

Research article

Adsorption Optimization for the Removal of Cadmium in Water by Aluminum (Hydr)oxide on Cation Exchange Resin

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Received: 7 March 2022, Revised: 27 April 2022, Accepted: 12 September 2022

DOI: 10.55003/cast.2022.02.23.012

Abstract

Keywords

cadmium;
adsorption;
water treatment;
optimization

In this study, we prepared aluminum oxide/hydroxide on a cation exchange resin and applied it for removing Cadmium (Cd) in water. The characteristics of the synthesized materials were determined by X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy, and Fourier transform infrared spectroscopy. The Cd removal tests were conducted in both batch and continuous adsorption experiments. The maximum treatment efficiency and adsorption capacity were determined to be 99.97% and 10 mg/g material, respectively, under the optimum conditions of 10 mgCd/L, 1 g/L of material, and pH 6.54 for 70 min at room temperature. The adsorption kinetics and isotherms followed pseudo-second-order kinetics and the Freundlich isotherm model, respectively. The adsorption of Cd on the material was mainly due to physical adsorption and was an exothermic process. This study gives an alternative method for heavy metal removal from water using a new, inexpensive, and available absorbent.

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1. Introduction

Heavy metal residues in water cause serious environmental pollution problem and has long-term impact on humans and ecosystems. Heavy metals present in the environment are mainly due to the activities of the metal plating industries, mining operations, tanneries, phosphate fertilizer use, insecticide use, and alloy manufacturing. Some of the notable heavy metals involved in these activities are cadmium, lead, chromium, and mercury [1]. Cadmium (Cd) is known to have no biological function but is highly toxic since it is one of the heavy metals that causes kidney damage, kidney disorders, high blood pressure, bone fractures, and the destruction of red blood cells [2, 3]. Cd entering the environment through wastewater is absorbed and accumulated by microorganisms and eventually transferring to humans through the food chain. In a study by Abdeldayem [4], Cd content in the aqueous environment ranged from 0.004 to 0.008 mg/L, which was higher than the allowable limit of WHO (2017), which is 0.003 mg/L. In Vietnam, the concentration of Cd found in river water in both the North and the South exceeded the allowable standard (QCVN 40:2011/BTNMT) by 4-16 times, typically in the Nhieu Loc-Thi Nghe canal area. In particular, in Tan Tru district (Long An), the Cd content ranged from 2-8 mg/L, which was 40-60 times higher than the allowable standard. Due to the particularly hazardous nature of Cd, Cd and other heavy metals must be thoroughly removed by treatment before being discharged into the environment.

There are many methods, technologies, and techniques that have been developed and used to remove Cd in water such as coagulation, flocculation, chemical precipitation, ion exchange, reverse osmosis, electrodialysis, ultrafiltration, and nanofiltration [5]. The treatment method is based on wastewater properties, concentration, and treatment costs. The coagulation method produces a significant amount of sludge after treatment. In addition, aluminum and iron salts that are used for coagulation, when hydrolyzed often release H^+ ions, which lowers the pH in the water, causing an imbalance for the receiving source. Filtering methods use membranes to remove contaminants, but often membrane clogging occurs, requires complex pretreatment systems, and is therefore not suitable for widely used in practical applications. These solutions almost have certain disadvantages when applied in practice, such as high cost and high expertise requirements during operation [5].

On the other hand, adsorption is a simple process and has been used for a long time in the removal of pollutants from water. Adsorption is a commonly used technology for the removal of metal ions from various wastewater industries [6, 7]. One solution has been proposed with more advantages such as the combination of ion exchange and adsorption methods, using adsorbent materials developed from oxides/hydroxides of metals (e.g., Al, Fe, and Mn). Such methods can remove heavy metals without generating sludge, take up less area for tank building, and involve materials that can be converted and reused [8, 9]. In particular, aluminum oxide/hydroxide can be applied due to the amphoteric properties of aluminum, which make regeneration and reactivation easier. However, there has not been any study on the synthesis of such material and optimization of the adsorption process for the removal of Cd in water.

In this study, we upgraded a commercially available cation exchange resin by adding aluminum oxide/hydroxide via a conventional impregnating method. The material was then applied for Cd adsorption in water in batch experiments. The factors affecting the adsorption process were investigated, and the adsorption kinetics, isotherms, and thermodynamics were studied. An optimization software was employed for experimental design to determine statistical significance and to optimize the adsorption process. A continuous column adsorption model was then also built and applied for evaluation of the adsorption process in practical applications.

2. Materials and Methods

2.1 Material synthesis

The cation exchange resin (CER) was from India (Indion 220Na). Chemicals such as $\text{Al.NH}_4(\text{SO}_4)_2.12\text{H}_2\text{O}$, $\text{CdSO}_4.8\text{H}_2\text{O}$, NaOH, H_2SO_4 , and HCl from China with analytical grade and were used without further purification.

Aluminum oxide/hydroxide on cation exchange resin (AOH@CER) was synthesized by the impregnation method [10-13]. First, the CER was rinsed with distilled water for 30 min and let to dry naturally at room temperature. Next, 20.1 g of $\text{Al.NH}_4(\text{SO}_4)_2.12\text{H}_2\text{O}$ was added into 1000 mL of deionized water and mixed well until complete dissolution had occurred. After that, the solution was added with 30 g of the prepared CER and stirred at 300 rpm for 2 h. The mixture was subsequently added with 200 mL of 0.2 M NaOH solution and continuously stirred at 300 rpm for 15 min. The material was then filtrated and washed with deionized water and dried naturally at room temperature to obtain the AOH@CER material, which was finally stored in a desiccator for further use.

2.2 Adsorption of Cadmium

Cadmium standard solution with a concentration of 50 mg/L was prepared by dissolving 0.0928 g of $\text{CdSO}_4.8\text{H}_2\text{O}$ in water in a 1000 mL volumetric flask. Synthetic wastewater containing Cd was then prepared from the stock Cd solution by dilution with an appropriate water volume ratio. The adsorption experiment was carried out by adding a certain amount of AHO/CER into the Cd-containing wastewater solution under mixing at 300 rpm. During the test, samples were taken and filtered, and the filtrate was sent for the determination of Cd concentration. The factors affecting the adsorption process (e.g., time, pH, dosage, reaction temperature, and Cd concentration) were investigated. After that, an experimental design software was used to set up a correlation equation between the influencing factors to determine the statistical significance through the analysis of variance (ANOVA) and the optimal value for the Cd adsorption. Besides, a continuous flow column model was also built and applied under optimal operating conditions for evaluating the performance of the material in practical applications. A burette with a volume of 10 mL, a height of 100 cm, and a tube diameter of 0.5 cm was used as the adsorption column. A fiberglass layer was used to seal the material as water flowed through it. The design flow rate was 0.7 mL/min, corresponding to 70 min of hydraulic retention time with 50 mL of wastewater flowing through the entire column of material. The dosage of AHO/CER was 1.5 g/L. To increase the reliability of the experimental results, the experiments for the effects of adsorption times, pH, and dosage were conducted three times while those for simultaneous reaction temperature and Cd concentration were done twice. Before each experiment, the adsorbent and the column were cleaned with distilled water.

2.3 Analysis

X-ray diffraction (XRD, D2 Phaser, Bruker) and Fourier transform infrared spectroscopy (FTIR, Alpha, Bruker) were used to determine the crystal structure and surface chemical properties, respectively. Scanning electron microscopy (SEM) provided the surface morphology of the materials while the composition and percentage of elements present in the material were determined by energy-dispersive X-ray spectroscopy (EDX) and elemental mapping (SEM-EDX, JCM-7000, JEOL).

The concentration of Cd in water was determined by atomic absorption spectroscopy (AAS 400, Pekin Elmer) according to the method of SMEWW 311B-2017. Cd removal efficiency (H, %) and adsorption capacity (a, mg/g) were calculated by the following equations.

$$H = \frac{(C_0 - C_e)}{C_e} \times 100\% \quad (1)$$

$$a = \frac{(C_0 - C_e)}{m} \times V \quad (2)$$

Where C_0 and C_e were the concentrations of Cd at the initial time and at the time of equilibrium (mg/L), respectively; m the mass of the material (g); and V the volume of solution (L).

For the optimization process, Design Expert software (Design Expert 11) was used to find the optimal operating parameters based on analyzed variance and nonconformity values. The operating factors were independent variables (reaction time: A, pH: B, material mass: C, initial Cd concentration: D), and the cadmium removal efficiency was the response variable. The extent and degree of independence of the variables are described in Table 1. Center composite design (CCD) was employed with 30 experiments at 5 levels ($-\alpha$, -1, 0, +1, $+\alpha$) including 16 planned experiments and 6 centered repeat experiments in order to evaluate errors. Moreover, 8 additional experiments were used at a point located a distance α from the center experiments (Table 1).

Table 1. Range of independent variables of Cd adsorption

| Independent variables | Unit | Range and level | | | | |
|------------------------------|------|-----------------|-------|-------|-------|-----------|
| | | $-\alpha$ | -1 | 0 | +1 | $+\alpha$ |
| Reaction time (A) | min | 30 | 60 | 90 | 120 | 150 |
| pH (B) | - | 4 | 5 | 6 | 7 | 8 |
| Material mass (C) | g | 0.035 | 0.045 | 0.055 | 0.065 | 0.075 |
| Initial Cd concentration (D) | mg/L | 5 | 10 | 15 | 20 | 25 |

3. Results and Discussion

3.1 Material characterization

Commercial CER is initially light yellow, and changes to silvery-white gold color in AHO/CER material with brighter color after impregnation with aluminum (hydr)oxide. During the synthesis process, the aluminum salt solution is hydrolyzed to Al^{3+} ions that exchange with Na^+ ions of the cation resin. Then, Al^{3+} ions react with the OH^- group in NaOH solution to form aluminum hydroxide ($Al(OH)_3$) on the surface of the resin [10]. SEM results of the AHO/CER material at different resolutions showed the appearance of tiny patches of new material on the surface of the CER after synthesis (Figures 1(a, b, e, f)), which were not seen in the original CER (Figures 1(c-d)). This probably indicated the successful impregnation of aluminum (hydr)oxide onto the CER surface. The results of EDX spectroscopy and mapping in Figure 2 show that the sample consists of four elements with different mass percentages. The major element was O (51.39%), followed by C (38.17%), Na (7.88%), and Al (2.56%). Thereby, it can be seen that aluminum (hydr)oxide on CER material was successfully synthesized by the ion exchange method and aluminum salts onto Na^+ cation resin.

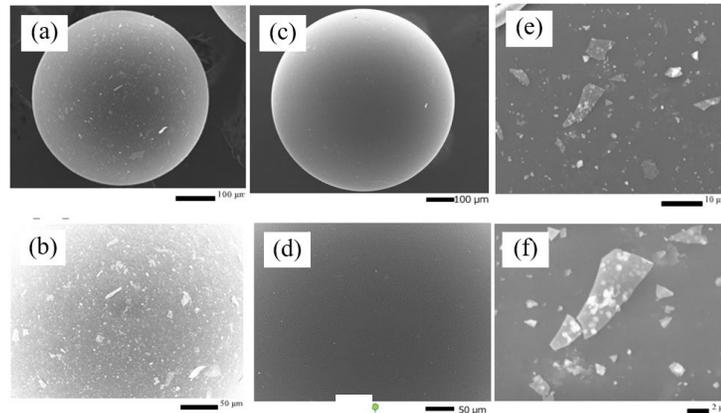


Figure 1. SEM images of AHO/CER (a, b, e, and f) and original CER (c and d) (magnification: $\times 200$ (a), $\times 400$ (b), $\times 140$ (c), $\times 300$ (d), $\times 2200$ (e), $\times 5500$ (f))

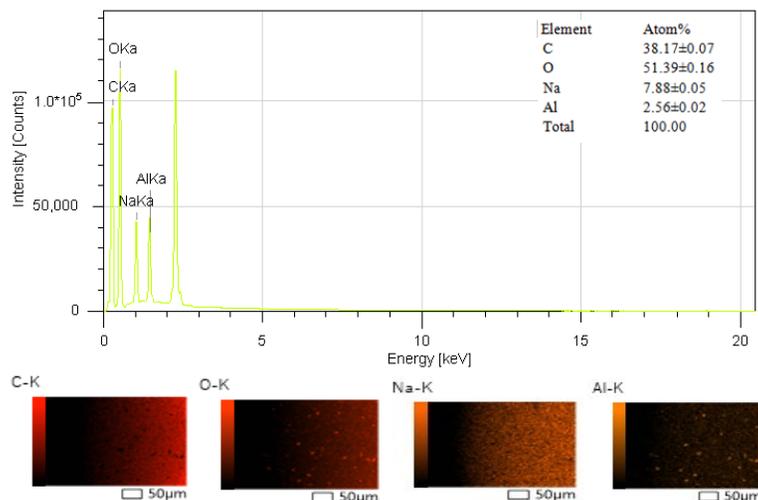


Figure 2. EDX spectra of AHO/CER material and its EDX-mapping

X-ray diffraction patterns of CER and AHO/CER are plotted in Figure 3(a), showing the high purity of the CER. For AHO/CER composite, more peaks and noise are observed and characteristic peaks of aluminum (hydr)oxide appear in the amorphous structure [14]. As seen in Figure 3(b), FTIR characteristic peaks of AHO/CER at wavenumbers of 2900, 1650, and 1419-1463 cm^{-1} can be assigned to the bonds of CH, C = C, and Al-OH [8], proving that the AHO/CER composite was successfully synthesized. After Cd adsorption, the FTIR spectrum of the material had a slight change with the appearance of new peaks at wavenumbers of 500, 720, and 860 cm^{-1} , which corresponded to the characteristic peaks of Cd-O [14], proving the successful adsorption of Cd on the AHO/CER composite.

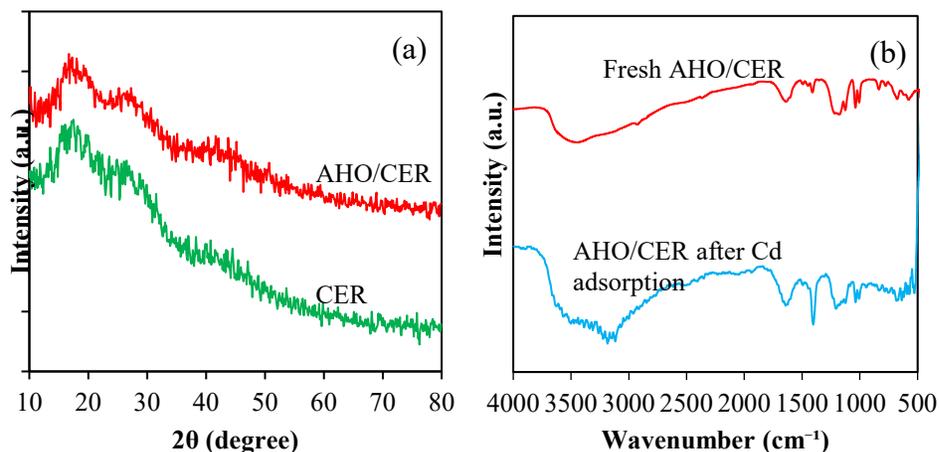


Figure 3. (a) XRD and (b) FTIR of AHO/CER composite

3.2 Batch adsorption of Cadmium

For AHO/CER composite, the Cd adsorption mechanism was related to the location of adsorption centers on the surface [15]. The surface of the alumina particles is hydrolyzed in an aqueous medium at a pH of around 6-7, and the H^+ ion reduction of the Al-OH group occurs to form Al-O⁻ groups, which are more attractive for adsorption of cations [16]. The OH groups on the surface also provide adsorption sites and form bonds with the cations [17].

Adsorption time plays an important role in the design of the reactor and in determining the inlet and outlet flow rates. The Cd adsorption capacity during 120 min is shown in Figure 4(a). The adsorption process of AHO/CER occurs rapidly in the first 30 min, then increases slowly, and is finally stable after 120 min. When the number of Cd ions adsorbed on the surface of the material becomes dense and the interaction force between Cd cations with the surface of the material decreases, the adsorption capacity is almost unchanged and reaches an equilibrium state after 90 min. Therefore, 90 min was chosen as the appropriate adsorption time for further experiments.

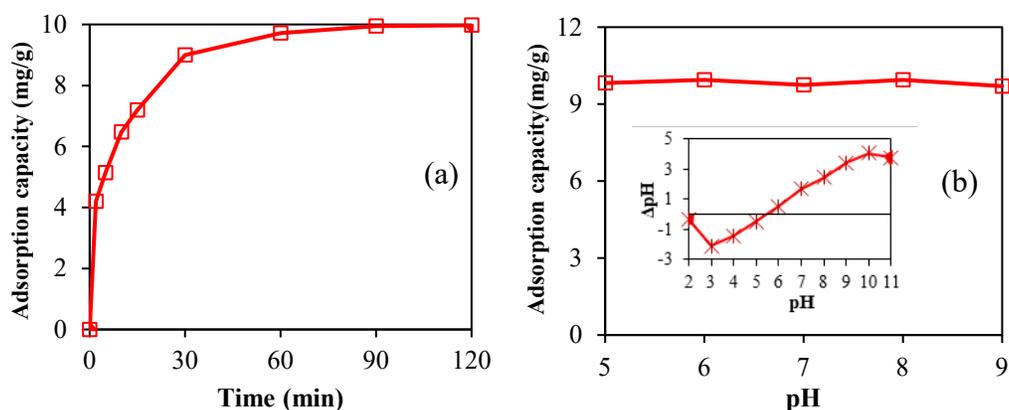


Figure 4. Effects of (a) time and (b) initial pH on Cd adsorption capacity using AHO/CER (inset of (b): determination of isoelectric point value of AHO/CER composite)

The effects of the initial pH effect on the Cd adsorption are demonstrated in Figure 4(b). Interestingly, there was no significant difference in adsorption capacity over the surveyed pH ranges from 5-9, proving that there was a wide application range of pH for the AHO/CER composite for actual water and wastewater treatment applications. The point of zero charges (pH_{pzc}) of the AHO/CER composite was determined at 5.5 (inset of Figure 4(b)). Since the adsorption of cations is preferential at $pH > pH_{pzc}$ [18], the adsorption capacity shows almost no significant change in the pH range from 5-9. The adsorption of Cd depends on the nature of the adsorbent surface and the distribution of metal cations in the solution. At $pH > 7$, little higher adsorption capacities are likely due to a combination of both adsorption and precipitation on the surface, where metal ions begin to precipitate at high pH values. In this study, pH 6, at which has a high adsorption capacity of 10 mg/g was observed, and which is similar to the actual condition of water and wastewater, was selected as the suitable value for the next experiments.

The effect of adsorbent mass on the adsorption efficiency is illustrated in Figure 5(a). The adsorption efficiency is directly proportional to the mass of the material, while the adsorption capacity is inversely proportional. As material mass increases, the number of adsorption sites increases, thus providing more surface area for contact between Cd and the adsorbent. However, the adsorption capacity decreases with the larger adsorbent amount since the Cd distributed on the surface of each adsorbent unit decreases. This is consistent with previous studies on the influence of adsorbent mass on the efficiency and adsorption capacity of the material [12, 19]. In this study, the mass of 50 mg of material in 50 mL of 10 mg/L Cd solution gave a Cd adsorption efficiency of 99.97%, an adsorption capacity of 9.97 mg/g, and a Cd concentration after treatment of 0.029 mg/L. This outlet concentration met the National technical regulation for industrial wastewater (QCVN 40:2011/BTNMT, 0.05 mg/L for Cd). Furthermore, the 50 mg of adsorbent mass had a negligible reduction in the adsorption capacity as compared with the others. Therefore, the appropriate mass of material was chosen at 50 mg (equivalent to the material dosage of 1 g/L) for further experiments.

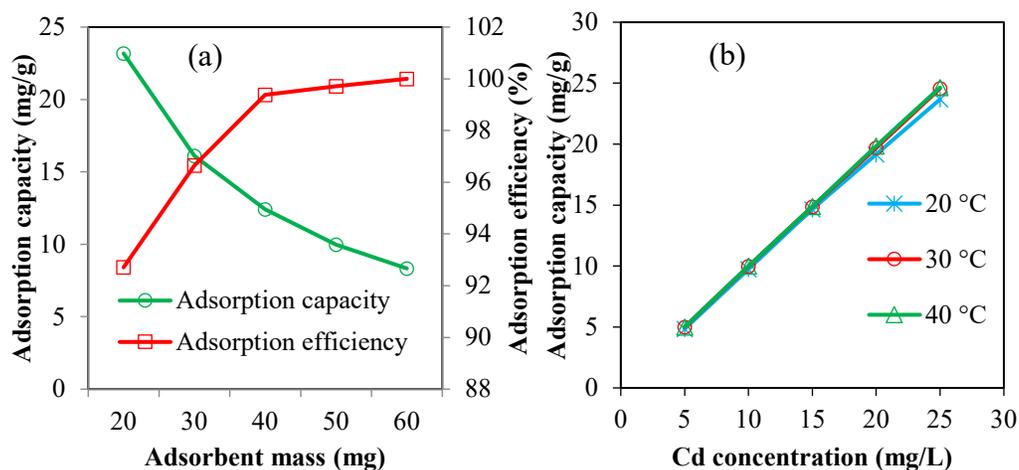


Figure 5. Effect of (a) material mass and (b) Cd concentration and temperature on the capacity using AHO/CER

Adsorption temperature and pollutant concentration both have a great influence on the adsorption capacity of materials. In this experiment, the cadmium adsorption capacity was investigated at different temperatures (20-40°C) and initial Cd concentration (5-25 mg/L). As shown in Figure 5(b), the adsorption capacity is proportional to both the variation of initial Cd concentration

and solution temperature. As the initial concentration and temperature increased, the adsorption capacity also increased. With a higher initial Cd concentration, the Cd ions become denser, which facilitates the interaction of Cd ions and the adsorbent, thus promoting contact and ion capture of the material. Moreover, the concentration gradient produced by the increase in the initial Cd concentration leads to higher Cd adsorption [20]. Similarly, when the solution temperature increases, the cadmium ions in the solution become more mobile, making the frequency of collisions between the material and Cd ions higher, so the possibility of Cd ions being captured is also greater. Particularly, this can be seen in solutions with a cadmium concentration of 15 mg/L or more when the temperature is increased from 20 to 40°C.

3.3 Adsorption kinetics, isotherms, and thermodynamics

For the Cd adsorption process, the adsorption kinetics were studied based on pseudo-first-order, pseudo-second-order, and diffusion kinetic models, as summarized in Table 2. Accordingly, the pseudo-second-order kinetic equation was more suitable for Cd adsorption on AHO/CER composite. The correlation coefficient of the pseudo-second-order model ($R^2 = 0.9982$) is higher when compared with the other two types of kinetic equations. This suggests that the adsorption process is a type of chemisorption, which relates to valency forces and the sharing or exchanging of electrons between AHO/CER and Cd [21, 22]. Furthermore, the theoretical Cd adsorption capacity calculated according to the pseudo-second-order equation was 9.28 mg/g, which was closed to the observed experimental Cd adsorption capacity (8.99 mgCd/g). Besides, the apparent rate constant of pseudo-second-order was determined to be 0.03 g/(mg.min).

Table 2. Kinetic model parameters for the adsorption of Cd on AHO/CER composite

| Kinetic model | Parameters | Values |
|--------------------------------|------------------------------------|--------|
| Pseudo-first-order | q_e (mg/g) | 58.47 |
| | k_1 (min^{-1}) | 0.017 |
| | R^2 | 0.4475 |
| Pseudo-second-order | q_e (mg/g) | 9.28 |
| | k_2 (g/(mg.min)) | 0.030 |
| | R^2 | 0.9982 |
| Intra-particle diffusion model | k_p (mg/(g.min ^{0.5})) | 0.692 |
| | C (mg/g) | 2.906 |
| | R^2 | 0.7701 |

Note: k_1 and k_2 are the first-order and second-order apparent adsorption rate constants, respectively. k_p is the intra-particle diffusion rate constant and C is the thickness of the boundary layer. q_e is the adsorbed amount at equilibrium.

The Langmuir and Freundlich isotherms were applied to evaluate and describe the nature of the Cd ion adsorption process on the surface of the AHO/CER composite. The agreement between theory and experiment is based on the value of correlation coefficient R^2 between the experimental values and the proposed model and the coefficient n in the Freundlich isothermal model. As shown in Table 3, the correlation coefficients of both models are gradually approaching 1 and have a high degree of suitability for the Cd adsorption process in the temperature condition from 20-40°C. However, the Freundlich isothermal model has a higher correlation coefficient R^2 , and the value of n ranges from 1 to 10, which is favorable for the adsorption process [23]. The material analysis results show that the surface is relatively uniform, thus it will have the same affinity for Cd at almost

all locations on the surface. The high agreement with the Freundlich model shows that both individual interactions with each Cd ion and the material and the mutual interaction between the Cd ions are important for the adsorption process. Also, the process is preferable to be chemical adsorption.

Table 3. Parameters in Langmuir and Freundlich adsorption isotherms

| Isotherms | | Temperature | | |
|------------|----------------|-------------|-------|-------|
| | | 20 °C | 30 °C | 40 °C |
| Langmuir | R ² | 0.88 | 0.96 | 0.95 |
| | | | | |
| Freundlich | R ² | 0.89 | 0.99 | 0.97 |
| | n | 1.47 | 2.71 | 4.94 |

The thermodynamics of the Cd adsorption process was studied to determine the energy values and trends of the process (Table 4). Cd adsorption has a Gibbs free energy of $\Delta G < 0$, proving that the adsorption of Cd ions by AHO/CER composite is a spontaneous process at standard conditions. The value of $\Delta H < 0$ indicates that Cd adsorption on AHO/CER is an exothermic process. With an ΔH value of -133.58 kJ/mol (e.g., higher than 40 kJ/mol), the adsorption of Cd by AHO/CER composite can be classified as a chemical adsorption process. The affinity of the adsorbent for Cd is expressed as ΔS with a value of 0.49, indicating a favorable process.

Table 4. Thermodynamic parameters of Cd adsorption by AHO/CER composite

| | Temperature | Values |
|------------|-------------|---------|
| ΔG | 293 K | -276.18 |
| | 303 K | -281.05 |
| | 313 K | -285.92 |
| ΔH | | -133.58 |
| ΔS | | 0.49 |

Based on the results of material characterizations and adsorption tests, especially kinetics, isotherms, and thermodynamics, the mechanism of Cd adsorption on the surface of AHO/CER can be suggested. In the structure of AHO/CER, the aluminum hydroxide particles are located in the matrix of the CER. It is likely that Cd adsorption can be accomplished via a dual interaction process of (i) ion exchange with cation exchange resin and (ii) adsorption on the aluminum hydroxide surface. Therefore, the adsorption of Cd onto AHO/CER likely forms a complex in which each Cd is surrounded by six oxygen atoms. This phenomenon may be similar to the study of Du *et al.* [24]. Thus, the coordination environment of Cd at the Al hydroxide-water interface in this study is a bidentate corner-sharing complex, which explains the high adsorption capacity of Al oxide at mid pH.

3.4 Results from optimization process

Based on the results of determining the individual factors (e.g., time, pH, material mass, and initial Cd concentration) affecting the Cd adsorption efficiency, this study continued to optimize the

relevant factors for the batch adsorption model. The empirical quadratic polynomial model for 4 parameters can be represented as the following equation.

$$Y = \beta_0 + \sum_{i=1}^4 \beta_i X_i + \sum_{i=1}^4 \beta_{ii} X_i^2 + \sum_{i=1}^3 \sum_{j=i+1}^4 \beta_{ij} X_i X_j \quad (3)$$

The results of analysis of variance (ANOVA) for the multivariable 2nd order model are shown in Table 5.

Table 5. ANOVA for Quadratic model

| Source | Sum of Squares | df | Mean Square | F-value | p-value | |
|------------------|----------------|-----------|-------------|-----------|----------|-------------|
| Block | 0.6050 | 2 | 0.3025 | | | |
| Model | 65.40 | 14 | 4.67 | 8.69 | 0.0002 | significant |
| A-Time | 38.10 | 1 | 38.10 | 70.83 | < 0.0001 | |
| B-pH | 0.4027 | 1 | 0.4027 | 0.7487 | 0.4026 | |
| C-Material mass | 2.54 | 1 | 2.54 | 4.72 | 0.0489 | |
| D-Initial conc. | 0.2702 | 1 | 0.2702 | 0.5024 | 0.4910 | |
| AB | 0.4587 | 1 | 0.4587 | 0.8528 | 0.3726 | |
| AC | 1.12 | 1 | 1.12 | 2.08 | 0.1733 | |
| AD | 0.0333 | 1 | 0.0333 | 0.0619 | 0.8074 | |
| BC | 0.0582 | 1 | 0.0582 | 0.1082 | 0.7475 | |
| BD | 0.0017 | 1 | 0.0017 | 0.0033 | 0.9554 | |
| CD | 0.0243 | 1 | 0.0243 | 0.0452 | 0.8349 | |
| A ² | 19.69 | 1 | 19.69 | 36.60 | < 0.0001 | |
| B ² | 0.0193 | 1 | 0.0193 | 0.0359 | 0.8527 | |
| C ² | 0.0053 | 1 | 0.0053 | 0.0099 | 0.9224 | |
| D ² | 0.0713 | 1 | 0.0713 | 0.1325 | 0.7217 | |
| Residual | 6.99 | 13 | 0.5379 | | | |
| Lack of Fit | 6.99 | 12 | 0.5827 | 1.049E+05 | 0.0024 | significant |
| Pure Error | 5.556E-06 | 1 | 5.556E-06 | | | |
| Cor Total | 73.00 | 29 | | | | |

P-values less than 0.05 indicate model terms are significant, and A (time), C (material mass), and A² are significant model terms (Table 5). The other values with P-values greater than 0.1000 indicate the model terms are not significant. For pH (B), the material can adsorb Cd well in an acidic environment. In a basic environment, metal ions begin to precipitate, thus affecting the Cd removal efficiency due to the combination of both adsorption and precipitation on the surface of the adsorbent. Therefore, in the survey range at pH = 4-8, there is no significant difference. By removing insignificant factors, the quadratic multivariate regression equation is rewritten as the following equation.

$$Y = 99.32 + 1.32x_1 + 0.34x_2 - 0.87x_1^2 \quad (4)$$

The three-dimensional surface and contour graph models describe the response of the independent factors on the output dependent variable through the regression equation. These two types of graphs give an overview of the best approach of the model concerning each pair of independent variables affecting the objective function. The results of the interaction between time and material mass on Cd removal efficiency are shown in Figure 6.

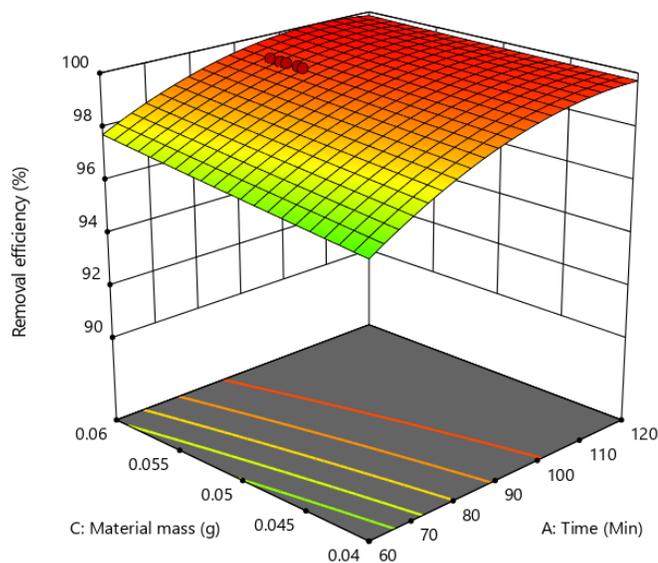


Figure 6. The combined effect of time (A) and material mass (C) on Cd removal efficiency

As the main objective of this study was finding the optimal conditions for Cd removal, the results suggest that the pH of the treated solution needs to reach neutral or sub-neutral if it is to be discharged into the environment; the initial pollutant concentration should match the solution's actual pollution value; and the material mass should be just enough to adsorb the pollutants to avoid excessive treatment costs. The combining of the above factors for optimization of the model suggested a material mass of 0.075 g, adsorption time of 70 min, pH 6.54, initial Cd concentration of 10 mg/L. Under these optimal conditions, the adsorption process achieved 99.50% Cd removal and met QCVN 40:2011/BNTMT. The experimental value of removal efficiency at this optimized condition was 99.53% (Figure 7(a)), which was similar to the predicted value of 99.50%.

3.5 Comparison with commercial CER and applicability of AHO/CER by column test

In the study, the Cd adsorption capacity of AHO/CER was compared with commercial cationic resins (220Na) under the same conditions of the material of 0.075 g, adsorption time of 70 min, pH 6.54, with 50 mL of 10 mg/L Cd solution, and at room temperature. As presented in Figure 7(a), the Cd removal efficiency of AHO/CER composite was higher than that of its precursor of 220Na CER.

Based on the results of the optimization study using batch model, a continuous flow model was operated under the experimental conditions of a flow rate of 0.7 mL/min, 10 mgCd/L, 1.5 g/LAHO/CER, and at room temperature. As shown in Figure 7(b), outlet Cd was not detected, and 100% treatment efficiency was achieved in the first 350 min. After 700 min of adsorption, the Cd concentration reached 0.048 mg/L with a removal efficiency of 99.52%. And in the next 1050 min, the cadmium concentration reached 0.05 mg/L with the removal efficiency of 99.5%, still meeting QCVN 40: 2011/BTNMT. After 1400 min, the outlet Cd concentration was 0.052 mg/L with a removal efficiency of 99.49%. From these results, the amount of the material can be adjusted based on the flow rate of wastewater, treatment purposes, and the source of receiving water after treatment (e.g. discharging standards).

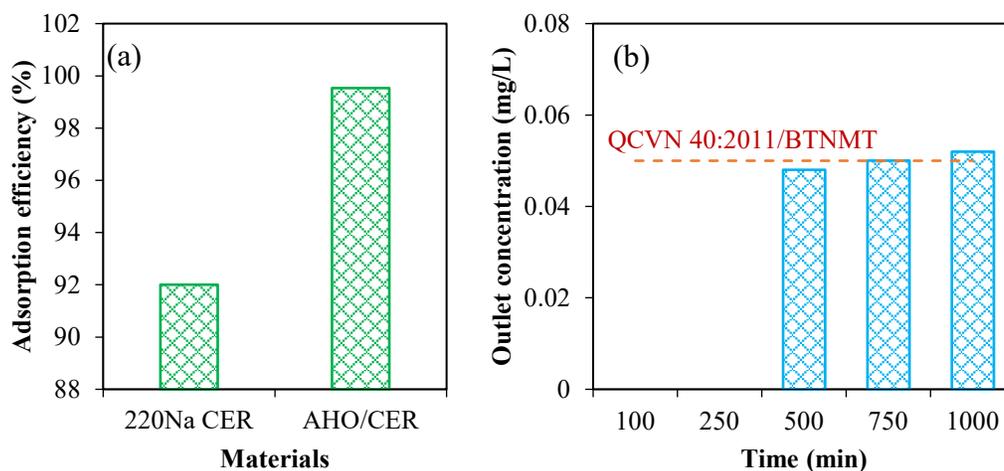


Figure 7. (a) Cd removal efficiency using AHO/CER composite in comparison with commercial CER and (b) Outlet Cd concentration in column test

4. Conclusions

The AHO/CER composite was successfully synthesized and characterized by FTIR, XRD, SEM, and EDX techniques. The results showed that the AHO/CER composite gave better Cd removal efficiency than 220Na cation resin. The interaction between the polymer structure and aluminum (hydr)oxide particles enhanced Cd adsorption efficiency in the solution. This Cd removal efficiency reached over 99% after only 70 min of adsorption from an initial Cd concentration of 10 mg/L at pH 6.5. This study provides a possible way to improve the adsorption efficiency of heavy metals in water based on commercially available ion exchange resins.

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