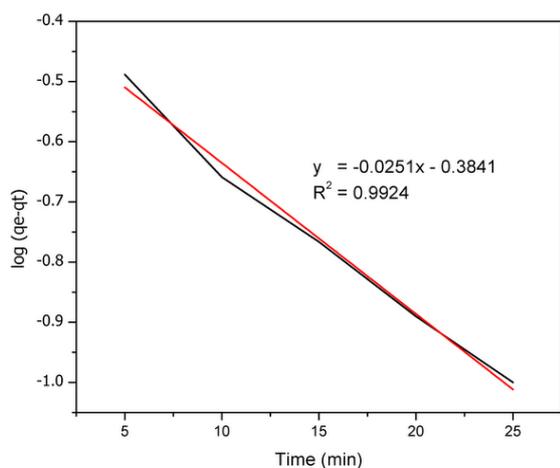

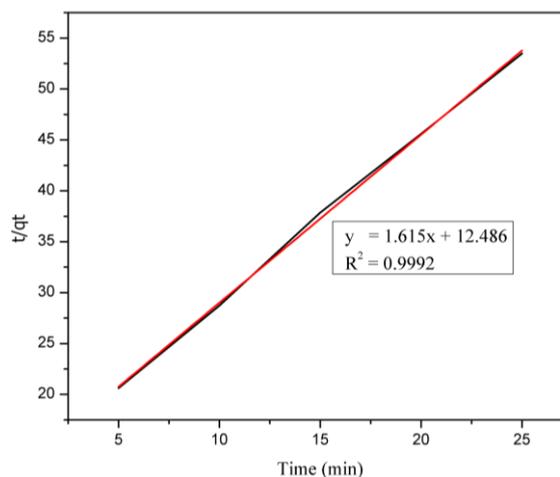**Figure 9.** The pseudo-first-order kinetic adsorption curve of Pb metal

Figure 10. The pseudo-second-order kinetic adsorption curve of Pb metal

From the obtained data, it can be concluded that the kinetics of the activated natural zeolite adsorption tend to follow a pseudo-second-order kinetics. This is evident from the R^2 value approaching 1. Furthermore, the values of calculated adsorption capacity (q_{cal}) from this model are closer to the measured q_e values. Based on the data, it can be concluded that the adsorption of Pb and Cr using the activated natural zeolite follows the pseudo-second-order kinetics equation. Cr(VI) adsorption onto ZnO-graphene oxide nanocomposite follows the pseudo-second-order kinetics equation [33]. The pseudo-second-order kinetics model is suitable for adsorbents with numerous active sites [30]. Zeolite possesses many active sites for the adsorption process to occur. Therefore, in this study, it can be assumed that the adsorption process using zeolite adsorbent is described by the pseudo-second-order kinetics equation.

The pseudo-second-order kinetic equation is a mathematical model to explain how the adsorption rate of activated natural zeolite changes over time. At the initial contact stage, the adsorption rate tends to be high because numerous empty adsorption sites are still ready to capture adsorbate molecules. However, as time progresses, the adsorption sites on the activated natural zeolite begin to fill up, causing the adsorption rate to slow down.
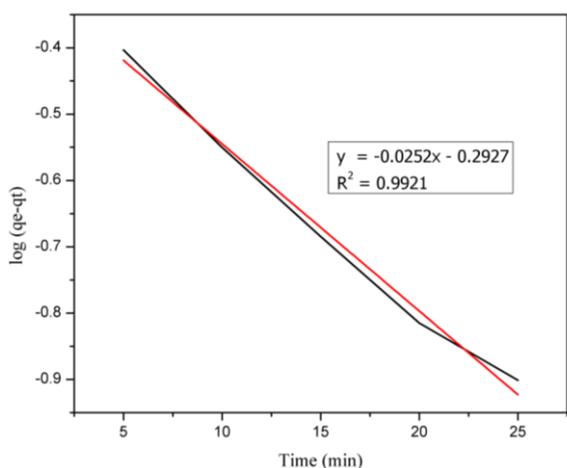
Table 4. Adsorption kinetic parameters

Adsorption Kinetic	Parameters	Pb	Cr
Pseudo-first-order	Equation	y = -0.0251x + 0.3841	y = -0.0252x - 0.2927
	R^2	0.9924	0.9921
	q_{cal} (mg/g)	0.4129	1.9620
	q_e (mg/g)	0.5674	0.6498
	k_1 (1/min)	0.0578	0.0580
Pseudo-second-order	Equation	y = 1.615x + 12.486	y = 1.3843x + 12.954
	R^2	0.9992	0.9992
	q_{cal} (mg/g)	0.6055	0.7223
	q_e (mg/g)	0.5674	0.6498
	k_2 (g/mg.min)	0.2184	0.1479

Figure 11. The pseudo-first-order kinetic adsorption curve of Cr metal
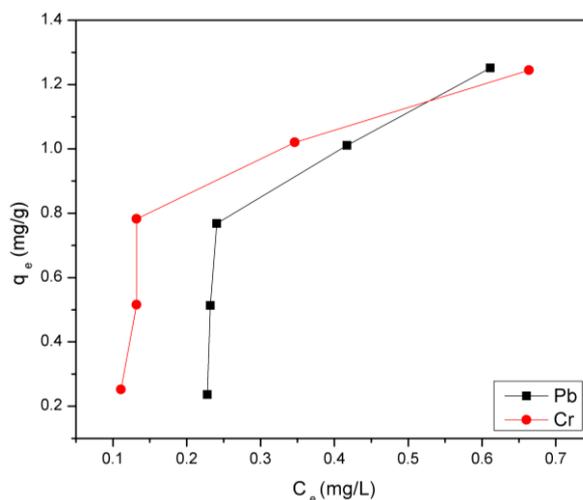
Figure 13. Adsorption isotherm graph
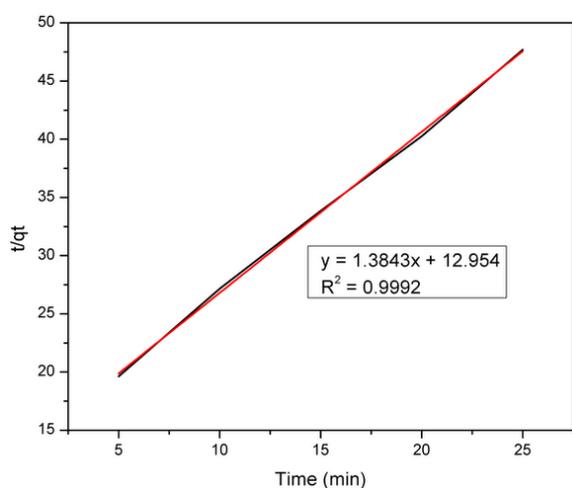
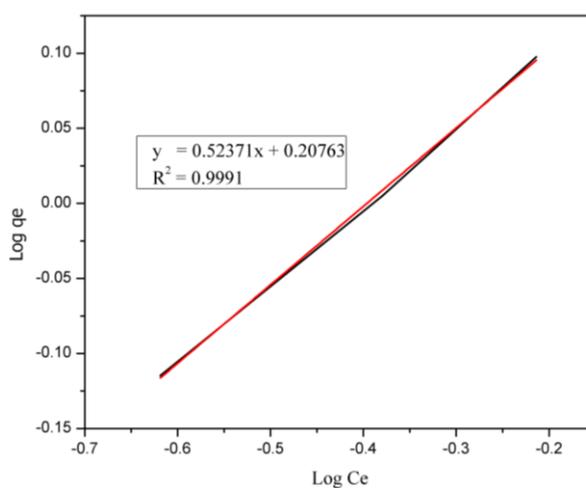**Figure 12.** The pseudo-second-order kinetic adsorption curve of Cr metal

3.3.6. Adsorption Isotherm Model

Adsorption isotherms indicate the amount of heavy metal ions that can be adsorbed per unit weight of adsorbent at equilibrium conditions [34]. The adsorption isotherm model is determined based on the linear regression equation generated from experiments. Generally, two adsorption isotherm models are commonly used to describe solid-liquid adsorption: the Freundlich and Langmuir models. The Freundlich isotherm model is obtained from a graph between $\log C_e$ (concentration at equilibrium) on the x-axis and $\log q_e$ (equilibrium adsorption capacity) on the y-axis.

Meanwhile, the Langmuir isotherm model is obtained from a graph between C_e on the x-axis and C_e/q_e on the y-axis. Determining the most suitable adsorption isotherm model is typically based on the coefficient of determination (R^2) value, which approaches 1. Additionally, the determination of the type of adsorption isotherm can also be carried out by considering the parameters Freundlich constant (K_F) and Langmuir constant (K_L), as well as comparing the values of calculated adsorption capacity (q_{cal}) and adsorption capacity (q_e) from experimental data. The adsorption isotherm graph is illustrated in Figure 13.

Figure 14. The Freundlich isotherm curve for Pb metal

Freundlich and Langmuir's adsorption isotherm curves were constructed from the adsorption data of Pb metal using activated natural zeolite as the adsorbent. Below are the Freundlich and Langmuir adsorption isotherm curves for Pb metal.

Freundlich and Langmuir's adsorption isotherm curves were constructed from the adsorption data of Cr metal using activated natural zeolite as the adsorbent. Below are the Freundlich and Langmuir adsorption isotherm curves for Cr metal. Table 5 compares two possible adsorption isotherm models, Freundlich and Langmuir. Table 5 presents a comparison of adsorption isotherm parameters.

The analysis of the experimental data found that the Langmuir constant (K_L) is larger than the Freundlich constant (K_F). These results indicate that the adsorption process on the adsorbent surface forms a monolayer under equilibrium conditions. The Langmuir isotherm equation effectively reflects the occurring adsorption phenomenon. Furthermore, the higher K_L value signifies that the adsorption sites are limited on the adsorbent surface.

Table 5. Adsorption isotherm parameters

Isotherm	Parameters	Pb	Cr
Freundlich	Equation	y = 0.5237x + 0.2076	y = 0.2868x + 0.1442
	R^2	0.9991	0.9992
	n	1.9094	3.4867
	K_F [(mg/g)(L/mg)$^{1/n}$]	0.6200	1.3938
Langmuir	Equation	y = 0.4694x + 0.2060	y = 0.6796x + 0.0884
	R^2	0.9888	0.9944
	q (mg/g)	2.1303	1.4714
	K_L (L/mg)	22.7864	7.6877
	R_L	0.0669	0.1638
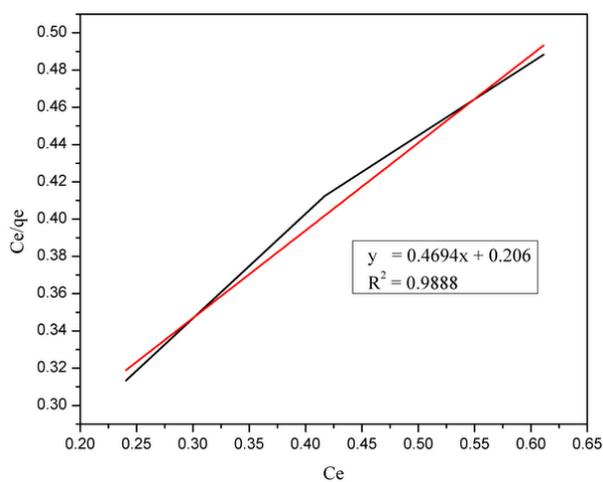
Figure 15. The Langmuir isotherm curve for Pb metal

Figure 17. The Langmuir isotherm curve for Cr metal

The Langmuir isotherm is a model that describes the adsorption process by forming a monolayer on the surface of a homogenous adsorbent [36]. The Langmuir isotherm model depicts the Pb and Cr adsorption process on the activated natural zeolite adsorbent. According to the Langmuir isotherm model, a single active site on the activated natural zeolite adsorbent can only bind to one cation molecule. The adsorption process of Pb and Cr metals on the activated natural zeolite adsorbent occurs selectively, forming a monolayer on the adsorbent's surface. Previous research on methylene blue using natural zeolite/Fe_2O_3 adsorbent followed Langmuir isotherm, the adsorption capacity is 32.258 mg/g [37]. Previous research on Pb, Cu, and Cd metals adsorption using ZSM-5 zeolite as the adsorbent aligns with the Langmuir isotherm [36].
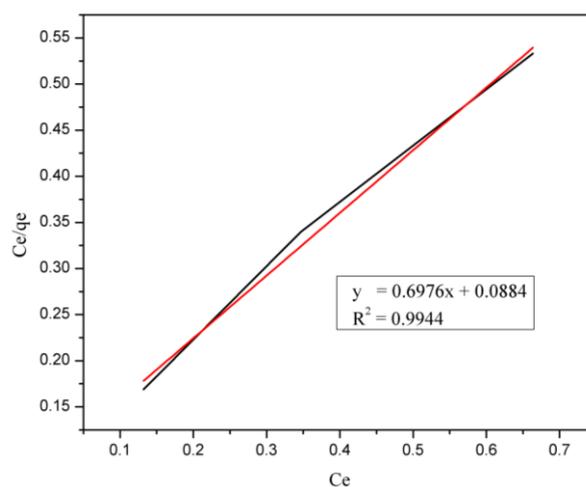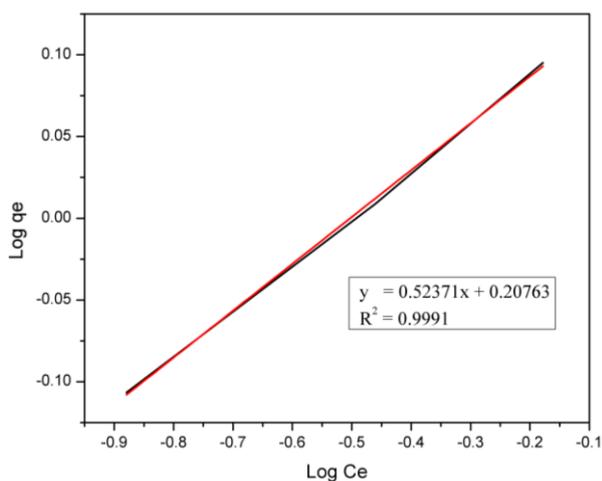

Figure 16. The Freundlich isotherm curve for Cr metal

The value in the Langmuir isotherm provides information about the dynamics of adsorption and desorption in a system at equilibrium. This research found that the R_L value is less than 1, indicating that the adsorption process is favorable [35]. Adsorption is more dominant than desorption, leading to the retention or adsorption of a significant amount of substances on the surface of the adsorbent at equilibrium conditions. Meanwhile, desorption is relatively limited, suggesting a strong interaction between the adsorbate and the adsorbent surface under these conditions.

4. Conclusion

Based on the conducted research, it can be concluded that natural zeolite can be physically and chemically activated. Activation and optimization were carried out to obtain activated natural zeolite that can be utilized as an adsorbent to its maximum potential. Activation leads to changes in its characteristics. Activation leads to an increase in the Si/Al ratio. The higher the Si/Al ratio, the larger the active sites for adsorption processes. The results of the adsorption study in the treatment of laboratory wastewater with simulated Pb and Cr metal waste showed that using activated natural zeolite as an

adsorbent is more effective than natural zeolite without activation. Activated natural zeolite adsorbs heavy metal ions through an ion exchange mechanism.

Acknowledgment

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