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Modification of CaO from Quail Egg Shells with Sodium Dodecyl Sulfate through Extraction and Precipitation Method as Adsorbent for Methylene Blue Dyes

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Abstract

Calcium oxide (CaO) is widely used as an adsorbent due to high adsorption effectiveness and can adsorb metals in wastewater and dye waste. The aim of this research is to synthesize CaO from quail egg shells and then modify it using sodium dodecyl sulfate surfactant. Synthesis of CaO was carried out through the extraction method using HCl 1% and precipitation method using Na_2CO_3 1M. Modified CaO was synthesized by the same method with the addition of Sodium Dodecyl Sulfate (SDS). Diffractogram peaks on CaO and CaO modifications are similar to JCPDS data No.88-1811. CaO IR spectrum modification after adsorption showed the addition of functional groups C-N and C=N from methylene blue. CaO and CaO's modifications had pHpzc of 11.82 and 11.62.CaO modification using SDS caused a decrease in the surface area of CaO from 3.9 to 2.5 m^2/g and an increase in the pore radius from 3.6 to 13.5 nm. Modification of CaO using SDS decrease the surface area of CaO but adsorption capacity increases 66.19% from 44.63 mg/g to 74.17 mg/g. Kinetic model and adsorption isotherm on CaO and CaO modifications occur in pseudo-second order by following the Langmuir isotherm model. The adsorption process is endothermic and adsorption occurs spontaneously with positive ΔH^o and negative ΔG^o values at each adsorption temperature.

Keywords: quail egg shells, extraction method, calcium oxide, sodium dodecyl sulfate, methylene blue

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Abstrak (Indonesian)

Kalsium oksida (CaO) banyak digunakan sebagai adsorben karena memiliki efektifitas penyerapan yang tinggi serta dapat menyerap logam pada air limbah dan limbah zat warna. Tujuan dari penelitian ini adalah untuk mensintesis CaO dari cangkang telur puyuh dan memodifikasinya menggunakan surfaktan natrium dodesil sulfat kemudian mengapilkasikan pada proses adsordpsi zat warna metilen biru. Sintesis CaO dilakukan melalui metode ekstraksi menggunakan HCl 1% dilanjutkan dengan metode presipitasi menggunakan Na_2CO_3. 1M. CaO termodifikasi disintesis dengan metode yang sama dengan menambahkan Sodium Dodesil Sulfat (SDS) pada saat presipitasi. Puncak difraktogram pada CaO dan CaO modifikasi mirip dengan data JCPDS No.88 – 1811. Spektrum Infra merah CaO modifikasi setelah adsorpsi menunjukkan adanya penambahan gugus fungsi C-N dan C=N dari biru metilen. CaO dan CaO modifikasi memiliki pHpzc 11,82 dan 11,62. CaO modifikasi menggunakan SDS menyebabkan terjadinya penurunan luas permukaan CaO dari 3,9 menjadiI 2,5 m^2/g dan peningkatan radius pori dari 3,6 menjadi 13,5 nm. Modifikasi menggunakan SDS menyebabkan terjadinya peningkatan kapasitas adsorpsi sebesar 66,19% dari 44,63 mg/g menjadi 74,17 mg/g. Model kinetika adsorpsi yang sesuai adalah pseudo orde dua. Isoterm adsorpsi yang sesuai adalah isoterm adsorpsi Langmuir. Proses adsorpsi bersifat endotermik dan adsoprsi terjadi secara spontan dengan nilai ΔH^o positif dan ΔG^o negatif pada setiap suhu adsorpsi.

Kata Kunci: cangkang telur puyuh, metode ekstraksi, kalsium oksida, natrium dodesil sulfat, metilen biru

INTRODUCTION

Methylene blue is a cationic dye that is widely used in the textile industry, easily soluble in water. Methylene blue dye waste in waters with levels of 20-30 mg/L is very difficult to decompose naturally. Methylene blue cause various kinds of human cancers, coming major challenging concerns for public health safty. However, methylene blue shows high stability and resistance to biodegradation [1,2]. An effective method to overcome methylene blue dye waste is adsorption [3-6]. The adsorption process has the advantage of economical handling costs, is able to remove organic materials and does not cause side effects [7]. This process has properties that are easy to apply and can use various types of adsorbents [8].

Calcium oxide (CaO) is widely used as an adsorbent because it has high absorption effectiveness and can absorb metals in wastewater and waste from dyes [9,10]. CaO is widely used because it has high base strength with relatively low production costs [11]. As an adsorbent, it has advantage,s such as large surface area, low cost, safe for humans, fast kinetics, and effective for removing heavy metal ions from water. In addition, it has been used to adsorb dyes from the textile, pharmaceutical, and agricultural waste industries, as well as to absorb the CO_2 gas and heavy metals [10,12,13] CaO can be obtained through the $CaCO_3$ calcination process. One source of $CaCO_3$ is quail eggshells with a calcium content of 9.69% [14]. Quail eggshells can be used as adsorbents derived from animals with shell pores that can be used as adsorbents. To increase the absorption of CaO as an adsorbent, modifications are made by adding surfactants. One of them is the surfactant SDS (Sodium Dodecyl Sulfate). The addition of SDS can reduce the size of the particles formed and in hollow or porous materials can help the formation of pore structures [15]. Jamrunroj et.al [16], synthesized CaO from calcium acetate monohydrate and modified the CaO structure by adding SDS surfactant. SDS-modified CaO has a different crystal size than CaO synthesized without SDS. SDS-modified CaO has a large surface area, pore volume, and pore diameter [16].

Based on the description above, CaO synthesis was carried out from quail egg shells through the HCl extraction method and the precipitation method using Na_2CO_3 then modified by adding SDS surfactant during precipitation. The synthesis results were characterized using X-Ray Diffractometer (XRD), Fourier Transform Infrared Spectrometer (FTIR), pH Point of Zero Charge (pHpzc) and Brunauer, Emmett and Teller (BET). SDS-modified CaO was applied to the adsorption process of methylene blue dye with parameters of contact time variation, methylene blue concentration, and temperature

MATERIALS AND METHODS

Materials

Quail egg shells obtained from quail farms in Simalungun Regency, North Sumatra Province. The chemical and reagent for CaO modified synthesize of modified CaO include HCl (37%), Na_2CO_3, Sodium Dodecyl Sulfate, Methylene blue dye were purchased from Merck. The distillated water was used to make the reagents.

Synthesis of Modified CaO

A total of 20 grams of quail eggshell powder was put into an Erlenmeyer flask then 500 mL of 1% HCl was added then the mixture was stirred for 6 hours. The extraction results were separated using suction filtration until the filtrate was obtained. The filtrate was then added with 10 g of SDS and stirred at temperature of 60^{o}C and speed of 400 rpm for 1 hour. The solution obtained was added with 500 mL of 1M Na_2CO_3 and stirred for 2 hours. The precipitate obtained was separated using filter paper then dried using an oven at a temperature of 100^{o}C and calcined at temperature of 1000^{o}C for 6 hours [17].

Determination of pHpzc

A total of 25 mL of 0.1M NaCl solution was put into an Erlenmeyer flask and then the pH was made from pH 2, 3, 4, 5, 6, 7.8, 9, 10, 11, and 12. The pH was adjusted by adding 0.1 M HCl or 0.1 M NaOH. After that, 0.1 g of CaO modified was put into each Erlenmeyer flask and stirred using a shaker for 2 hours at a speed of 150 rpm. The solution was left for 48 hours and the pH was measured again. [18]. This treatment is the same for CaO modified.

Determination of Optimum Conditions

Optimum conditions were conducted by determining the adsorption capacity at contact time variations of 20 - 80 minutes, concentration variations of 25 - 250 mg/L, temperature variations of 30 - 80^{o}C. Determination of adsorption capacity refer to the equation (1):

$$q_e = \frac{C_o - C_e}{w} \times V \quad (1)$$

where q_e is adsorption capacity (mg/g), Co (mg/L) is the initial concentration of methylene blue and Ce (mg/L) is the remaining concentration after adsorption.

V is the volume of the remaining solution (L), while w is the weight of the adsorbent (g) [19-22].

RESULTS AND DISCUSSION

Synthesis of CaO and modification of CaO

Synthesis of CaO compounds and modification of CaO were carried out using the HCl extraction method and precipitation method using Na_2CO_3. The synthesis of CaO and modification of CaO consists of 3 stages, that were dissolving calcium compounds found in quail egg shells using 1% HCl solvent, precipitation using 1M Na_2CO_3 solution, and calcination of $CaCO_3$ according to the reaction [17]:

$$CaCO_{3\,(s)} + HCl_{(aq)} \longrightarrow CaCl_{2\,(aq)} + H_2O_{(l)} + CO_{2\,(g)}$$

Extraction using 1% HCl aims to isolate the main content of quail egg shells in the form of $CaCO_3$. The resulting product was $CaCl_2$ then reacted with Na_2CO_3 to re-form $CaCO_3$.

$$CaCl_{2\,(aq)} + Na_2CO_{3\,(aq)} \longrightarrow CaCO_{3\,(s)} + 2\ NaCl_{(aq)}$$

Calcination of $CaCO_3$ produced CaO according to the reaction:

$$CaCO_{3\,(s)} \longrightarrow CaO_{(s)} + CO_{2\,(g)}$$

Synthesis of SDS modified CaO at the precipitation stage and calcination according to the reaction:

$$CaCl_2/SDS_{(aq)} + Na_2CO_{3\,(aq)} \longrightarrow CaCO_3/SDS_{(s)} + 2NaCl_{(aq)}$$

$$CaCO_3/SDS_{(s)} \longrightarrow CaO/SDS_{(s)} + CO_{2\,(g)}$$

The synthesis of CaO and SDS-modified CaO was carried out through the stages of extraction and precipitation then calcination with the aim of obtaining purer CaO compared to direct calcination on quail egg shells.

XRD Characterization

The synthesis of CaO and modified CaO was characterized using XRD to identify the diffractogram peaks of CaO and modified CaO. **Figure** 1 shows that modified CaO has five diffractogram peaks at 2θ angles of 32.22, 37.37, 53.89, 62.62 and 64.24 and CaO forms four diffraction peaks at 2θ angles of 32.24, 37.40, 62.65, 64.24. If compared based on JCPDS No.88-1811 data, the 2θ angle formed has almost the same similarity with both adsorbents. From the calculation using the Debye-Scherrer formula, the crystal size of modified CaO and CaO were 33.52 nm and 29.81 nm, respectively.

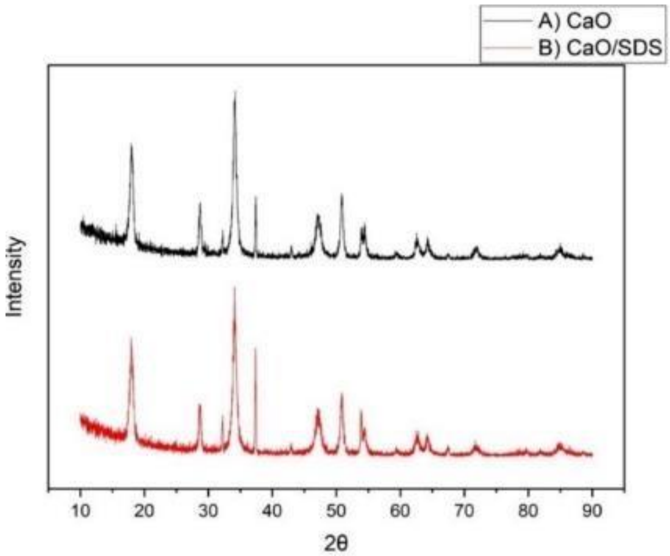

Figure 1. Diffractogram Peaks of CaO and Modified CaO

BET Characterization

BET characterization was carried out to determine the surface area and volume of CaO and modified CaO adsorbents. Surface area influences the adsorption process so that the larger the size of the absorbing pores can influence the greater the adsorption power.

Table 1. BET characterization of the synthesized material

Adsorbent	Surface area (m^2/g)	Pore volume (cc/mg)	Pore radius (nm)
CaO	3.94667	0.01083	3.6115
Modified CaO	2.52869	0.01197	13.5529

Table 1 shown that modified CaO has a smaller surface area than CaO. This is due to the large number of doped SDS components resulting in a smaller CaO surface area. Modifying CaO using SDS affects the surface area of CaO and helps to spread SDS throughout the CaO surface compared to CaO without SDS [11]. This is similar to research by Jamrunroj et.al that CaO added with SDS has a smaller surface area than CaO synthesized without the addition of surfactants [16]. The calcination process affects the decrease in surface area of modified CaO and the resulting pore size increases [23]. The larger pore size of modified CaO proves that SDS has succeeded in opening the pore structure in the synthesis of CaO.

FTIR Characterization

The results of FTIR characterization of modified CaO compounds before and after adsorption are shown in Figure 2. The results of FTIR characterization of modified CaO compounds showed that in the wave number region of 3641.60 cm^{-1} there is an O-H group, the band region at wave numbers 2852.72 - 2922.16 is the peak of the C-H group. samples containing CaO appear in C-H stretching (3000-2800 cm^{-1}) [22]. Wave numbers in the region of 873.75 cm^{-1}, 1126.43 cm^{-1}, 1458.18 cm^{-1} are characteristics of the carbonyl region functional group.

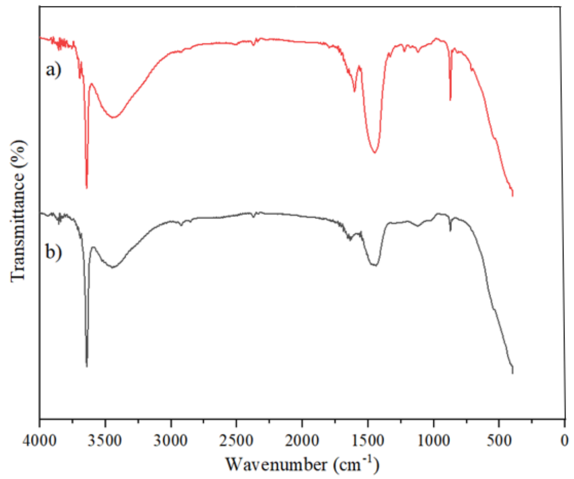

Figure 2. FTIR Spectrum of Modified CaO – Methylene Blue (a) and Modified CaO (b)

The band that appears at wave number 1458.05 cm^{-1} is the region of the -O-C-O bond group originating from carbonate. The wave number 1332.81 cm^{-1} indicates the presence of C-N vibrations of the aromatic ring originating from methylene blue. A new peak indicates that methylene blue is adsorbed on the modified CaO compound. The wave number 3431.36 – 3643.53 cm^{-1} indicates the presence of O-H vibrations. The adsorption of methylene blue is a physical adsorption where the dye only sticks to the surface of the adsorbent.

Determination of pH Point Zero Charge (pHpzc)

At pHpzc, the material has a neutral charge. Determination of pHpzc is very important in the adsorption process where the adsorption process can occur optimally if the adsorbent charge is opposite to the adsorbate charge. The pHpzc of CaO and modified CaO are shown in **Figure** 3.

Figure 3 shows that the pHpzc value of CaO was 11.82 and modified CaO was 11.62. If the pH is greater than pHpzc then the adsorbent surface is negative, if the pH is less than pHpzc then the adsorbent surface is positive, while if the pH value is the same as the pHpzc value then the adsorbent surface is neutral.

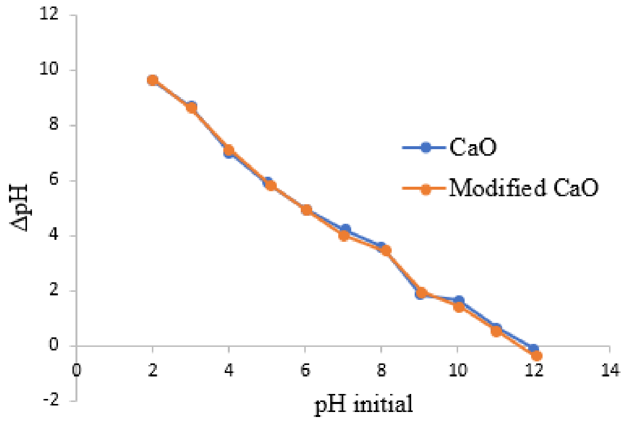

Figure 3. pHpzc Curves of CaO and Modified CaO

Methylene blue is a cationic dye, so the adsorption process can occur optimally at a pH above pHpzc. The methylene blue adsorption process was carried out at pH 12.

Determination of Optimum Contact Time

Determination of the optimum time variation was carried out to determine the interaction of the CaO compound adsorbent and modified CaO with methylene blue dye when varying the contact time. The adsorption curve of methylene blue with variations in contact time is shown in **Figure** 4. **Figure** 4 shows that CaO and modified CaO experienced a significant increase in adsorption at a contact time of 20-40 minutes and tended to be constant for 60 minutes and above.

The highest uptake capacity of CaO and modified CaO compounds occurred at contact times of 90 and 70 minutes. This occurs because at the beginning of the adsorption process there is a lot of empty space on the surface of the adsorbent. At the time the interaction between the adsorbent and the adsorbate increase so that the adsorbed methylene blue increases with time [5,24].

In the adsorption process using CaO, uptake capacity decreased at a contact time of 100 minutes and modified CaO at a time of 80-100 minutes. This happens because the contact time between the adsorbent and methylene blue that is too long. It can cause the methylene blue that has been absorbed will be released again [25].

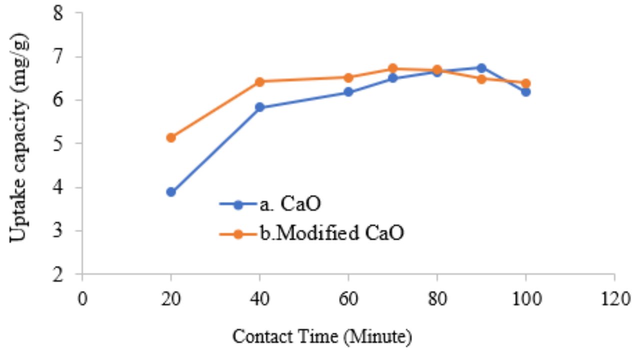

Figure 4. Methylene Blue Adsorption Curve with Variation of Contact Time with CaO and Modified CaO

Determination of Optimum Concentration

The adsorption stage will increase from the beginning and decrease gradually until it reaches the equilibrium point. Therefore, the influence of the initial concentration of methylene blue on the absorbency of the adsorbent was studied. The adsorption curve of methylene blue with varying concentration is shown in **Figure** 5.

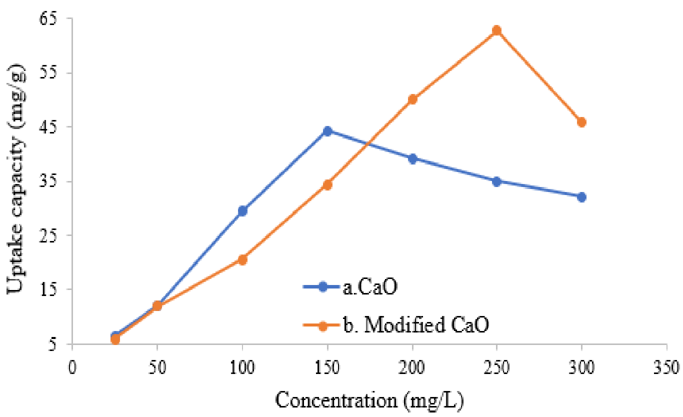

Figure 5. Methylene Blue Adsorption Curve with Concentration Variations with CaO and Modified CaO

In **Figure** 5, CaO experienced a significant increase in adsorption at a concentration of 25-150 mg/L and modified CaO at a concentration of 25-250 mg/L. The highest adsorption capacity occurred at concentrations of 150 and 250 mg/L. This occurs because the surface of the unsaturated adsorbent can still be used by the adsorbent to absorb methylene blue dye. when passing the optimum condition, the adsorption capacity decreased at a concentration of 200 mg/L by CaO adsorbent and 300 mg/L by modified CaO adsorbent. This occurs because of the large amount of adsorbent that enters the pores and when the pores are full, the remaining pores on the surface of the adsorbent will be difficult to occupy because the adsorbate molecules in the solid phase are bulk so that they have a repulsive force [26].

The difference in adsorption capacity occurs in CaO and modified CaO compounds. The pore volume of CaO was smaller so that the absorption capacity during the adsorption process was smaller than modified CaO. This is because when SDS surfactant is added, the pore volume and pore size of the modified CaO are larger so that when the adsorption process is carried out, the absorption of methylene blue is greater than that of CaO.

Determination of Optimum Temperature

Temperature has an important role in adsorption because it can play a role in the amount of substance adsorbed. The adsorption capacity and reaction rate will increase when the temperature increases. An increased adsorption rate can cause a strong adsorption force between the active site of the adsorbent and the adsorbate phase. The adsorption curve of methylene blue with variations in temperature is shown in **Figure** 6.

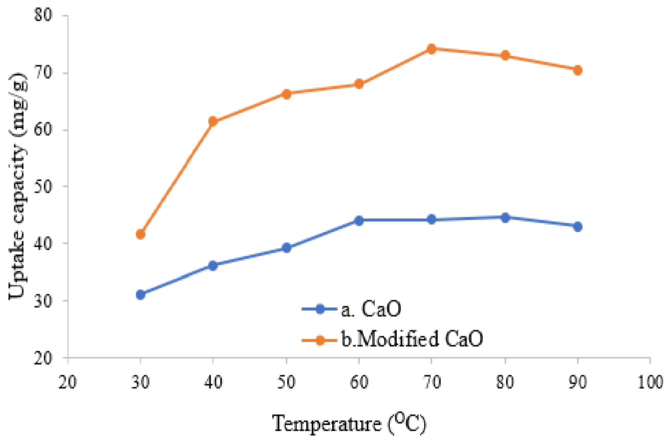

Figure 6. Methylene Blue Adsorption Curve with Temperature Variation with CaO and Modified CaO

The uptake capacity for methylene blue increases until it reaches its optimum temperature and then slowly decreases. The decrease in uptake capacity occurs because the higher temperature produces greater kinetic energy so that the molecules move faster. This causes the adsorbate that was initially adsorbed to be released from the adsorbent pores [27].

Adsorption Kinetics CaO and Modified CaO

The study related to the results of determining the optimum time for methylene blue dye aims to find out how to model the adsorption kinetics. The value of pseudo first order and pseudo second order is determined from the equilibrium value (Qe) and correlation coefficient (R^2). The greater the contact time between the adsorbent and the adsorbate, the greater the t/qt value. The adsorbent's ability to quickly adsorb methylene blue dye can produce high constant rate values [28]. **Table** 2 shows that the adsorption kinetics model of the CaO adsorbent and modified CaO were in pseudo second order with a correlation coefficient R^2 value that were almost close to one. CaO and Modified CaO Pseudo Second Order Curve shown in **Figure** 7.

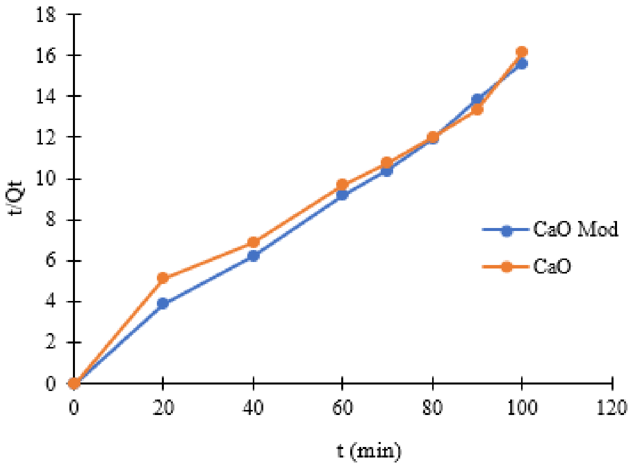

Figure 7. CaO and Modified CaO Pseudo Second Order Curve

Table 2. Data on Adsorption Kinetic Parameters of Modified CaO and CaO to Methylene Blue Dye

Kinetic Model	Parameter	Adsorbent	
		CaO	Modified CaO
Pseudo First Order	Qe Experiment (mg/g)	6.748	6.734
	Qe Calculation (mg/g)	1.03	1.262
	K_1 (min^{-1})	0.012	0.021
	R^2	0.098	0.242
Pseudo Second Order	Qe Experiment (mg/g)	6.748	7.445
	Qe Calculation (mg/g)	6.951	7.435
	K_2 (mg/g.menit)	0.114	0.751
	R^2	0.9797	0.9999

It is assumed that the adsorption rate is influenced by the interaction of adsorption sites on the adsorbent surface with the adsorbent during the adsorption process.

$$\frac{dq}{dt} = k2(qe - qt)^2 \qquad (2)$$

The pseudo-second-order kinetic model can be expressed as in Equation (2). It is assumed that the adsorption capacity is proportional on the number of active sites on the adsorbent [19].

Adsorption Isotherms CaO and Modified CaO

Adsorption isotherm was carried out to see the interaction between modified CaO and CaO as adsorbent on methylene blue dye as adsorbate. The adsorption isotherm models studied are the Langmuir and Freundlich isotherm models are listed in **Table** 3.

Table 3. Data on Adsorption Isotherm Parameters of Modified CaO and CaO to Methylene Blue Dye

Isotherm Model	Parameter	Adsorbent	
		CaO	Modified CaO
Langmuir	Q_m (mg/g)	34.48	56.82
	K_L (L/mg)	0.192	0.035
	R^2	0.983	0.831
Freundlich	n	8.291	1.480
	1/n	0.121	0.676
	K_F (mg/g)	17.183	2.772
	R^2	0.114	0.716

In **Table** 3, it can be seen that R^2 value of the Langmuir model isotherm for CaO and modified CaO adsorbents were greater than the Freundlich model isotherm. This means that CaO and modified CaO follow the Langmuir adsorption isotherm model. Both CaO and modified CaO adsorbents assume that the surface of the adsorbent is homogeneous with an adsorption energy equivalent to each adsorption active site. Adsorption on CaO and modified CaO occurs chemically where the interaction between the active side of the adsorbent and the adsorbed substance occurs in a single layer, namely only on the surface of the adsorbent [7,29].

Adsorption Thermodynamics Parameters of Modified CaO and CaO

The effect of temperature on adsorption using modified CaO and CaO as an adsorbent to adsorb methylene blue dye was studied is listed in **Table** 4. **Table** 4 shows that the energy is released in the process adsorption depends on the type of interaction between the CaO adsorbent and modified CaO. The enthalpy parameter value (ΔH°) in **Table** 4 is positive, indicating that the adsorption process of CaO and modified CaO is endothermic with the adsorption capacity increasing as the temperature increases. The adsorption process of modified CaO and CaO has a positive ΔS° value, meaning that during the adsorption process irregularities occur at the solution interface.

Table 4. Data on Adsorption Thermodynamics Parameters of Modified CaO and CaO to Methylene Blue Dye

Adsorbent	ΔH° (KJ/mol)	ΔS° (J/K.mol)	ΔG (KJ/mol) 30	40	50	60	70	80	90
Modified CaO	51.805	0.167	1.21	-0.46	-2.13	-3.8	-5.47	-7.14	-8.81
CaO	80.154	0.259	1.66	-0.93	-3.52	- 6.11	-8.70	-11.30	-13.88

The ΔG° value for CaO and modified CaO is negative, indicating that the adsorption reaction occurs spontaneously. Increasing temperature results in lower ΔG° values. High temperatures produce greater pushing forces which result in a decrease in the adsorption process of adsorbate molecules on the adsorbent. In this study, the values of ΔH° and ΔG° are in the range for physical adsorption.

CONCLUSION

The synthesis of CaO and modified CaO using SDS has been successfully carried out. The addition of SDS changes the surface area, pore volume and pore radius. Adsorption capacity CaO modified to methylene blue increased by 66.19% when compared to CaO. The adsorption process occurs spontaneously, and follows the pseudo second order kinetic model and Langmuir isotherm.

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