

# UTILIZATION OF TEA WASTE ACTIVATED BY USING HYDROCHLORIC ACID AS AN ADSORBENT FOR CALCIUM (II) IONS IN HARD WATER

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## ABSTRACT

Water is an important natural resource for human survival. Groundwater in calcareous soil areas contains high levels of  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Mg}(\text{HCO}_3)_2$  salts and will have a negative impact if consumed continuously. In this study, an adsorption method using tea waste (*Camellia sinensis*) was conducted to reduce the concentration of Ca(II) ions that cause water hardness. Tea waste was activated with 0.1 N HCl for 24 hours. Tea waste was characterized by Fourier Transform Infrared (FTIR) and Scanning Electron Microscopy (SEM). The optimum condition of Ca(II) adsorption by the tea waste was obtained at pH 8, with a contact time of 30 minutes and an adsorbent weight of 0.5 grams. The maximum adsorption capacity was obtained at Ca(II) solution concentration of 70 mg/L with an adsorption capacity value of 6.704 mg/g. The adsorption isotherm corresponding to the tea waste adsorbent is the Freundlich isotherm ( $r^2 = 0.9199$ ). The highest absorption of Ca(II) metal ions in well water samples from the concentration of Ca(II) metal ions was 72.7702 mg/L to 4.877 mg/L, with adsorption efficiency of 93.3% and adsorption capacity of 6.7893 mg/g.

**Keywords:** Water hardness, Adsorption, Tea waste, Activation, Calcium

## 1. INTRODUCTION

Water is an important natural resource for human survival. In daily life, humans use water for various purposes such as drinking, washing, bathing, and other activities. The water used contains many natural and polluted minerals. According to Permenkes RI Number 32 of 2017 concerning "Environmental Health Quality Standards and Water Health Requirements for Sanitary Hygiene Purposes" states that all water produced must meet the criteria for clean water quality requirements, including in terms of biologically, physical, and chemical.

One of the chemical requirements in water quality requirements is the amount of Ca and Mg metal content in water whose presence is commonly referred to as water hardness [1]. Water hardness is when there are certain minerals in the water, generally calcium ions ( $\text{Ca}^{2+}$ ) and magnesium ions ( $\text{Mg}^{2+}$ ) in the form of carbonate salts. In general, the cause of

hardness is due to the presence of metals or cations with valences of 2, such as Fe, Sr, Mn, Ca, and Mg.

The disadvantages caused by the presence of hard water, among others, can cause soap not to foam (foamy). The soap will foam if  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions are precipitated. Hard water causes a decrease in the cleaning power in the soap so that use of soap becomes excessive. In addition, it can also cause a crust on the kettle that will clog the kettle valves. This causes the heat conductivity of the kettle to decrease so that the use of fuel is greater, and the time used will be longer.

Several residents in Bojongrangkas Village, Ciampea, Bogor Regency have complained about the white crust like lime found on cooking utensils. The crust is a lime sediment that comes from several sources that have been boiled. Also, the water when used for washing does not produce much foam.

One way to reduce hardness is by adsorption method. Adsorption is a process of absorption of

substances by solids that occurs on the surface of solid due to the attractive force between atoms or molecules on the surface of solids without participating in the absorption of the substance. Adsorption methods by natural adsorbents have been widely used in reducing water hardness. Of the several natural adsorbent materials that can be used, tea waste has considerable potential to be used as an adsorbent. The ability of tea waste to absorb heavy metals results from the functional groups of the cell wall of tea leaf consisting of cellulose, hemicellulose, lignin, tannin publication and structural proteins [2].

According to research conducted by Maulana [3], adsorption of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  metal ions by tea waste can be done with the result of  $\text{Ca}^{2+}$  metal ion adsorption efficiency of 31.56% and for  $\text{Mg}^{2+}$  metal ion adsorption of 26.28% under pH 8 conditions and contact time of 10 minutes. Because of there are shortcomings in the previous research, further research is needed to get the efficiency and capacity of calcium metal ion adsorption from tea waste adsorbent to the maximum.

## 2. METHODS

The research method used in this study is a laboratory experiment method to determine the adsorption efficiency of calcium metal in well water samples by adsorbents made from tea waste. This research consists of four stages. The first stage, the preparation and characterization of adsorbents; second, adsorbent optimization; third, determination of adsorption isotherm model; and the fourth is the application of calcium metal adsorption in the sample.

### 2.1. Tools and Materials

The tools used in this research include containers, stirrers, beaker glass, measuring glass, ovens, analytical balances, glassware, pH meters, hotplate stirrer, Whatman No. 41 filter paper and several instruments such as Inductively Coupled Plasma (ICP), Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR).

The materials used in this research include tea waste obtained from stalls and restaurants, hard water samples, aquabidest,  $\text{HNO}_3$  65%, NaOH p.a., HCl 37%, Ca metal standard 1000 mg/L.

### 2.2. Preparation of 0.1 N HCl Activated Tea Waste Adsorbent

The collected tea waste was washed with water until the water was colorless. Then the clean tea waste was mashed and sieved to obtain an adsorbent of 100 mesh. Tea waste was dried using an oven at  $110^\circ\text{C}$  to dry. Tea waste that has been dried, then soaked in 0.1 N HCl solution  $\pm$  24 hours. After that, the tea waste was filtered and rinsed with distilled water until pH 7 (neutral) was obtained, oven at  $110^\circ\text{C}$  to dry and put in the desiccator for  $\pm$  15 minutes, and the tea waste was ready for use.

### 2.3. Characterization of Tea Waste Adsorbent

The activated tea waste adsorbent was tested using Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) to determine the morphology of the activated and non-activated adsorbents. To identify the functional groups, present in tea waste adsorbents.

### 2.4. Optimization of Adsorption Conditions

#### 2.4.1. pH Optimization of $\text{Ca}^{2+}$ Metal Adsorption

1 gram of tea waste that had been activated with 0,1 N HCl added to 50 mL of 5.0 mg/L calcium standard solution that had been regulated by adding 0.1 N  $\text{HNO}_3$  or 0.1 N NaOH until pH 4, 6, and 8 were obtained. Then the sample and adsorbent were stirred for 30 minutes at 100 rpm. After that, it was filtered, the filtrate was taken and analyzed by atomic absorption spectrophotometer to determine the optimum pH.

#### 2.4.2. Optimization of Contact Time for $\text{Ca}^{2+}$ Metal Adsorption

1 gram of tea waste that had been activated with 0,1 N HCl was added to 50 mL of 5.0 mg/L calcium standard solution. The pH was adjusted according to the results of determining the optimum pH. Stirred at 100 rpm using the stirrer during the specified contact time of 30, 60, and 90 minutes. After that, it was filtered and measured calcium content with an atomic absorption spectrophotometer.

### 2.4.3. Optimization of Weight of Tea Waste Adsorbent

A total of 50 mL of 5.0 mg/L calcium standard solution was put into 4 different beaker glasses. Adjust the pH according to the results of determining the optimum pH. Tea waste that had been activated with 0.1 N HCl was added as much as 0.5; 1; 1.5; and 2 grams. Then the sample and adsorbent were stirred at 100 rpm during the optimum contact time obtained. After that it was filtered and measured the calcium content with an atomic absorption spectrophotometer.

### 2.5. Determination of Maximum Capacity and Isotherm Adsorption of Tea Waste Adsorbent on Calcium Metal Ions

Tea waste adsorbent as much as the optimum weight that has been determined was added to 50 mL of calcium metal solution with concentrations of 30, 50, and 70 mg/L under optimum conditions. Then stirred with stirrer at the optimum contact time. After that, it was filtered and measured the calcium content with an atomic absorption spectrophotometer. Then the data obtained was processed by graphical method.

### 2.6. Reduction of Calcium Metal Level in Well Water by Tea Waste Adsorbent

Activated tea waste adsorbent was tested on well water samples. Well water samples as much as 50 mL were put into a beaker glass, then adjusted the pH at the optimum pH that has been determined by the addition of HNO<sub>3</sub> 0.1 N or NaOH 0.1 N. Then put the tea waste adsorbent as much as the optimum weight that has been determined, then stirred with a stirrer at 100 rpm during the optimum contact time that has been determined. Then filtered with filter paper, then the filtrate was analyzed using Inductively Coupled Plasma (ICP).

## 3. RESULTS AND DISCUSSION

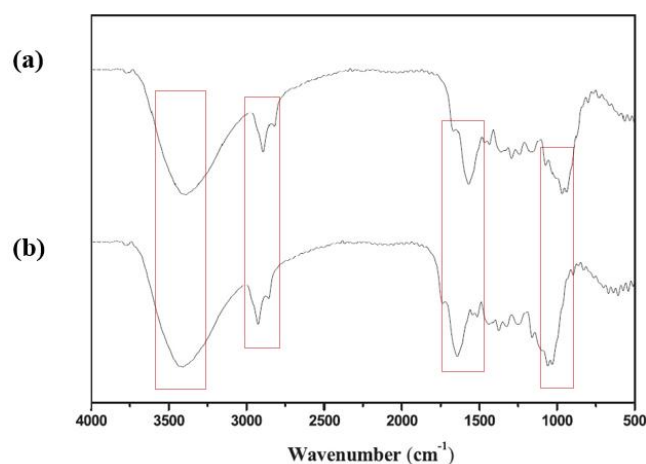
### 3.1. Characteristic of Tea Waste Adsorbent

The following are the results of characterization of tea waste with Fourier Transform Infrared

Spectroscopy (FTIR) to determine the functional groups contained in the adsorbent and Scanning Electron Microscopy (SEM) to see the morphological results on activated and non-activated tea waste adsorbents.

#### 3.1.1. Characteristic of Tea Waste Adsorbent with Fourier Transform Infrared Spectroscopy (FTIR)

Tea waste was analyzed by FTIR to determine the functional groups contained in the tea wastes.



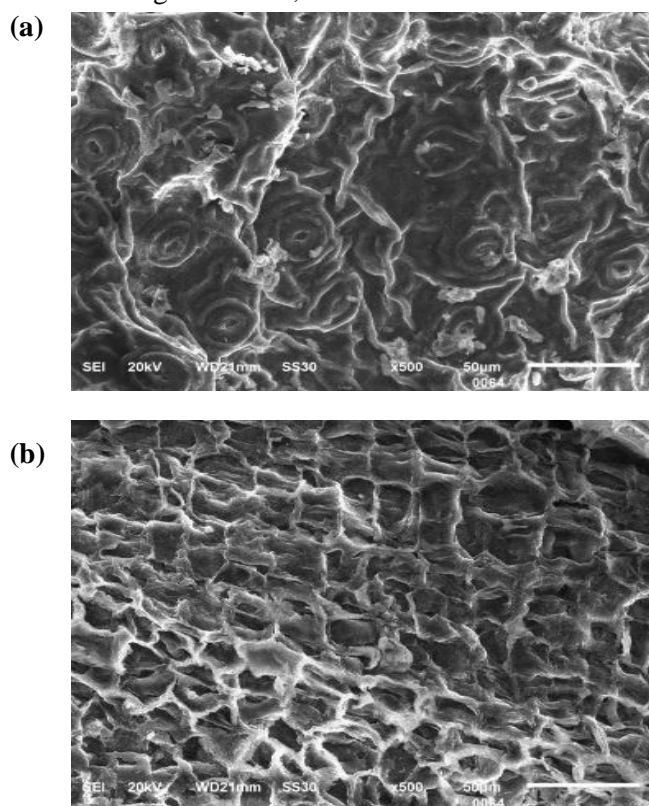
**Figure 1.** FTIR spectra of (a) Tea waste before activation and (b) Tea waste after activation

In the spectrum of tea waste before (a) and after (b) activation, there is a broad peak at wave number 3392.96 cm<sup>-1</sup> which indicates the O-H functional group [4]. Furthermore, an absorption band of wave number 2921.06 cm<sup>-1</sup> was obtained in tea waste before activation and an absorption at wave number 2924.82 cm<sup>-1</sup> in tea waste after activation, indicating the presence of aliphatic C-H groups which are the building blocks of lignocellulose structure [5]. Then there was a shift in absorption between activated and non-activated tea waste from wave number 1704.91 cm<sup>-1</sup> to wave number 1718.27 cm<sup>-1</sup>, which indicates the presence of C=O group. The absorption band at wave number 1018.32 cm<sup>-1</sup> found in tea waste before activation shifted to wave number 1043.99 cm<sup>-1</sup> indicating the presence of C-O absorption from carboxylic acids and alcohol vibrations [6].

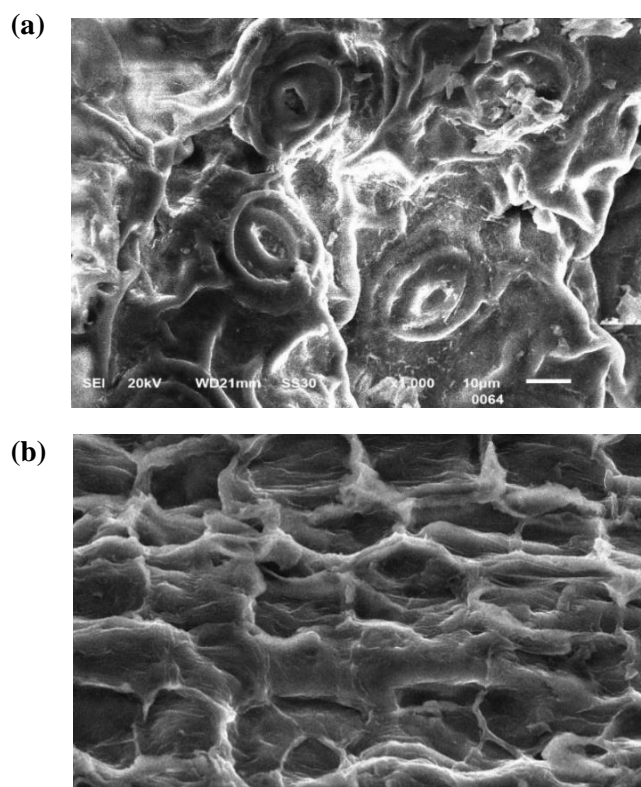
The presence of this O-H functional group is an important absorption site for adsorbents [7]. The presence of O-H and C-O functional groups indicates that the resulting tea waste adsorbent tends to be more polar in nature. The activation process with HCl aims to clean the impurities contained in the tea waste, thus increasing the surface area of the tea waste without damaging the structure. The reduction of mineral salts indicates the formation of -COOH and -OH functional groups on the adsorbent so that more Ca metal ions will be adsorbed by the tea waste adsorbents.

### 3.1.2. Characteristic of Tea Waste Adsorbent with Scanning Electron Microscopy (SEM)

The characterization process of tea waste with SEM was carried out to observe the morphology of the activation treatment with 0.1 N HCl on tea waste. Characterization of tea waste was carried out with different magnifications, which are 500x and 1000x.



**Figure 2.** Characteristic of Tea Waste Adsorbent 500x magnification (a) Tea Waste before activation (b) Tea waste after activation



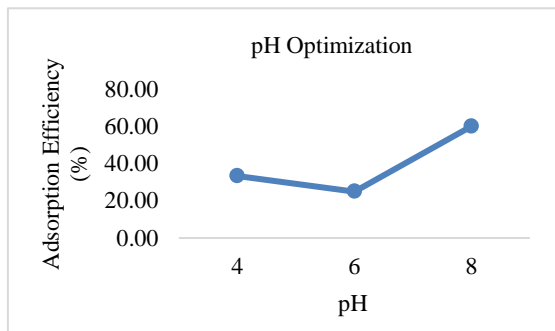
**Figure 3.** Characteristic of Tea Waste Adsorbent 1000x magnification (a) Tea Waste before activation (b) Tea waste after activation

Based on the results of SEM analysis on tea waste adsorbents before activation and after activation, both adsorbents have different morphological structures. In tea waste before activation, the surface is still closed, and no pores have been formed. While in tea waste after activation, the pores formed are more and more open. According to Purwaningsih [8], the activation process on tea waste using HCl solution aims to remove impurities in adsorbent pores, so that the pores are open and the absorption process by the active group against metal ions is not inhibited.

## 3.2. Optimization of Adsorption Conditions

### 3.2.1. pH Optimization of Ca<sup>2+</sup> Metal Adsorption

The adsorption process was carried out at various pH variations to determine the optimum pH of the adsorbent in absorbing calcium metal ions. Determination of the optimum pH was carried out with pH variations of 4, 6, and 8.

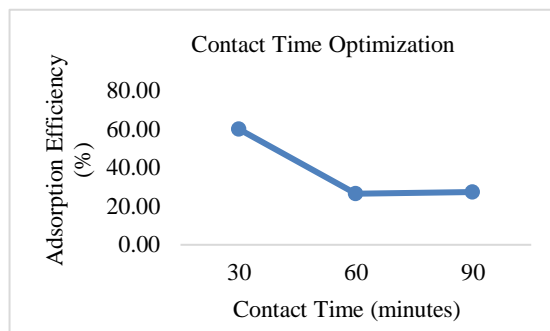


**Figure 5.** Graph of pH Optimization Results of  $\text{Ca}^{2+}$  Metal Adsorption

Based on Figure 4, the pH value with the largest adsorption efficiency value is at pH 8 with an adsorption value of 60.03%. The adsorption process is influenced by many protons in the solution that complete with metal ions on the adsorbent surface. In acidic conditions the adsorbent surface is positively charged, this causes repulsion between the adsorbent surface and metal ions, so that the adsorbent's ability to absorb calcium metal ions decreases. In acidic conditions the adsorbent surface is positively charged, this causes repulsion between the adsorbent surface and metal ions, so that the adsorbent's ability to absorb calcium metal ions decreases. This occurs during adsorption conditions at pH 4, where the absorption process of calcium metal ions is low. At pH 6 adsorption decreased, this is because at that pH metal ions can hydrolyze so that the solution is unstable and causes the ability to absorb metal ions to decrease [9]. While at alkaline pH there is an optimum absorption of calcium metal because the adsorbent surface is surrounded by  $\text{OH}^-$  so that the adsorbent surface becomes negative. This causes an attractive force between the adsorbent surface and positively charged calcium metal ions and results in the highest calcium metal ion adsorption.

### 3.2.2. Contact Time Optimization of $\text{Ca}^{2+}$ Metal Adsorption

Contact time is the time required for the adsorbent to adsorb its adsorbate. Determination of the optimum contact time was carried out at 30 minutes, 60 minutes, and 90 minutes.

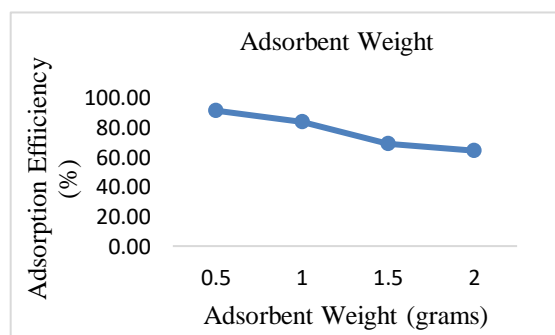


**Figure 4.** Graph of Contact Time Optimization Results of  $\text{Ca}^{2+}$  Metal Adsorption

Based on the graph above, the optimization of contact time for calcium metal ion adsorption is at 30 minutes. The adsorption efficiency continues to decrease as time passes. This can be due to the contact time between the adsorbent and adsorbate having exceeded the optimum contact time or the adsorbent is already in saturated condition or experiencing adsorption equilibrium. At contact times of 60 minutes and 90 minutes there is a decrease in adsorption efficiency due to too long physical contact between calcium metal ions and adsorbents, then calcium metal ions will be released back into solution. This condition can be caused by the weak interaction that occurs between metal ions and adsorbents to bond to the adsorbent surface [10].

### 3.2.3. Weight Optimization of Tea Waste Adsorbent

Determination of the optimum adsorbent weight aims to obtain the optimum weight of tea waste adsorbent in adsorbing calcium metal ions carried out at the optimum pH and contact time by looking at the highest adsorption efficiency. The mass of adsorbent contacted was 0.5; 1; 1.5 and 2 grams.



**Figure 6.** Graph of Adsorbent Weight Optimization

Based on the graph above, it can be concluded that the optimum adsorbent weight is at 0.5 grams with an adsorption efficiency of 91.47%. The adsorption efficiency value decreases as the adsorbent weight increases. This is possible because the adsorbent surface is saturated or close to saturation of the adsorbate, the reason could be due to two things, the first is the formation of the second adsorption layer and so on above the adsorbate that has been bound on the surface, or it can be called multilayer adsorption. While the second can also occur because the second layer is not formed and so on so that the adsorbate that has not been adsorbed diffuses out of the pore and returns to the fluid flow [11].

### 3.3. Determination of Maximum Capacity and Adsorption Isotherm of Tea Waste Adsorbent on Calcium Metal Ions

#### 3.3.1. Relation of Adsorption Capacity of Calcium Metal Ion Adsorption by Tea Waste Adsorbent

Adsorption capacity shows how much the ability of tea waste adsorbent activated with 0.1 N HCl and non-activated in adsorbing calcium metal ions. The adsorption capacity was determined by making concentration variations in artificial calcium metal solutions of 30, 50 and 70 mg/L.

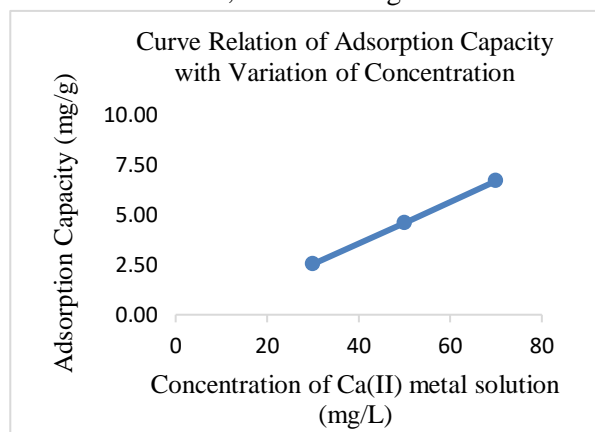


Figure 7. The Correlation Between the Variation of Starting Concentration with Adsorption Capacity

Based on the graph above, it can be shown that the increase in the amount of metal adsorbed is directly proportional to the increase in concentration. The higher the concentration, the more Ca (II) molecules interact with the adsorbent so that adsorption increases [12]. The highest adsorption increase is at the calcium concentration of 70 mg/L with an adsorption capacity of 6.70 mg/g on 0.1 N HCl-activated tea waste adsorbent.

#### 3.3.2. Determination of Adsorption Isotherm Results

Determination of the type of adsorption isotherm by tea waste adsorbent was carried out at optimum conditions with different concentration variations by adsorbent that had been activated by 0.1 N HCl. Based on the data obtained, a linear regression test was carried out using the Langmuir and Freundlich equations.

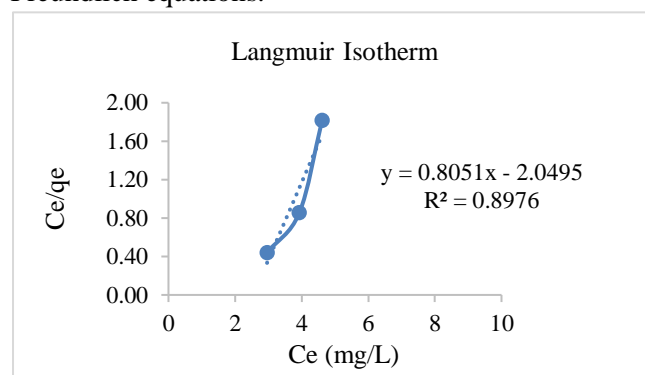


Figure 9. Graph of Langmuir Isotherm of Adsorption of Ca(II) Metal Ions by Tea Waste

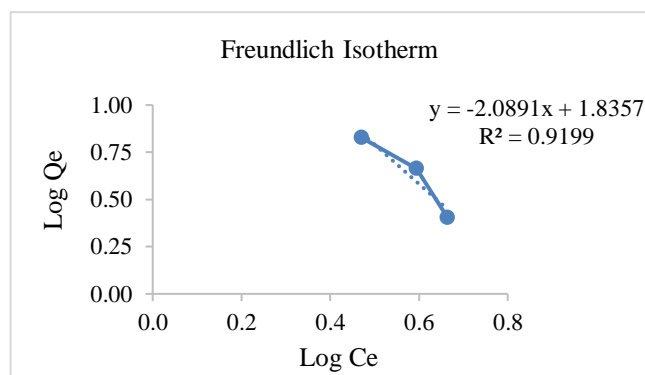


Figure 8. Graph of Freundlich Isotherm of Adsorption of Ca(II) Metal Ions by Tea Waste

**Table 1.** Adsorption Isotherm Parameters of Ca(II) in Hard Water

Isotherm	Parameters	Results
Langmuir	$Q_m$ (mg/g)	1.2421
	$K_L$ (L/mg)	-0.3928
	$R_L$	-0.0377
	$R^2$	0.8976
Freundlich	$K_F$ (m/mg)	0.0146
	$n$	-0.4787
	$R^2$	0.9199

Based on the comparison of each equation, it is known that the  $R^2$  value of the Freundlich isotherm equation is greater than the  $R^2$  value of the Langmuir isotherm equation. For Langmuir isotherm obtained  $R^2$  is 0.8976 while for Freundlich isotherm obtained  $R^2$  is 0.9199. So, it can be concluded that the adsorption experiment of calcium metal ions by this tea grounds adsorbent follows the Freundlich isotherm equation and the interactions that occurred physically.

The other parameters related to adsorption process are equilibrium parameter or adsorption dimension ( $R_L$ ). The  $R_L$  value indicates the suitability of the Langmuir isotherm pattern to the adsorption process, if the  $R_L > 1$  value, the adsorption process is unfavorable; if the  $R_L = 1$  value, the adsorption process is linear; if the value is  $0 < R_L < 1$ , the adsorption process is favorable and if  $R_L = 0$ , the adsorption process is irreversible. However, the  $K_L$  parameter value obtained in this study is negative (Table 4), so the  $R_L$  value becomes negative. A negative  $R_L$  value cannot be applied to describe the nature of the adsorption process [13].

### 3.4. Removal of Calcium Metal Content in Well Water by Tea Waste Adsorbent

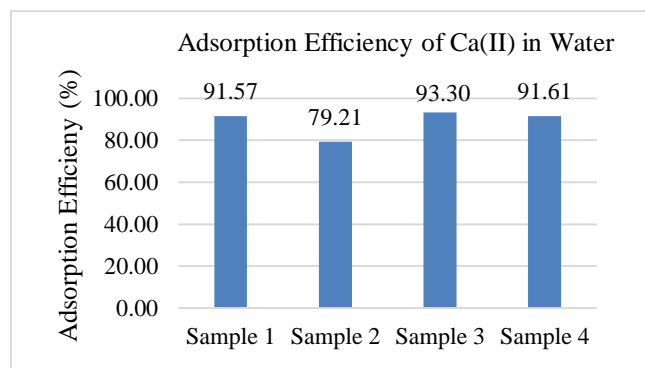
The determination of calcium metal content by tea grounds adsorbent was carried out by preliminary analysis using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) on 4 well water samples around the limestone mountain. The results of the analysis of calcium content in well water can be seen in the following table.

**Table 2.** Analysis of Ca(II) Metal Adsorption in Well Water

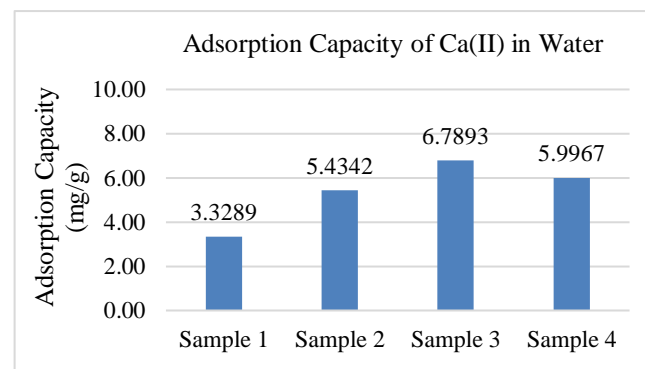
Sample Name	Concentration of Ca(II) (mg/L)	
	Before adsorption	After adsorption
Sample 1	36.3542	3.065
Sample 2	68.6009	14.259
Sample 3	72.7702	4.877
Sample 4	65.4564	5.489

From the analysis of the adsorption of Ca (II) metal in well water, the concentration of calcium metal before and after adsorption was obtained, then the adsorption efficiency and adsorption capacity of calcium metal absorption in well water were calculated and the graphics were created as follows.

Based on the results of adsorption of Ca(II) metal in well water, the efficiency and capacity of adsorption were calculated and the graphic was created below.



**Figure 10.** Graph of Adsorption Efficiency of Ca(II) Metal in Well Water



**Figure 11.** Graph of Adsorption Capacity of Ca(II) Metal in Well Water

Figures 10 and 11 show that the concentration of calcium metal in well water after adsorption by tea waste adsorbent has decreased. The highest absorption

of calcium metal occurred in the third well water sample, which was previously 72.7702 mg/L to 4.8770 mg/L with an adsorption efficiency of 93.30% and an adsorption capacity of 6.7893 mg/g.

#### 4. CONCLUSION

Based on the results of the research conducted, it can be concluded that the optimum conditions for adsorption of Ca (II) metal ions by tea grounds that have been activated with 0.1 N HCl are as follows: 0.5-gram weight of adsorbent, at pH 8, and 30 minutes of contact time. The adsorption isotherm model obtained follows the Freundlich isotherm model with an  $R^2$  value of 0.9199. The highest removal of Ca(II) metal ions by tea waste activated with 0.1 N HCl is in the third well water sample from concentrations of 72.7702 ppm to 4.877 ppm with an efficiency of 93.3% and an adsorption capacity of 6.7893 mg/g.

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