ADSORPTION OF CADMIUM METAL IONS BY A PHYSICALLY-CHEMICALLY ACTIVATED ADSORBENT FROM CANDLENUT (*ALEURITES MOLUCCANA*) SHELLS

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Abstract: Cadmium (Cd) is a pollutant that is highly toxic, dangerous to blood vessels, and bioaccumulative in water. The purpose of this paper is to investigate the kinetics and isotherms of cadmium ion adsorption using candlenut shell-activated carbon. Adsorbents were prepared by chemically activating with 0.5M HCl, physically activating via pyrolysis at 700°C, and a combination of both methods. Adsorptions were conducted using Cd solutions with initial concentrations of 100-300 mg/L, at 100 rpm stirring, and contact times of 5-50 minutes. The chemical functional properties and surface morphology of the adsorbents were studied using Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM), respectively. The characterization revealed that the adsorbent prepared by the physical-chemical activation method was the best and was used to test its performance in adsorbing Cd(II) solutions. The results showed that adsorption capacity increased with contact time and reached equilibrium at 50 minutes with a *qm* value of 12.6 mg/g. The adsorption process followed the Langmuir isotherm model with a constant of 0.14 and R^2 value of 0.986, while the kinetic model was pseudo-second order with R^2=0.999. The results demonstrated that candlenut shells are effective as adsorbent media for treating Cd(II) waste.
Keywords: Adsorption; Cadmium; Candlenut shells; Activated carbon

Abstrak: Kadmium (Cd II) merupakan salah satu bahan pencemar yang sangat beracun, berbahaya bagi tubuh dan mengalami biokumulasi dalam perairan. Artikel ini bertujuan untuk mengkaji kinetik dan isoterm penyerapan logam kadmium menggunakan arang aktif dari cangkang kulit kemiri. Adsorben cangkang kemiri dipreparasi dengan tiga variasi perlakuan aktivasi yaitu aktivasi kimia dengan larutan HCl 0,5M, aktivasi fisika melalui pirolisis pada suhu 700°C, dan kombinasi kimia dan fisika. Adsorpsi dilakukan dengan menggunakan larutan Cd dengan konsentrasi awal 100-300 mg/L, pengadukan 100 rpm dan waktu kontak 5-50 menit. Adsorben dikarakterisasi menggunakan *Fourier-transform infrared spectroscopy* (FTIR) untuk mempelajari kandungan fungsional kimianya, dan menggunakan *Scanning Electron Microscopy* (SEM) untuk mengobservasi morfologi permukaan. Hasil karakterisasi menunjukkan bahwa adsorben dengan aktivasi kimia fisika menunjukkan karakteristik terbaik dan dipakai sebagai representatif dalam pengujian performa adsorpsi larutan Cd(II). Performa kerja adsorben ditinjau dari segi kapasitas adsorpsi terhadap waktu kontak dan konsentrasi awal larutan

Cd(II). Selain itu, studi isotherm dan kinetika adsorpsi juga dilakukan untuk mempelajari mekanisme adsorpsi yang terjadi. Hasil eksperimen menunjukkan bahwa kapasitas adsorpsi meningkat seiring bertambahnya waktu kontak, dan kesetimbangan dicapai pada 50 menit dengan nilai qm sebesar 12,6 mg/g. Proses adsorpsi Cd(II) menggunakan adsorben cangkang kemiri teraktivasi kimia fisika mengikuti model *isotherm Langmuir* model dengan nilai konstanta 0,14 dan dan R^2 = 0,986. Model kinetika adsorpsi ini adalah orde dua semu dengan R^2=0,999. Hasil yang diperoleh membuktikan bahwa cangkang kemiri sangat efektif untuk dijadikan media adsorben untuk pengolahan limbah Cd(II).

Kata kunci: Adsorpsi; Cadmium; Cangkang kemiri; Karbon aktif.

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Introduction

Heavy metal pollution is a serious global environmental issue Khan et al., 2022; Nriagu and Pacyna, 1988), with industries discharging waste in various forms without proper treatment every year (Ahmed et al., 2022). Metals with specific gravities greater than 5 g/cm^3 and densities five times that of water are considered heavy metals. These heavy metals essentially pollute the soil, water, and air. These metals include chromium, nickel, lead, copper, mercury, cadmium, iron, and many others (Nagajyoti et al., 2010). Cadmium, a highly toxic metal classified as a carcinogen and teratogen, is one of the heavy metals of concern. It can remain in the body and harm the lungs, liver, and kidneys (Kisling et al., 1987).

The challenge of removing Cd(II) from wastewater lies in finding environmentally friendly and cost-effective technologies. This is especially important for developing countries like Indonesia where maintaining environmental harmony and health is crucial for sustainable development. One of the key considerations in selecting a waste treatment method is to balance the need for low operating costs and ease of operation (Han et al., 2022; Pyrzynska, 2019; Qasem et al., 2021).

Physical, chemical, biological, and their combinations are traditional methods for removing pollutants from wastewater. Some of the most effective methods, such as membrane technology and chemical oxidation, have limitations in terms of economic feasibility (Pyrzynska, 2019). Other options, such as ion exchange, flocculation, electrochemical oxidation and adsorption (Qasem et al., 2021) have been considered. Among these, adsorption is a popular method due to its high efficiency, ease of recovery, renewability, and cost-effectiveness (Kwikima et al., 2021. However, choosing an ideal adsorbent remains a challenge as it must have a large amount of surface area, high adsorption efficiency and capacity, good stability, and be simple to regenerate (Kumar et al., 2015).

Agricultural waste materials have been found to be inexpensive, environmentally friendly, and capable of high biosorption capacities. Using agricultural waste as adsorbents has several advantages over conventional methods, such as the ability to regenerate and recycle the biosorbent, minimal sludge formation, high efficiency, and low cost (Bhatnagar and Sillanpää, 2010). Available literature reports many types of agricultural waste-based materials that have been successfully used as adsorbents, such as rice and wheat husks, sawdust from woody plants, tree bark, coconut and peanut shells, tea leaf waste, jatropha deoiled cake, and fruit peels (apple, banana, coffee and orange), bagasse (Bashir et al., 2020; Brown et al., 2000; Farooq et al., 2011; Farooq et al., 2010; Feng et al., 2011; Jalali and Aboulghazi, 2013; Singh, 2020). These agricultural waste materials have high carbon content, porous structures, and functional groups that increase their adsorption capacity (Dai et al., 2018). Utilizing this biomass waste addresses solid waste management and contributes to environmental preservation.

In this study, candlenut shells were selected as a biomass waste-based adsorbent for Cd removal in wastewater. Candlenut (*Aleurites moluccana*) is a widely used natural product in Indonesia, particularly in Aceh, that has many benefits in cooking, medicine, beauty, energy, and biofuel (Sihombing and Wijayanto, 2013). Traditionally, only the meat of candlenut is utilized, resulting in the disposal of its shells as waste. With a shell-to-meat ratio of 64.57%, higher than the 30% of coconut and oil palm shells (Sugiani, Wayan N et al., 2021), and a lack of proper management, candlenut shells are a potential source of environmental pollution. However, their hard characteristics make them suitable for use as candlenut shell charcoal.

Previous studies have used activated carbon from candlenut shells to remove heavy metals such as mercury (Mariana et al., 2022), Lead (Sugiani, Wayan N. et al., 2021; Zakir et al., 2019b), and chromium (Zakir et al., 2019a). To our knowledge, only a few studies on the adsorption of cadmium ions using candlenut shells have been conducted. The effectiveness of activated carbon derived from candlenut shells in removing cadmium from solution will be investigated in this study. The adsorbent properties, adsorption capacity, kinetics, and adsorption isotherm were explored.

Materials and Methods

Materials

Candlenut shells sourced from Aceh Besar were used as the base material for adsorbents. Cd(II) solution (MERCK 1.19777.0500) was used as an artificial waste sample, while 0.05 M hydrochloric acid (HCl) solution (Sigma-Aldrich) served as a chemical activator, and distilled water was used as a solvent and for other purposes such as washing.

Methods

Preparation of adsorbent

The preparation of candlenut shell-based activated carbon adsorbents was carried out in three ways: chemical activation (C), physical activation (P), and physical-chemical activation (PC). The procedure began with washing and drying the candlenut shells in the sun to reduce water content. The dried shells were then crushed (PM100-RETSCH, Shimadzu, Japan) and sifted to produce a uniform size of about 100 mesh. For chemical activation, the shells were immersed in 0.5 M HCl solution for 3 hours with occasional stirring, washed with water until pH was neutral, filtered, and oven-dried. For physical activation, the shells were carbonized at 700°C for 5 hours. For physical-chemical activation, the shells were first carbonized at 700°C for 5 hours and then immersed in 0.5 M HCl solution.

Evaluating the effects of contact time

Cd(II) solutions containing 100, 200, and 300 mg/L were added to 100 mL chemical glass and 1 gram of physically-chemically activated candlenut shells adsorbent was added. The mixture was stirred at 100 rpm to facilitate contact between the adsorbent and adsorbate. Contact time for adsorption was varied for 10-250 minutes. After the process, the filtrate was separated using filter paper for 15 minutes. The resulting filtrate was then analyzed using an atomic absorption spectrophotometer (AAS, AA-7000, Shimadzu, Japan).

The results of the Cd metal ions' final concentration obtained from the analysis using AAS were used to calculate the adsorption capacity. The adsorption capacity was calculated using the equation below:

$$q_{t=n} = \frac{(C_{t=0} - C_{t=n}) V_S}{m_{AC}} \quad \text{.....(1)}$$

Where:

$q_{t=n}$ = adsorption capacity at t = n (mg/g)
$C_{t=0}$ = initial adsorbate concentration at t = 0 (mg/L)
$C_{t=n}$ = final adsorbate concentration at t = n (mg/L)
m_{AC} = mass of activated carbon (g)
V_S = volume of the solution at the specific time t = n (L)

Characterization of adsorbent

The characteristics of the prepared candlenut shell adsorbents, which were activated in three different ways, were examined using FTIR ((FTIR Prestige-21, Shimadzu, Japan) to recognize the functional groups in the activated candlenut shell adsorbent. The morphological effects of each activation treatment were also examined using scanning electron microscopy (JEOLJSM 6510 LA, Shimadzu, Japan).

Adsorption isotherm

The Langmuir and Freundlich models were used to examine the adsorption isotherm. The Langmuir equation is written as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{1}{q_m} Ce \quad \text{.....(2)}$$

where C_e is the concentration of adsorbate in solution (mg/L), qe is the maximum adsorption capacity per gram of adsorbent (mg/g), q_m is the adsorption capacity at time t per gram of adsorbent (mg/g), and K is a constant related to the adsorption capacity. To determine the constants in the Langmuir equation, a linear plot of C_e/q_e against C_e is drawn.

Meanwhile, for the Freundlich isotherm model, the following equation is used:

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

where K_f is the Freundlich isotherm constant which relates to adsorption capacity and $\frac{1}{n}$ is an indicative constant that indicates the intensity of the adsorption process. To determine the constants in the Freundlich equation, a graph is constructed by plotting log q_e against *log* C_e. The values of $\frac{1}{n}$ and log K_f are determined from the linear equation from the graph.

Adsorption Kinetics

To evaluate the adsorption kinetics of Cd(II) ions, Lagergren's rate equation was applied. This equation includes pseudo-first (Equation 4) and second-order (Equation 5) kinetic model:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad \text{.....(4)}$$

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad \text{.....(5)}$$

Pseudo-first-order reaction

Equation (4) can be integrated into equation (6)

$$ln(q_e - q_t) = ln\, q_e - k_1\, t \quad \text{.....(6)}$$

The calculation of the pseudo-first-order kinetic rate can be done by constructing a graph of the relationship between *ln* $(q_e - q_t)$ as the Y-axis and t as the X-axis and determining the slope and intercepts. This can be used to calculate the *ln* q_e and K_1 values, which in turn can be used to determine q_e and K_l. Specifically, the q_e and K_1 values are obtained from:

- Slope = -k, becomes k = slope
- ln qe = Intercept, becomes Intercept = ln qe

Pseudo-second-order reaction

Equation (5) can be incorporated into equation (7):

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} t \quad \text{.....(7)}$$

The second-order kinetic rate can be determined by creating a linear equation from a graph of the relationship between *t/qt* as the Y-axis and *t* as the X-axis. The linear equation will result in $1/q_e$ and $1/k_2.q_e$ values, which are used to obtain the q_e dan K_2 values by using the following equation:

- Slope$=\frac{1}{\text{qe}}$ becomes qe$=\frac{1}{\text{slope}}$
- Intersep$=\frac{1}{\left(\text{k}^2\right)(\text{qe})}$ becomes $\text{K}^2=\frac{1}{(\text{qe})(\text{Intersep})}$

Results and discussion

Analysis of the functional groups

Previous research has shown that carbon from candlenut shells typically contains functional groups such as OH, C-H, and C=O. O-H, C=C, C-H from methyl and methylene groups, and C-H from aromatic structures were identified as functional groups in carbonized candlenut shells. The O-H, C=C, and C-H from methyl and methylene groups, and C-H from aromatic structures were identified as functional groups in carbonized candlenut shells.(Zakir, et al., 2019; Risdiana, et al., 2021).

The IR spectra of the C, P, and PC adsorbents in Figure 1 show a sloping absorption band in the 2280 cm^{-1} wavenumber region, indicating the presence of hydroxyl groups (OH). The chemically activated candlenut shell adsorbent has a wider peak area which shrinks after going through the carbonization (Risdiana et al. 2019), indicating that the carbonization process has caused the loss of non-carbon elements. The carbonization process was designed to convert hydrocarbon compounds like cellulose and hemicellulose into pure carbon and yield granules with high adsorption power (Zakir et al. 2019). Previous research reported similar findings, where the IR results for the candlenut shell-based adsorbents were dominated by the presence of OH groups (Mariana et al., 2022).

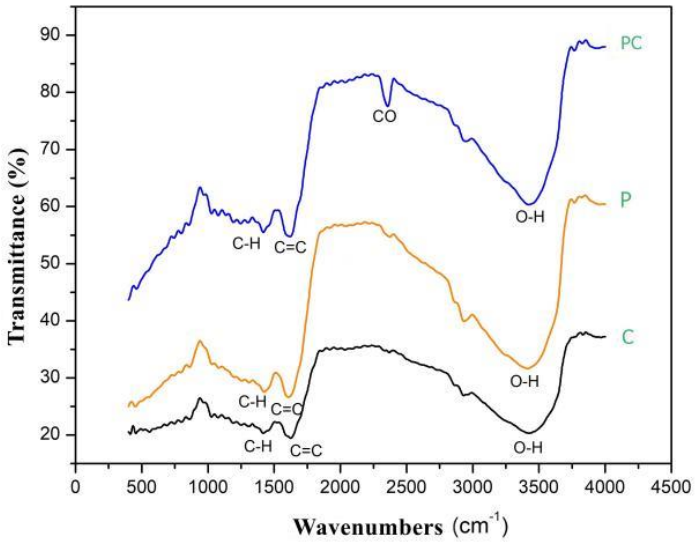

Figure 1. IR spectra of candlenut shell adsorbents after chemical (C), physical (P), and combined physical-chemical (PC) activation

The absorption band at a wavenumber of 2280 cm^{-1}, which is indicative of the bending vibrations of the C=O group, is more pronounced in the KF adsorbent compared to those that were only physically (P) or chemically (C) activated. This is believed to aid in the adsorption of heavy metal ions, as the presence of CO and OH bonds on the adsorbent surface makes it more polar (Zakir, et al., 2019).

The IR spectra of the samples show an absorption band in the range of 1409-1425 cm^{-1} indicating the presence of a C-H asymmetric vibration. Additionally, there is an absorption band at 1592 cm^{-1}, which is associated with a C=C bond in an aromatic ring and C-O-C vibration, indicating an ether structure. The peak intensity of the C=C aromatic group in samples P and CP is higher than in sample C, indicating that carbonization (physical activation) increases the presence of aromatic compounds, which are a crucial component of the hexagonal structure of carbon.

Analysis of Pore Morphology

The surface morphology and pore characteristics of the candlenut shell adsorbents activated in three different ways were examined and are presented in Figure 2.

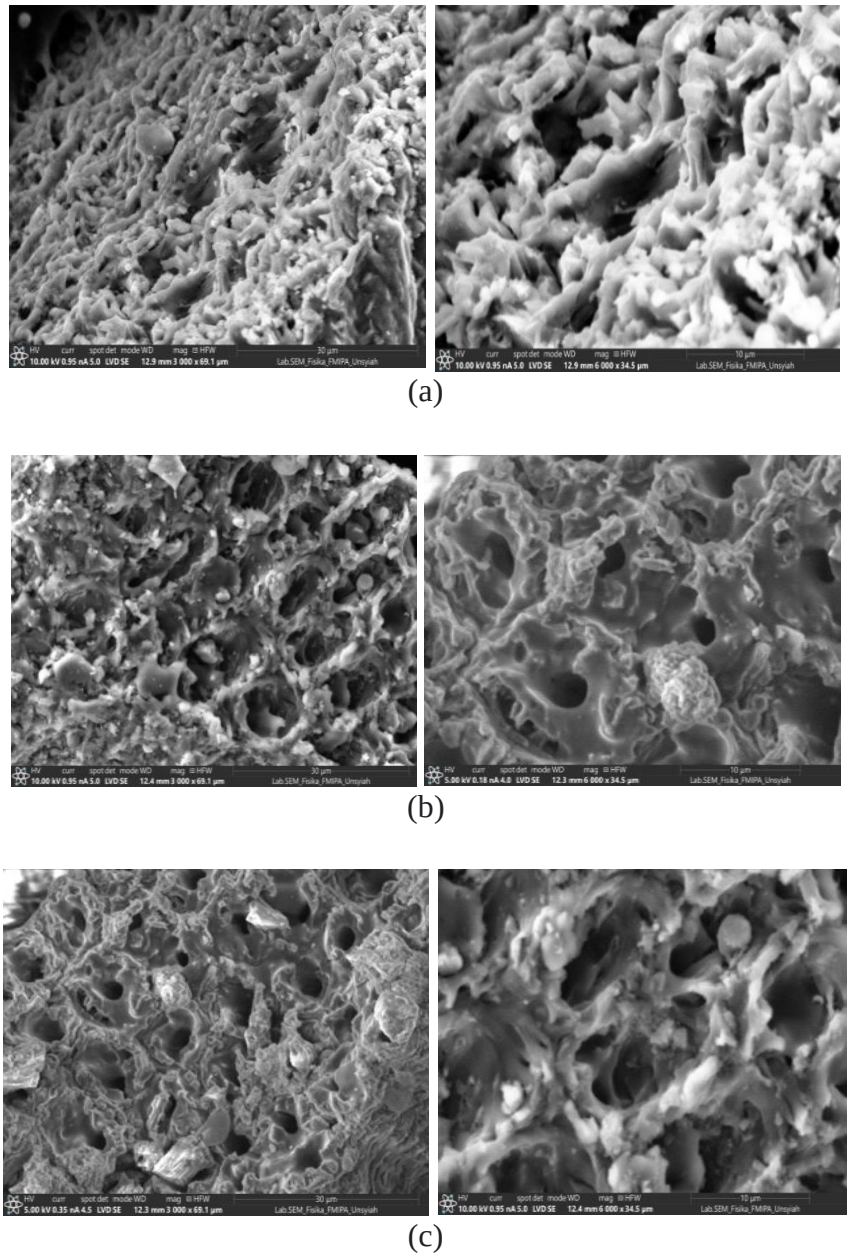

Figure 2. SEM images of the candlenut shell adsorbent after chemical (a), physical (b), and physical-chemical (c) activation

Figure 2 shows the different surface characteristics of the candlenut shell adsorbents by three different activation methods. The surface of the adsorbent activated by chemical only (Fig. 2a) appears to have tighter or closed pores, likely due to the dehydrating effects of the added hydrochloric acid (HCl) which reduces the stretching of H bonds in the surface pores (Nguyen and Dang, 2020; Wahyuni et al., 2021). However, this treatment alone does not produce optimal pore openings. On the other hand, physical activation (Fig. 2b) results in clear surface pores resulting in the release of volatile compounds throughout carbonization at

700°C (Mariana et al., 2022), which effectively opens the initially closed pores. Meanwhile, the physically-chemically activated adsorbent (Fig. 2c) has a better surface morphological structure with a greater number, size, and uniformity of pore shape, likely due to the stretching of chemical bonds and removal of impurities by HCl and evaporation during physical activation.

Overall, the SEM analysis suggests that the adsorbent that underwent both physical and chemical activation exhibits the most optimal surface and pore morphological properties. Therefore, in the subsequent adsorption performance testing, only PC adsorbents will be considered.

Effect of Contact Time on Adsorption Capacity

The duration of the adsorption process, known as contact time, is important in determining an adsorbent's adsorption capacity. To evaluate the optimal contact time, this study examined the relationship between contact time and Cd adsorption capacity using PC adsorbents at three different initial concentrations of Cd, as shown in Figure 3.

The adsorption capacity specifies the amount of adsorbate that can accumulate on the surface of the adsorbent during the adsorption process (Lo et al., 2012), and the optimum contact time is the point at which the maximum amount of Cd is adsorbed by the adsorbent (Kurniawati et al., 2021).

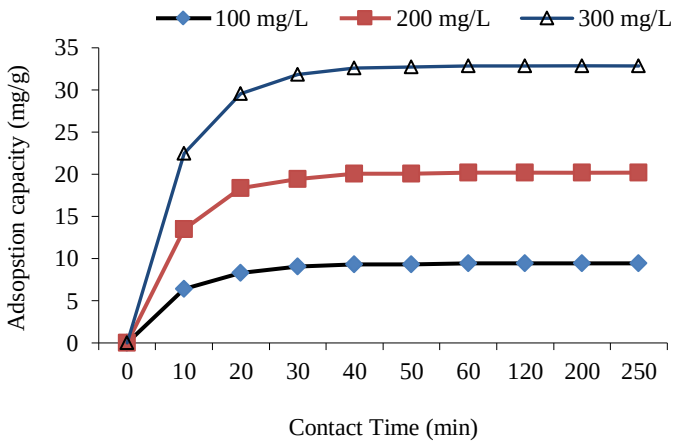

Figure 3. The effect of contact time on the adsorption capacity of Cd at various initial concentrations

Figure 3 illustrates the association between contact time and Cd adsorption capacity of physically-chemically activated candlenut shell adsorbent (PC) at three different initial concentrations of Cd. The adsorption capacity increases along with the contact time, as the amount of adsorbed Cd also increases until reaching equilibrium. Within the first 50 minutes, the Cd adsorption rate is high. However, after this point, the rate of adsorption appears to plateau, indicating that the

equilibrium state has been reached. This suggests that the optimal contact time for adsorption using the physical-chemical activated candlenut shell adsorbent is 50 minutes. If the adsorbent has a higher capacity to absorb more adsorbate, a longer contact time is required. Adsorbents with high capacities have more available reactive sites on their surface for adsorbate molecules to bind to (Mariana et al., 2021). It can also be observed from Figure 3 that the trend graphs for the three concentrations tend to be similar, with only the adsorption capacity being lower in experiments using a lower concentration of Cd solution. This is because, at lower concentrations, fewer adsorbate particles are present in the solution.

Adsorption Isotherm

Adsorption isotherms play a crucial role in describing the distribution of adsorbate between the solid and solution phases in an adsorption process (Andres et al., 2022). In this study, the adsorption isotherm behavior of the physically-chemically activated candlenut shell adsorbent for Cd removal was studied using the Langmuir and Freundlich models. The Langmuir isotherm is signified by a plot of *Ce* against *Ce/qe*, as shown in Figure 4, and the Freundlich isotherm by a plot of *log Ce* vs *log qe*, as shown in Figure 5.

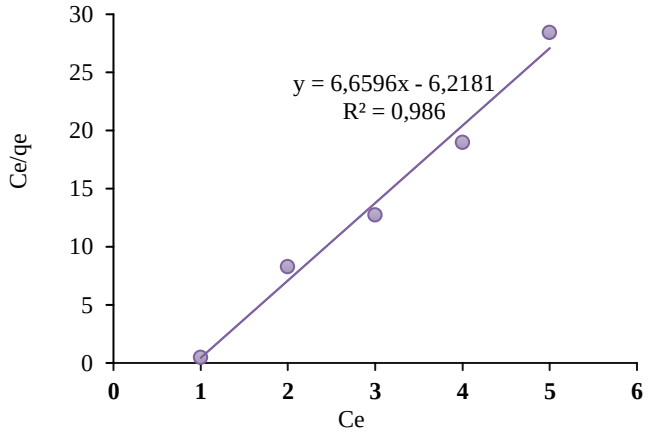

Figure 4. Langmuir isotherm model of Cd(II) metal ion adsorption on physically-chemically activated candlenut shell adsorbent

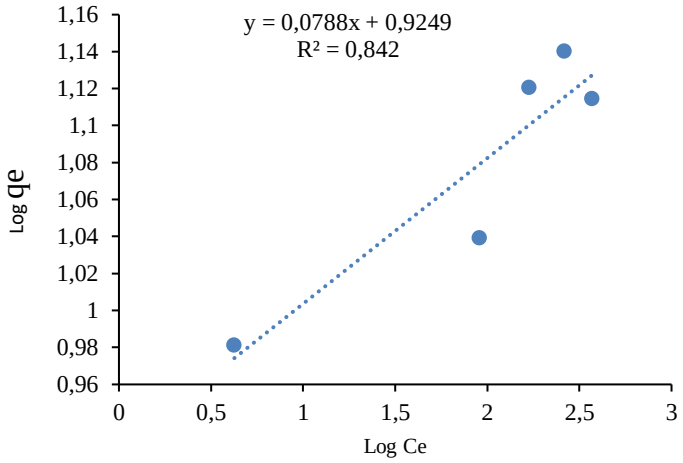

Figure 5. Freundlich isotherm model of Cd(II) metal ion adsorption on physically-chemically activated candlenut shell adsorbent

Both Figures 4 and 5 provide coefficient of determination data, slope, and intercept, which can be used to calculate isotherm constants, as presented in Table 1.

Table 1. Isotherm constants of Cd(II) adsorption using physically-chemically activated candlenut shell adsorbent on Langmuir and Freundlich isotherm models

Langmuir			Freundlich		
q_m	K_L	R^2	n	K_F	R^2
13.51	0.14	0.986	12.7	-0.034	0.842

Table 1 presents the Langmuir and Freundlich isotherm constants of Cd(II) adsorption using physically-chemically activated candlenut shell adsorbent. The data shows that the Langmuir isotherm model is more suitable for this adsorption process, as indicated by the higher coefficient of determination (R^2) of 0.986 compared to the Freundlich isotherm model with a coefficient of 0.842. This implies that the active sites on the adsorbent surface are uniform, allowing for the adsorption of one Cd ion per site without interaction between Cd and the active site.

This finding is supported by other research studies, such as the work done by Huang and the research team, who found that the adsorption of Cd on nitric acid oxidized granular activated carbon also follows the Langmuir model with q_m values in the range of 24-51 µmol/g and R^2 values greater than 0.96 across varying temperatures (Huang et al., 2007).

Adsorption Kinetics

The examination of adsorption kinetics offers insight into the rate and mechanism of the adsorption process, which can be used to understand the nature of the interaction between the adsorbent and adsorbate as well as the mechanism for removing the adsorbate (Silva-Yumi et al., 2018). To determine the underlying

mechanism of the adsorption process, the data obtained were fitted to two kinetic models, as can be seen in Figures 6 and 7.

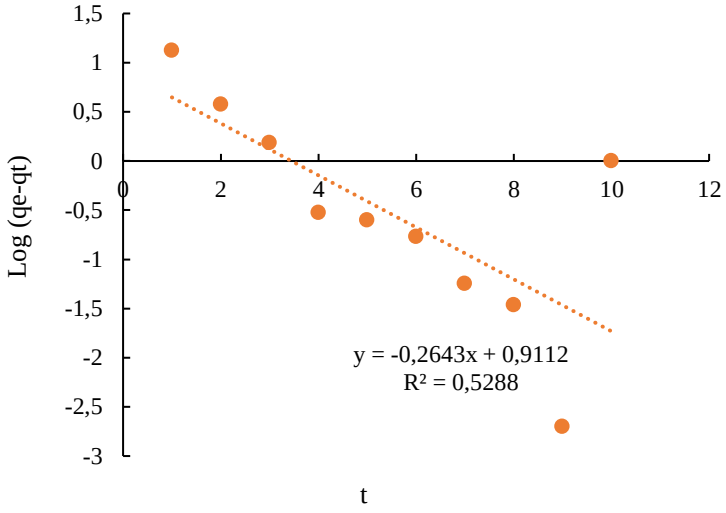

Figure 6. Pseudo-first-order kinetics model for Cd adsorption on physically-chemically activated candlenut shell adsorbents

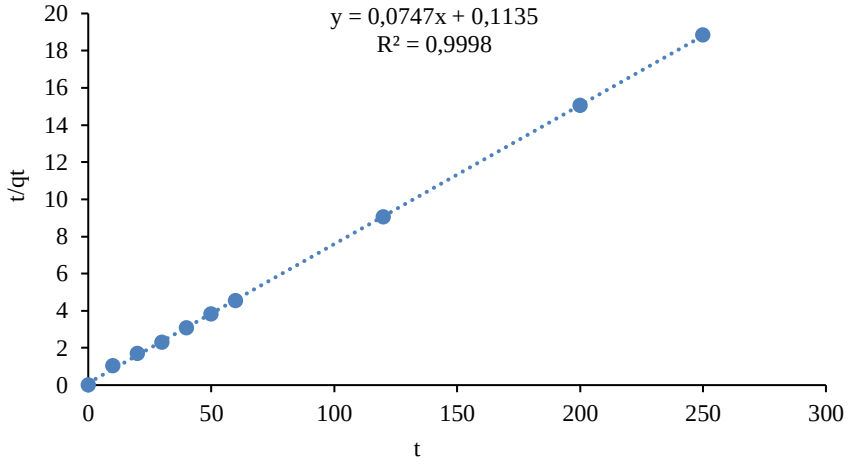

Figure 7. Kinetics of Cd adsorption on physically-chemically activated candlenut shell adsorbent by the pseudo-second-order model

The data of slope and intercept from Figures 6 and 7, showing the plots of the pseudo-first-order and pseudo-second-order adsorption kinetic equations, were used to calculate the values of the pseudo-first-order rate constant (k_1), the pseudo-second-order rate constant (k_2), the theoretical adsorption capacity (qe_{calc}), and the regression coefficient (R^2). The kinetic constants are summarized in Table 2.

Table 2. Kinetic constants obtained from the adsorption kinetics data

Pseudo-first Order			Pseudo-second Order		
q_e	K_1	R^2	q_e	K_2	R^2
0,911	1,608	0,528	0,074	8,810	0,999

Table 2 presents the constants of the pseudo-first and second-order kinetic models for the Cd adsorption process using physically-chemically activated candlenut shell adsorbent. As seen from the R^2 values, the adsorption process follows the pseudo-second-order kinetics more closely, with an R^2 of 0.9998, compared to the R^2 of 0.5288 for the pseudo-first-order kinetics. This is consistent with previous studies, such as (Asuquo et al., 2017), who adsorbed Cd using commercial activated carbon, and (Huang et al., 2007) who found that Cd adsorption using activated carbon followed the pseudo-second-order model with a coefficient of determination (R^2) of 0.9998. This model describes the adsorption process that occurs due to chemical bonding between the adsorbate and the functional groups on the adsorbent's surface, which determines the adsorption capacity. This mechanism is based on adsorption equilibrium, which is determined by the amount of adsorbate adsorbed on the adsorbent surface as well as the amount of adsorbate adsorbed at equilibrium. (Ho, 2006).

Conclusion

A study on the performance of physically-chemically activated candlenut shell adsorbent to remove Cd(II) ions in waste has been carried out. The results indicate that the adsorption process follows the Langmuir isotherm model with a coefficient of determination (R^2) of 0.995 and the pseudo-second-order kinetics model with R^2 = 0.9998. The equilibrium time was found to be 50 minutes. These findings suggest that candlenut shell is a promising material for Cd(II) waste treatment.

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