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The Modification of Coal Fly Ash Adsorbent Using Dithizone Immobilization for Cd(II) Ions Removal

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Abstract

The adsorption of Cd(II) ions onto an adsorbent of dithizone-immobilized coal fly ash (DCFA) was done using batch experiments. In this study, coal fly ash was initially activated using hydrochloric acid, and then its surface was modified by dithizone. The immobilization of activated coal fly ash (ACFA) with dithizone has been carried out to increase the adsorption capacity as the adsorbent of Cd(II) ions. The synthesized adsorbents (DCFA and ACFA) were characterized by FT-IR, XRD, TGA-DTA, adsorption-desorption N_2 (BET), and SEM to confirm the successful immobilization of dithizone on the activated coal fly ash. The adsorption parameters, such as pH, adsorbent dosage, contact time, and initial concentration of Cd(II) ions on the adsorption efficiency, were optimized. Optimal adsorption was achieved at pH 7, an adsorbent dosage of 0.1 g, a contact time of 75 minutes, and an initial Cd(II) concentration of 50 mg L^{-1}. The results showed that the adsorption kinetics were found to follow a pseudo-second-order kinetic model, and their adsorption isotherms were best described by the Langmuir model. Kinetics and adsorption isotherm studies suggested that the capacity, equilibrium constant, and energy of the DCFA in adsorbing Cd(II) ions are improved compared to those of non-immobilized ACFA. A sequential desorption study using different solvents of H_2O, KNO_3, $HONH_2HCl$, and Na_2EDTA revealed that binding Cd(II) ions to the adsorbents primarily involves chemisorption. The type of interaction shifts significantly from being predominantly electrostatic or ion-exchange in ACFA to primarily involving chelate complexation in DCFA.

1. Introduction

Heavy metal contamination has emerged as a critical public health issue worldwide, particularly due to its association with various health risks and environmental degradation. The most common heavy metals arising from various industries, including cadmium (Cd), lead (Pb), arsenic (As), chromium (Cr), mercury (Hg), and nickel (Ni), are among the most harmful pollutants of water [1]. These metals are highly toxic due to non-biodegradable properties that can accumulate in living organisms and their ability to remain and mobility in the environment for a longer duration of time [2].

Cadmium (Cd) is a toxic heavy metal that poses significant health risks when present in drinking water. Cadmium ions contaminate the environment through industrial effluents from plating and nickel-cadmium battery manufacturing [3]. A significant amount of cadmium is absorbed through the respiratory system. This metal has been identified as a carcinogen, and it can affect the prostate, lungs, pancreas, and urinary tract [4]. Regulatory bodies have established permissible limits for cadmium in drinking water to protect public health. The World Health Organization (WHO) recommends a maximum concentration of 0.003 mg/L [5]. Similarly, the United States Environmental Protection Agency (USEPA) sets the maximum contaminant level (MCL) for cadmium at 0.005 mg/L [6].

In recent years, research and development initiatives have produced various kinds of technologies for heavy metal removal from industrial effluent. These techniques, such as electrochemical, ion exchange, reverse osmosis, chemical precipitation, coagulation-flocculation, ultrafiltration, photocatalysis, and membrane separation, have emerged as promising techniques for removing heavy metals [7].

However, the majority of these techniques need further treatments, high operational and maintenance costs, the energy-intensive use of hazardous substances, and the disposal of toxic sludge as a byproduct, which may indicate the presence of more pollutants [8]. As a result, they may not be appropriate for small-scale industries, especially in developing countries where affordable solutions are required. The adsorption method has shown great promise and advantages such as cost efficiency, availability, ease of operation, high efficiency, lack of production of by-products, and the possibility of regeneration. The production of high-quality effluent and the lack of hazardous substances and free radical formation are among the other advantages of this method [9, 10].

Coal fly ash (CFA), a by-product of coal combustion in thermal power plants that use coal as fuel [11]. It is a globally abundant waste with substantial dust emission that not only harms the atmospheric environment but also threatens human health [12]. Recently, CFA-based adsorbent emerged as an effective adsorbent for removing potential water pollutants such as heavy metals, organic, and dyes due to its availability, environmental consideration, and low cost [12, 13, 14]. However, CFA typically has a low adsorption capability due to its low surface area and crystalline structure. In order to improve the adsorption efficiency, CFA modification using chemical and physical methods has been studied [15].

More advancements are now being made in the surface modification and functionalization of CFA employing a sensitive and specific ligand to increase the capacity and selectivity of the adsorbent material [16, 17]. According to Nguyen *et al.* [18] mercaptobenzothiazole (MBT) and sodium dodecyl sulfate (SDS) are used to modify the CFA surface to remove Cd and Hg ions. On the other hand, dithizone, 1,5-diphenyl-thiocarbazone, is widely known for its outstanding analytical and spectroscopic uses as a chelating compound that contains nitrogen and sulfur donor atoms.

Dithizone offers distinct advantages that make it particularly suitable for Cd(II) analysis, such as showing high selectivity, good stability, and sensitivity for cadmium. Dithizone showed high selectivity toward Cd(II) ions due to its strong affinity and the formation of stable, easily extractable chelates [19].

It is a suitable ligand for heavy metals complexation, more specifically to chelate heavy metal ions, including Pb(II), Cd(II), Cu(II), and Hg(II) [20, 21]. Because of its selectivity, dithizone has been reported to be used as the ligand to modify the adsorbent surface in the wastewater treatment polluted with those metal ions. For example, Mudasir *et al.* [16] have introduced zeolite and bentonite [22] immobilized by dithizone for the removal of Hg(II) ions.

In the current study, we investigate the ability of DCFA adsorbent to remove Cd(II) ions from aqueous solution. Several adsorption parameters influencing the effectiveness of the adsorption process, such as the effect of pH, adsorbent dosage, contact time, and initial concentration of Cd(II) ions, were systematically studied. The adsorption kinetics and isotherms were investigated. Furthermore, the sequential desorption study using different solvents of H_2O, KNO_3, $HONH_2HCl$, and Na_2EDTA was also carried out to further investigate the different types of interaction that occur between Cd(II) ions and the active sites of both the DCFA and unmodified ACFA.

2. Experimental

2.1. Materials

Coal fly ash (CFA) was obtained from PT. Solusi Bangun Indonesia (Cement Factory in Cilacap, Indonesia). Dithizone or 1,5-Diphenylthiocarbazone (Merck), toluene (Merck), HCl 37% (Merck), and distilled water were used for the synthesis of dithizone-immobilized coal fly ash adsorbent. Salts of $Cd(NO_3)_2$ (Merck) were used for the standard solution of Cd(II) ions. Solution of KNO_3, $HONH_2HCl$, Na_2EDTA (Merck), and double-distilled water were used for the sequential desorption study.

2.2. Preparation of Adsorbent

CFA (10 g, 200 mesh) was activated by refluxing with 6 M HCl at 100°C for 4 hours. The resulting mixture was filtered, and the product was washed with distilled water until a neutral pH was achieved, then dried at 160°C for 6 hours. The ACFA (4.0 g) was then modified by adding 1.03 g of dithizone in a toluene medium. The mixture was stirred and heated at 50°C for 4 hours. The product was filtered and sequentially washed with toluene, ethanol, and distilled water, followed by drying at 45°C for 6 hours to obtain DCFA.

The activation of the adsorbent using hydrochloric acid (ACFA), the adsorbent characterization, and dithizone immobilization on the surface of ACFA using toluene medium, have been previously described in detail in our earlier paper [17].

2.3. Characterization of Activated Coal Fly Ash (ACFA) and Dithizone-Immobilized Coal Fly Ash (DCFA) Adsorbent

The pH of buffer and metal ion solutions was measured using a Mettler Toledo SevenCompact pH meter. Functional groups of the adsorbents were identified by Fourier Transform Infrared (FT-IR) spectroscopy (Shimadzu FT-IR/8201 PC), while crystal structures were analyzed via X-ray diffraction (XRD; Philips PW 3710). Post-adsorption morphology and elemental composition of ACFA and DCFA were examined using scanning electron microscopy with energydispersive X-ray spectroscopy (SEM-EDX; JEOL JSM-6510LA). Thermal stability was assessed through thermogravimetric analysis (TGA; Rigaku Thermoplus TG 8120) and differential thermal analysis (DTA; Thermoplus Evo Rigaku DSC 8230). Specific surface area and pore size were determined by nitrogen adsorption–desorption (Belsorp 28SA), and metal ion concentrations were quantified using atomic absorption spectroscopy (AAS; GBC 932 AA).

2.4. Adsorption Study of Cd(II)

2.4.1. Optimization of pH

An aqueous solution containing Cd(II) was prepared by dissolving $Cd(NO_3)_2$ salts in double-distilled water. The pH of the metal solution was adjusted by adding a buffer solution of nitric acid or aqueous ammonia in the range pH of 3.0-8.0. For each experiment, 20 mg of adsorbent was added to 10 mL of Cd(II) solution with an initial concentration (C_0) of 10 mg L^{-1}. The resulting suspension was stirred for 60 minutes at room temperature. After filtering the mixture, the concentration of Cd(II) ions in the filtrate was measured using AAS. A control solution was also prepared under the same conditions. All experiments were performed in triplicate. The adsorbed amount of Cd(II) metal ions from the solution (q_e) was determined using Equation 1.

$$q_{e=}(C_o - C_e)\,\frac{V}{m} \tag{1}$$

Where C_0 and C_e are the initial and equilibrium concentrations of metal in the solution (mg L^{-1}), respectively, and V and m are the volume of the aqueous metal solution (L) and the dosage of adsorbent (g), respectively.

2.4.2. Optimization of Adsorbent Dosage

Using different adsorbent dosages ranging from 10 to 100 mg, each adsorbent of ACFA and DCFA was reacted with 10 mL of Cd(II) metal ions at the optimum pH. The resulting suspension was then stirred for 60 minutes at room temperature. The experiment was conducted in triplicate. Atomic absorption spectrometry was then used to measure the concentration of Cd(II) in the filtrate.

2.4.3. Adsorption Kinetics Study

The effect of contact time of metal ions adsorption on the ACFA and DCFA adsorbent was examined in the range of 10-120 minutes. During these experiments, the optimal adsorbent dosage, pH, and volume of the Cd(II) solution were maintained constant to isolate the effect of contact time. The resulting data were used to evaluate the adsorption kinetics by applying both the pseudo-first-order (Equation 2) and pseudo-second-order (Equation 3) kinetic models.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

Where q_t (mg g^{-1}) is the amount of metal ions adsorbed at time t (min); q_e (mg g^{-1}) is the maximum amount of metal ions adsorbed per mass of material at equilibrium; k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the rate constant of pseudo-first and pseudo-second-order, respectively.

2.4.4. Adsorption Isotherm Study

The initial concentration of Cd(II) ions was varied in the range of 10-100 mg L^{-1}. The optimum adsorbent dosage, pH, and contact time—determined from the previous experiments—were maintained constant, along with a fixed volume of 10 mL for the Cd(II) solution. The resulting data were analyzed using the Langmuir and Freundlich isotherm models (Equations 4 and 5, respectively) to determine the adsorption capacity and equilibrium constants. A basic assumption of the Langmuir isotherm model is that sorption occurs at specific sites that are uniformly distributed throughout the surface of the adsorbent. Meanwhile, the Freundlich isotherm, which is based on multilayer adsorption, implies a heterogeneous adsorption surface and active sites with different energies.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max} K_L} \tag{4}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

Where, q_e (mg g^{-1}) is the equilibrium adsorption capacity, q_{max} (mg g^{-1}) is the maximum adsorption capacity, C_e (mg L^{-1}) is the equilibrium concentration after the adsorption process, K_L (L mg^{-1}) and K_F ((mg g^{-1}) (L g^{-1})$^{1/n}$) are the Langmuir and Freundlich isotherm model constants, respectively.

2.4.5. The Sequential Desorption of Adsorbed Cd(II) Ions

The desorption process was done using four type of solvents, such as double-distilled water, 1 M KNO_3, 0.3 M $HONH_2HCl$ in 25% acetic acid, and 0.1 M Na_2EDTA to investigate the physical, electrostatic or ion-exchange, hydrogen bonds, and complex interactions between the active sites of the adsorbent and metal ions, respectively [23]. To desorb the adsorbed metal ions, the adsorbent was successively stirred with the adsorbed Cd(II) metal ions in each solvent of 10 mL for 60 60-minute contact time for each solvent. AAS was then used to determine the concentration of metal ions that leached or dissolved into each solvent. The types of interaction between metal ions and the adsorbent were identified by analyzing the collected data.

3. Results and Discussion

3.1. Characterization of Dithizone-Immobilized Coal Fly Ash

The adsorbent materials, including ACFA and DCFA, were characterized using XRD. The analysis focused on the d-spacing and 2θ angle values characteristic of CFA and dithizone to assess the successful immobilization of dithizone on the adsorbent surface. The XRD pattern of CFA is presented in Figure 1. The results confirm the successful immobilization of dithizone compounds onto the fly ash adsorbent, as evidenced by the appearance of diffraction peaks at 2θ = 17.23°, 9.57°, and 8.69° with d- spacings of 5.142 Å, 9.236 Å, and 10.162 Å, respectively, which correspond to the characteristic of dithizone.

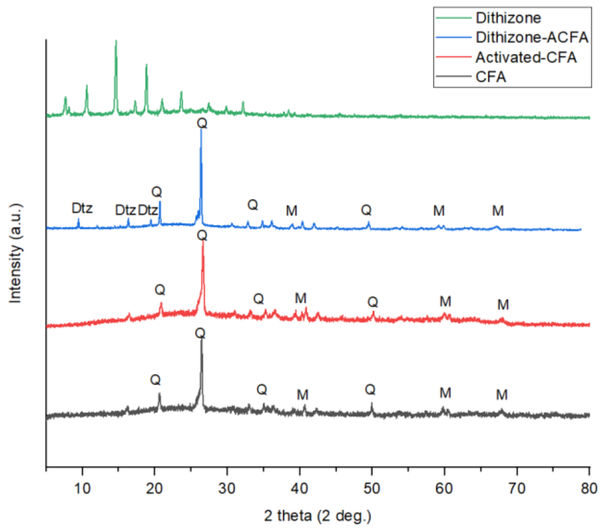

Figure 1. The XRD diffractogram of dithizone, DCFA, ACFA, and CFA (Dtz =Dithizone; Q = Quartz; M = Mullite)

In addition, the diffractogram of the DCFA still exhibits prominent peaks of the original fly ash composition. Specifically, peaks at 2θ = 20.97°, 26.75°, 36.65°, and 50.23° with d-spacings of 4.232 Å, 3.378 Å, 2.450 Å, and 1.815 Å, respectively, indicating the existence of quartz mineral, while mullite is identified by its characteristic peaks at 40.95°, 60.89°, and 68.38° with d- spacings of 2.202 Å, 1.520 Å, and 1.371 Å. Moreover, the complete characterization of CFA, ACFA, and DCFA using FTIR, SEM-EDX, TGA-DTA, and Nitrogen Adsorption-desorption analyses has been thoroughly discussed in our earlier paper [17].

3.2. Adsorption Study

3.2.1. The pH Optimization on Cd(II) Ions Adsorption

The adsorption process is significantly influenced by the pH of the solution. It is because the speciation of metal ions and the functional groups or active sites of the adsorbents in solution both affect the effectiveness of adsorption. The effect of pH solution on the adsorption of Cd(II) ions was presented in Figure 1. In this investigation, the pH range of 3 to 8 was varied while maintaining the other parameters constant using a 20 mg adsorbent dosage, 60 minutes of contact time, and an initial Cd(II) concentration of 20 mg L^{-1}.

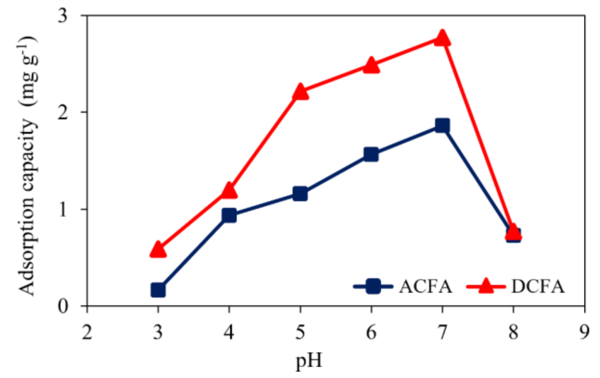

Figure 2. Effect of pH on the adsorption of Cd(II) ions onto ACFA and DCFA (20 mg of adsorbent, 10 mL of 10 mg L^{-1} Cd(II) solution, 60 minutes contact time at room temperature)

According to Figure 2, there are initially low adsorbed Cd(II) metal ions on either ACFA or DCFA at pH values of 3 and 4. These ions then gradually increase as the pH of the solution rises to its maximum value, after which they decline with further pH increase. At low pH, the high concentration of H$^+$ ions leads to protonation of the adsorbent surface, resulting in a positively charged surface. Since Cd(II) ions also exist as positively charged species under these conditions, electrostatic repulsion occurs between the Cd(II) ions and the protonated (H_3O^+-occupied) adsorbent surface. This repulsion reduces the efficiency of adsorption at low pH levels.

The optimum adsorption of Cd(II) on both ACFA and DCFA is achieved at pH 7. This suggests that there may have been an ion-exchange or electrostatic interaction between Cd(II) and the adsorbent materials, particularly in ACFA. Meanwhile, the DCFA adsorbent may interact with Cd(II) through the dithizone functional group that is present on its surface. This interaction may involve not only electrostatic or ion exchange, but also hydrogen bonding and complexation. This interpretation is further supported by the results of the subsequent sequential desorption study.

However, further increases in pH reduced Cd(II) adsorption, likely due to the hydrolysis-induced precipitation of Cd(II) ions [24]. Additionally, the functional groups on the adsorbent surface undergo deprotonation, resulting in partially negatively charged active sites. At higher pH values, excess OH$^-$ ions promote the formation of negatively charged Cd(II) complexes, leading to electrostatic repulsion between the adsorbent surface and metal complexes, which hinders adsorption. Based on these findings, pH 7 was identified as the optimum pH for Cd(II) adsorption onto DCFA and was used in all subsequent experiments. This result is consistent with the study by Linda *et al.* [25], who found that the optimum pH for Cd(II) adsorption using tetraethylene glycol (TEG)-modified silica was also pH 7.

Based on Figure 2, it can be concluded that the adsorption of Cd(II) metal ions on DCFA is relatively higher than that onto ACFA. The adsorption capacity of ACFA is attributed to its porous structure and the presence of active sites, such as aluminol, silanol, and siloxane functional groups. In contrast, the enhanced adsorption performance observed for DCFA may be due to the introduction of additional functional groups from dithizone, particularly –SH and –NH groups, which are known to interact strongly with metal ions. These additional groups likely contribute to the increased number of active binding sites and improved affinity for Cd(II) ions on the surface of the adsorbent.

3.2.2. The Adsorbent Dosage Optimization on Cd(II) Ions Adsorption

Figure 3 shows how the adsorbent dosage of ACFA and DCFA affects the adsorption capacity. The adsorption capacity of Cd(II) ions onto ACFA and DCFA increased with increasing adsorbent dosage up to a certain point and then reached a plateau. At 100 mg, the optimum dosage of adsorbent is achieved, where a significant adsorption of Cd(II) concentration is achieved.

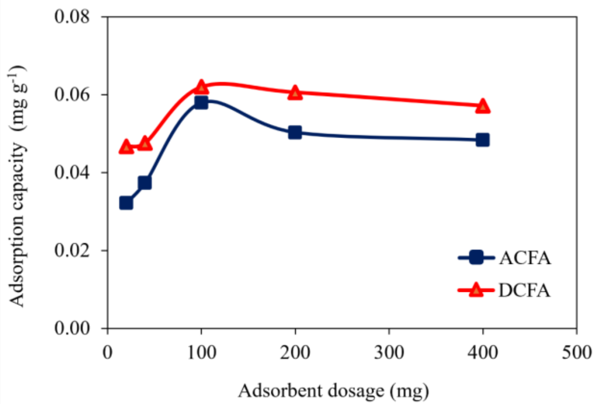

Figure 3. Effect of adsorbent dosage on adsorption capacity of Cd(II) on ACFA and DCFA (The optimum pH of 7, 10 mL of 10 mg L^{-1} Cd(II) ions, 60 min contact time at room temperature)

It can be explained by the interaction process between the ACFA and DCFA adsorbent materials and the metal ions as an adsorbate, which completely utilizes the active sites at low fly ash masses. Since the majority of the accessible binding sites are already occupied, the saturation of active sites on the adsorbent surface limits further adsorption, leading to the adsorption capacity plateaued beyond the optimum adsorbent dosage [26].

Similar adsorption behavior has been reported for Cd(II) ions adsorption, where the saturation of active sites prevents additional increases from appreciably improving removal efficiency [27, 28]. This may be due to particle agglomeration and limited mass transfer. Moreover, the aggregation of adsorbent particles at larger dosages may result in decreased surface area availability, which would lower the quantity of exposed active sites available for metal adsorption [26].

3.2.3. Adsorption Kinetics Study

The adsorption kinetic parameters can be investigated by carrying out adsorption experiments at various contact times. The effect of contact time of 20, 40, 60, 80, 100, and 120 minutes on the adsorption of Cd(II) metal ions have been investigated in the present study while maintaining other adsorption parameter constant such as the optimum pH of 7, the adsorbent dosage of 100 mg, and Cd(II) initial concentration of 20 mg L^{-1}. The result of this experiment is presented in Figure 4. Table 1 illustrates the results of evaluating the acquired data using pseudo-first-order and pseudo-second-order kinetic models.

According to Figure 4, the results indicate that as the contact time increases, the amount of Cd(II) ions adsorbed on the ACFA and DCFA adsorbents also increases until equilibrium is reached, after which it remains constant. The adsorption of Cd(II) occurs in two stages: an initial rapid uptake within the first 30 minutes of adsorbate–adsorbent interaction, attributed to the large surface area of the adsorbent material available for metal ion binding.

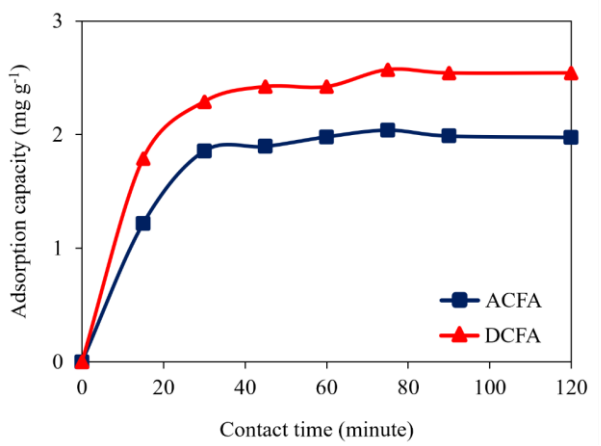

Figure 4. Effect of contact time on the adsorption of Cd(II) ions on ACFA and DCFA (The optimum pH of 7, 100 mg adsorbent, 10 mL of 10 mg L^{-1} Cd(II) ions, stirred at room temperature)

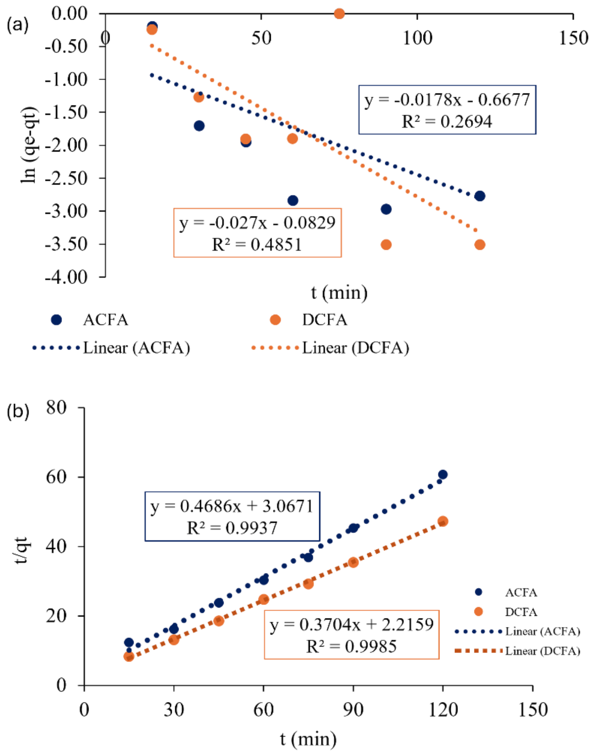

Figure 5. Kinetic study of Cd(II) ion adsorption on ACFA and DCFA: (a) pseudo-first-order and (b) pseudo-second-order kinetic models

Following the initial rapid uptake, a slower phase of Cd(II) ion removal occurred over the next 75 minutes, during which the adsorption sites on the adsorbent surface were assumed to have reached equilibrium. Furthermore, the results indicate that the amount of Cd(II) ions adsorbed by DCFA is higher than that of ACFA. This suggests that dithizone immobilization enhances the adsorption capacity of the adsorbent, likely due to the presence of active functional groups, such as −SH and − NH, introduced by dithizone on the surface of DCFA. These groups provide a greater number of active sites suitable for binding Cd(II) ions.

Table 1. Kinetic parameters for Cd(II) adsorption on ACFA and DCFA

Kinetic model	ACFA	DCFA
Pseudo-first-order		
k_1 (min^{-1})	0.02	0.03
Q_e (mg g^{-1})	2.04	2.57
R^2	0.27	0.49
Pseudo-second-order		
k_2 (g mg^{-1} min^{-1})	0.07	0.06
Q_e (mg g^{-1})	2.13	2.70
R^2	0.99	0.99
h (mg g^{-1} min^{-1})	0.33	0.45

Adsorption kinetics of Cd(II) by ACFA and DCFA were examined by assessing the adsorbent rate constant and adsorption equilibrium constants. In order to describe the mechanism of adsorption processes, the pseudo-first-order and pseudo-second-order kinetic models were applied to present the kinetics of Cd(II). Based on Figure 5 and Table 1, the adsorption of Cd(II) ions on ACFA and DCFA is better represented by the pseudo-second-order kinetic model, with a high correlation coefficient (R^2 = 0.99) for both adsorbents. This model suggests that the adsorption rate is more dependent on the availability of active sites on the adsorbent surface and the concentration of Cd(II) ions, indicating a chemisorption process.

One notable study by Liu et al. demonstrated that the adsorption of Pb(II), Cd(II), and Cu(II) ions onto a functionalized graphene oxide adsorbent was best described by the pseudo-second-order kinetic model. The research highlighted that the rate-limiting step in the adsorption process involved bimolecular interactions between the adsorbent and the metal ions, supporting the applicability of the pseudo-second-order model [29].

Similarly, Zhang *et al.* [30] focused on the removal of Cd(II) and Pb(II) ions using a biochar derived from spent mushroom substrate. The authors reported that the adsorption kinetics were well described by the pseudo-second-order model, indicating a chemisorption process that involved the formation of chemical bonds between the metal ions and the biochar. Furthermore, a similar result reported that the adsorption of ammonia-nitrogen on zeolite molecular sieves prepared from coal fly ash followed the pseudo-second-order kinetics model [31].

According to the data provided in Table 1, it is observed that the value of adsorption capacity (q_e) for Cd(II) adsorbed on DCFA is higher than that adsorbed on ACFA. The reason is possibly due to the active groups available on DCFA adsorbent that are also derived from dithizone molecules, such as –SH and –NH groups, thus increasing the adsorption capacity of DCFA towards Cd(II) ions. Meanwhile, in the adsorption of Cd(II) on ACFA, the metal ion interacts only with active groups of silanol, siloxane, and aluminol from the coal fly ash adsorbent. The rate of Cd(II) adsorption on DCFA is slightly slower than ACFA because this adsorption involves the complexation mechanism with the active sites from dithizone. Hence, the reaction requires a longer time for completion. Data from sequential desorption investigations support this explanation, which is discussed in more detail in a later section.

3.2.4. Adsorption Isotherm

The adsorption isotherms of Cd(II) ions were conducted with various initial concentrations of 10-100 mg L^{-1} to analyze how the adsorption capacity is affected by the initial concentration of metal ions. The other adsorption conditions were kept constant at an optimum pH of 7, the adsorbent dosage of 0.1 g, the contact time of 75 minutes, and 10 mL of Cd(II) solution. To comprehend the adsorption mechanism of Cd(II) on both ACFA and DCFA adsorbents, the Langmuir and the Freundlich isotherm models were then used to assess the results.

The effect of the initial concentration of Cd(II) on the amount of adsorbed Cd(II) ions on ACFA and DCFA is shown in Figure 6. It has been observed that the initial concentration of metal ions affects the adsorption capacity of adsorbed Cd(II) ions on the adsorbents that generally the amount of Cd(II) adsorbed increases from 10 to 50 ppm, suggesting that the metal ions have not yet completely occupied all the active sites that are accessible on the surface of the adsorbents. Then, further increasing the initial concentration of metal ions has no noticeable impact on the adsorption capacity of either ACFA or DCFA adsorbents. This result indicates that the equilibrium has been reached between Cd(II) metal ions and the adsorbents, and the metal ions can no longer occupy the active sites of the adsorbents.

The study of adsorption isotherms is crucial for understanding the interaction between adsorbates, such as metal ions, and adsorbents. Two of the most used models to describe these interactions are the Langmuir and the Freundlich isotherm models. These models were then used to study the nature of adsorption of Cd(II) ions on both adsorbents. Each model provides insights into the adsorption characteristics and mechanisms, which are essential for designing effective adsorption systems for removing contaminants from aqueous solutions.

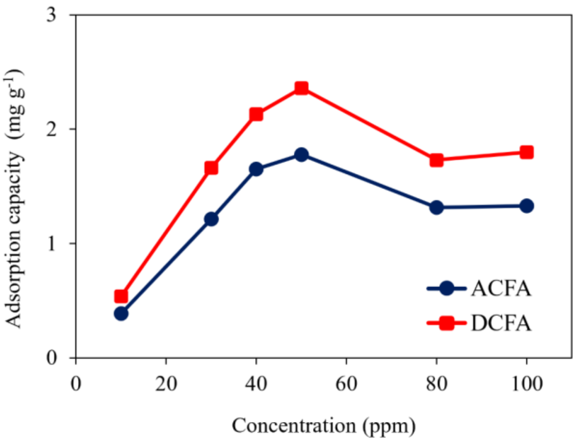

Figure 6. Effect of concentration on the adsorption of Cd(II) ions on ACFA and DCFA (the optimum pH of 7, 100 mg of adsorbent, 10 mL of Cd(II) ions, 75 minutes of contact time at room temperature)

Table 2. Isothermal adsorption parameters on activated ACFA and DCFA

Adsorbent	Langmuir isothermal adsorption parameters			
	Adsorption capacity (*b*) (mol g^{-1})	Equilibrium constants (*K*) (mol^{-1} L)	Adsorption energy (kJ mol^{-1})	Plot linearity (R^2)
ACFA	13.994×10^{-6}	2.65×10^4	25.23	0.8732
DCFA	17.240×10^{-6}	8.40×10^4	28.09	0.9406

Adsorbent	Freundlich isothermal adsorption parameters		
	Freundlich constant (K_F) (mg g^{-1})	Intensity of adsorption (1/n)	Plot linearity (R^2)
ACFA	0.3081	0.504	0.7357
DCFA	0.6343	0.416	0.726

The Langmuir isotherm model is based on the assumption that adsorption occurs at specific homogeneous sites within the adsorbent, leading to the formation of a monolayer of adsorbate on the surface. In contrast, the Freundlich isotherm model is an empirical model that describes adsorption on heterogeneous surfaces and allows for multilayer adsorption. Table 2 shows the adsorption isotherm parameters of the ACFA and DCFA adsorbents.

Table 2 demonstrates that the Langmuir isotherm is the best isotherm model for the adsorption of Cd(II) on both ACFA and DCFA, with the R^2 value closest to 1. These results indicate a chemical interaction between the adsorbents and the metal ions through the active sites on the surface of the adsorbent, compared to the pores. Furthermore, the Langmuir model was then used to calculate the parameters of isotherm adsorption. Compared to ACFA, DCFA has a greater adsorption capacity, equilibrium constants, and adsorption energy for the adsorption of Cd(II) ions. This demonstrates that the dithizone immobilization on the adsorbent materials has a significant impact on the isotherm adsorption parameters and strengthens the adsorbent-adsorbate interaction.

The enhanced interaction is attributed to the complexation mechanism between Cd(II) ions and the dithizone functional groups (−SH and −NH) attached to the DCFA surface. The mechanism of interaction between the metal ions and the adsorbents is discussed in more detail in the desorption section. Adsorption can occur through chemical interactions (chemisorption), physical interactions (physisorption), or a combination of both. Adsorption processes with an energy below 20.92 kJ mol^{-1} are classified as physisorption, while those with an energy above 20.92 kJ mol^{-1} are considered chemisorption. Based on this classification, the adsorption of Cd(II) on both ACFA and DCFA can be categorized as chemisorption.

3.3. Sequential Desorption Study

The adsorbed metal ions on the surface of the adsorbents were successively desorbed using several solvents to obtain more knowledge of the interaction mechanism between the adsorbents and Cd(II) metal ions. These studies can be used to evaluate the types of interaction that occur during the adsorption process. Adsorbents containing metal ions that had been adsorbed were sequentially submerged in several types of solvents, such as double-distilled water (for capturing mechanism), KNO_3 (for ion-exchange mechanism), NH_2OHHCl (for hydrogen bonds mechanism), and Na_2EDTA (for complexation reaction mechanism). Furthermore, the physical, electrostatic, hydrogen, and complexation mechanisms involved in the Cd(II) metal ions adsorption were sequentially assessed by analyzing the metal ions that were desorbed into each solvent at each desorption stage. The detailed results are presented in Figure 7.

Based on Figure 7, it can be inferred that the interaction between ACFA and Cd(II) ions involves electrostatic attraction, followed by the formation of hydrogen bonds. This is evidenced by the highest desorption rates observed with KNO_3, followed by $NH_2OH{\cdot}HCl$. The dominance of electrostatic interactions during the adsorption process with ACFA is likely attributed to the adsorbent's relatively high cation exchange capacity. Additionally, hydrogen bonding may also play a role, as the metal ions become hydrated, forming a hydration complex of Cd(II) that facilitates the formation of hydrogen bonds with the active sites of the adsorbent. The H_2O ligand attached to the metal ion in the hydrated complex possibly formed hydrogen bonds with the active groups of the adsorbents. In the case of DCFA, the hydrogen interaction was higher than that of ACFA due to the additional active groups from dithizone attached to the adsorbent surface.

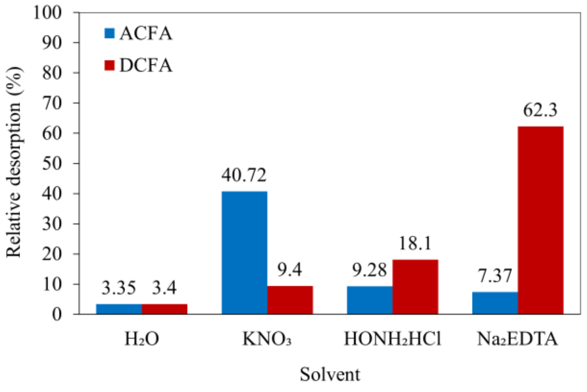

Figure 7. Sequential desorption of adsorbed Cd(II) on ACFA and DCFA

Furthermore, in the DCFA adsorbent, complexation appears to be the dominant mechanism driving the interaction with Cd(II) ions. This suggests that dithizone, once immobilized on the adsorbent surface, forms coordination bonds with Cd(II) ions. The continued activity of the -NH and -SH functional groups on the immobilized dithizone indicates their critical role in binding metal ions during the adsorption process. Additionally, a reduction in metal ion adsorption via electrostatic or ion-exchange interactions is observed, accompanied by an increase in hydrogen bonding. This shift is likely attributed to the immobilization of dithizone, which occupies certain active sites on the ACFA surface, thereby modifying the adsorbent's surface characteristics. As a result, the formation of hydrogen bonds between metal ions and surface functional groups is facilitated on the DCFA adsorbent.

3.4. After Adsorption

Figure 8 shows the FTIR spectra of ACFA and DCFA before and after Cd(II) adsorption, indicating that the adsorption process is primarily driven by chemical rather than physical interactions. This is indicated by the increment or decrement of the peaks situated at 1496.76 cm^{-1}, which demonstrate the presence of C=C of the aromatic phenyl group in DCFA shifted toward 1487.87 cm^{-1}. Furthermore, the adsorption band at 1319.31 cm^{-1} indicates the presence of the C–N stretching vibration in DCFA adsorbent shifted toward 1313.34 cm^{-1}. The absorption bands which are characteristics for coal fly ash still appears in DCFA before and after adsorption, such as Si–O and Si–O–Si, –OH bending vibration of Si–OH group, and the bending vibration of Si–O–Si.

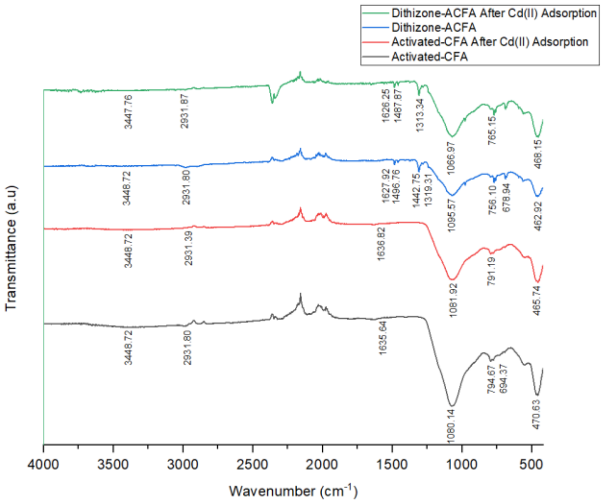

Figure 8. FTIR spectra of ACFA and DCFA adsorbent before and after adsorption

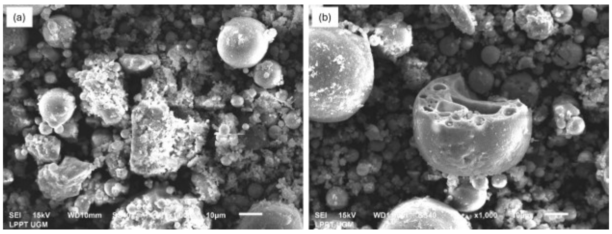

Figure 9. SEM images of (a) DCFA before and (b) after adsorption

The morphology of the DCFA adsorbent both before and after Cd(II) ions adsorption is shown in Figure 9. The SEM images show the presence of crevices on the adsorbents. After the adsorption processes of Cd(II), the surface of the adsorbent became rougher and disaggregated. It is possibly related to the sorption effect as the adsorbent material interacts with the metal ions.

4. Conclusion

Dithizone immobilization study of coal fly ash adsorbent demonstrated a strong affinity towards Cd(II) ions. A two-stage kinetic profile was observed in the kinetics of Cd(II) on DCFA adsorbent. The pseudo-second-order model fits the adsorption of Cd(II) on DCFA. Furthermore, compared to ACFA, DCFA has a higher rate of Cd(II) adsorption. The Langmuir is the best isotherm for describing Cd(II) adsorption on DCFA, with an adsorption capacity, equilibrium constant, and energy higher than ACFA.

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