

Sludge-based activated carbon for removal of Cadmium in the water resource; Financial feasibility

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Abstract

Sludge-based activated carbon (AC) was prepared for the cadmium (Cd) removal from the aqueous solution. X-ray diffraction and Fourier transform infrared were applied as two main techniques to investigate the surface characterizations of the adsorbent. Response surface methodology (RSM), which was coupled with central composite design (CCD), was applied to study the impact of three major parameters, such as pH, dosage (D) and initial concentrate (C) on the percentage of Cadmium removal. The RSM model indicates that the optimum points of Cd removal were 90% at pH = 8.74 and D/C = 50. The Financial Feasibility and Investment Strategy was also investigated to consider key indicators in the financial feasibility of water treatment projects. The present study shows the systematic investigation of an attractive adsorbent to remove Cd from an aqueous solution. Also, in this study, modern investment strategies and efficient financing methods for water treatment projects are provided. The results showed that this type of adsorbent is appropriately able to eliminate Cd from water and aqueous solution.

Keywords: Wastewater; Cadmium removal; optimization; RSM; Financial feasibility; Sludge-based activated carbon

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1. Introduction

Water is one of the most important elements, which is a critical source for the human body and life on the earth. While water carries away waste material, it circulates through the land just as it does through the dissolving, transporting, organic matter, replenishing nutrients and the human body. Groundwater is considered as the major drinking water resource [1, 2]. The wastewater treatment approach should satisfy two main objectives, such as conserving freshwater sources and protecting the environment. Two major water resources (brackish water and industrial wastewater) are fully considered as waste which is mostly thrown [3, 4]. This is mainly because the main contaminants including toxic heavy metals are in wastewater. The pollutants resulted from the industries where are considered as the point sources are transferred into the surface water. The contaminated surface water migrates far away and near the places where populations who live there and causes severe health problems for them. To prevent releasing toxic metals into the environment, the removal of these harmful heavy metals from industrial sewage is an important approach that should be done [5, 6]. Previous researches developed various methods to treat wastewater [7,8].

Normally wastewater contains a high concentration of heavy metals such as lead, barium, uranium, and cadmium, which are toxic for the environment and humans [9]. Cadmium heavy metal is one of the common pollutants that are in different industrial wastewaters such as battery and pigment production, petrochemical complexes, cement and metal production, and etc. Cadmium causes severe health issues like the liver and kidneys. The maximum amount of cadmium in drinking water is reported to be 0.003 mg.L^{-1} [7]. Generally, to reduce the negative impacts of cadmium on the environment, it should be separated from the effluents which are released into the environment. Several separation methods have been developed to remove this type of pollutant from wastewaters [10]. The adsorption technique is recently considered as an alternative method compared to the other methods as this process contains many opportunities, such as easy control and operation, high efficiency and potential and low costs [5, 11].

Considering an appropriate adsorbent is one of the most important factors that affect the efficiency of the process [12, 13]. A variety of materials including carbon-based sorbents, biosorbents, natural sorbents, miscellaneous adsorbents, farm wastes, and industrial waste have been checked for the removal of Cadmium heavy metal from wastewater [14]. Among the available industrial adsorbents, waste activated sludge (WAS) has attracted high attention due to its high chemical and unique mechanical resistance, and porous structure [5]. To date, a huge amount of WAS is produced during the urban sewage treatment process, resulted in numerous problems. WAS is generally composed of nutrients, microbial cells, extracellular polymeric substances (EPS) and minerals [15]. Since the disposal and treatment of sludge are responsible for almost 50% of the sewage treatment cost [16], the available traditional disposal process and sludge treatment such as incineration, aerobic and anaerobic digestion, composting, land use and landfill should be considered [17]. As these methods are generally limited due to the production of secondary pollution and its high costs, the carbonization of produced sludge results in attractive researchers' attention because of its harmlessness. For example, Cheng et al. used the sludge activated carbon (SAC) modified with an aluminum salt to remove organic pollutants from anaerobic digestion fluid. The results showed that the efficiency of the organic matter reached at 45% [18]. Wang et al. also performed SAC as a skeleton agent which was modified with organic polymer flocculant to eliminate the soluble biopolymer in sludge synchronously [19].

The main objective of the present study was to use a sewage sludge-based activated carbon (SBAC) to significantly increase the efficiency of Cd removal. Furthermore, since economic and environmental aspects that previously been studied have not covered the details of the application of SAC in heavy metals removal and using sewage SBAC as an economical and simple adsorbent, the optimization and financial aspect were also investigated. To demonstrate the potential of this adsorbent for application in industries, pH and D/C as critical factors were systematically analyzed by using RSM-CCD technique to obtain the high efficiency.

2. Material and method

2.1. Solution preparation

Stock solutions of Cd^{2+} were prepared by dissolving Copper (II) Sulfate (CuSO_4) and Cadmium (II) Sulfate (CdSO_4) (analytical grade), respectively in deionized water to a specific concentration. The initial pH of the Cd solution was regulated before the adsorption tests with hydrochloric acid and sodium hydroxide solutions. The pH was assessed using a Metrohm digital pH meter.

2.2. Synthesis of sludge-derived activated carbon

The activated carbon was synthesized from the sewage sludge obtained from a paper mill industry wastewater treatment. The sludge was washed to remove the contaminated grits and dried at $110\text{ }^\circ\text{C}$ for 36 h. Finally, it was crushed with a grinder and sieved to a size range of 2-4 mm. For the pyrolysis step, about 70 g of crushed sewage sludge was heated in a vessel to $450\text{ }^\circ\text{C}$ under a N_2 atmosphere and kept at this temperature for 3 hours. The obtained sample (char) was crushed and sieved to a size smaller than 0.25 mm and then dried at $110\text{ }^\circ\text{C}$ for 3 h. For the activation step, 150 mL of H_3PO_4 solution was mixed with 8 g of char. The liquid/solid phases were shaken at a constant rate of 300 rpm for 1 h. The supernatant was then separated by filtration and the remaining solid was washed until the pH of filtrate was constant. Subsequently, it was carbonized in a fixed-bed tank at the carbonization temperature (approximately $800\text{ }^\circ\text{C}$) under a N_2 atmosphere, then held at this temperature for 50 min. The obtained samples were washed with concentrated HCl to remove other contaminants and then with distilled water until the pH becomes neutral. The obtained sample was dried at $110\text{ }^\circ\text{C}$ for 24 h and then the AC was obtained.

2.3. Adsorption study

The Cd removal on the sludge-based activated carbon was studied under batch conditions. For this purpose, thirteen sample solutions (50 ml) with distinct concentrations between 4 to $20\text{ mg}\cdot\text{l}^{-1}$ were prepared for the Cd samples. 200 mg of the adsorbent was then added to the sample solution and stirred for 60 minutes in 150 ml bottles which were held in a shaker rotating with a speed of 150 rpm.

The temperature was assumed at $25\text{ }^\circ\text{C}$ during experimental conditions. After which the adsorbent was separated by using a centrifugation, a UV-VIS spectrophotometer was applied to measure the Cd concentration in the solutions. The percentage of Cd removal was proposed using Eq. 1:

$$R\% = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

Where C_t and C_0 are the final and initial concentrations in mg.l^{-1} . All experimental tests were conducted in triplicate to ensure the repeatability of the outputs.

2.4. Characterization tests

FT-IR was obtained with a Nicolet iS10 from Thermo Fisher Scientific for the investigation of the functional groups of nanoparticles, nanocomposites in the range of $4000\text{-}500\text{ cm}^{-1}$. The XRD of nanoparticles and nanocomposites were measured using a diffractometer using a Cu Ka radiation ($\lambda = 1.54056\text{ \AA}$).

3. Results and discussion

3.1. Characterization of Sludge-based activated carbon

The XRD and FTIR of as-synthesized AC are shown in Fig 1. From the XRD pattern, overall two broad peaks around 24.9° as well as 42.8° are due to the amorphous nature of AC. The certain sharp peaks are may be due to the existence of residual ash in the carbon. The broad absorption band at $3590\text{-}3100\text{ cm}^{-1}$ in the FT-IR spectra is characteristic of the stretching vibration of OH group in the AC. The band at $2790\text{-}3100\text{ cm}^{-1}$ shows the presence of an aliphatic – CH stretching. The band at 1635 cm^{-1} is due to the C=C stretching vibration in the AC.

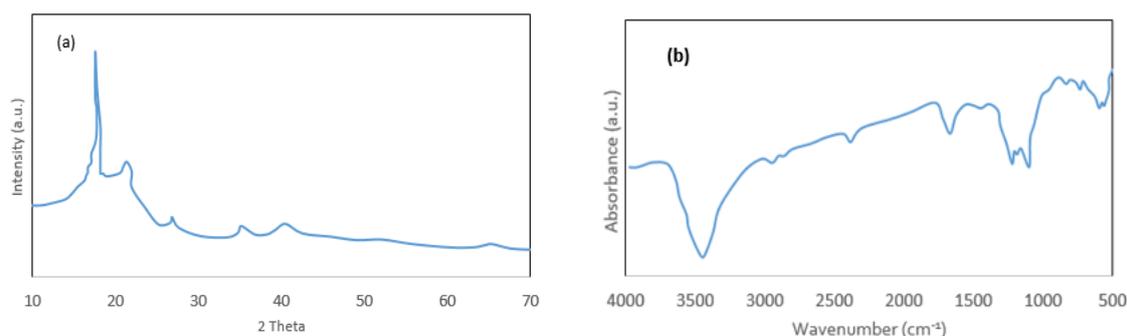


Figure 1. Characterization analysis of activated carbon (a) XRD diffraction pattern and (b) FTIR spectra

3.2. Experimental design

To perform the CCD based on its suitability, a quadratic surface model is needed to obtain a model that works well for optimization of the process. D/C and pH parameters were assumed as control parameters [20]. The design generally contains one center point, four-star points and two levels of full factorial design ($2^2 = 4$). In addition, three reproduces at the central point were assumed to investigate the pure error among each experiment. A none linear formula was proposed by the software to estimate the responses as a role of independent variables involving their quadratic interactions and squared terms. The obtained quadratic equation is presented as below.

$$Y = \beta_0 + \sum_{j=1}^3 \beta_j X_j + \sum_{j=1}^3 \beta_{jj} X_j^2 + \sum_{i < j} \beta_{ij} X_i X_j \quad (2)$$

The multiple regression analysis techniques (MRATs) in the RSM-CCD were applied to estimate the model coefficients. Factors and levels for CCD study and design matrix with their corresponding results are represented in Tables 1 and 2, respectively.

Table 1. Factors and levels for CCD study. Level pH, D/C

level	pH	D/C
$-\alpha$	5.00	10.00
-1	3.96	1.71
0	7.50	30.00
+1	10.00	50.00
$+\alpha$	11.03	58.28

Table 2. Design matrix and experimental data of the main products for removal study. Run Factor Final

Run	Factors		Cadmium	Pure Error	P-value (Model)	R ²
	pH	D/C	Removal %			
1	5.00	50.00	68			
2	10.00	10.00	51			
3	7.50	30.00	70			0.9347
4	7.50	1.71	40			
5	3.96	30.00	29			
6	7.50	58.28	98			
7	5.00	10.00	46		0.005 (significant)	
8	7.50	30.00	70			
9	11.03	30.00	64			
10	10.00	50.00	82			
11	7.50	30.00	71			
Sum of squares	-	-	-	0.6667		
Mean square	-	-	-	0.3333		

The determined coefficients were used to estimate a model and were extracted from the software, as shown in Eq. (3):

$$R1 = -68.04529 + 28.27487 \times \text{pH} + 0.456402 \times \text{D/C} + 0.0450 \times \text{pH} \times \text{D/C} - 1.74667 \times (\text{pH})^2 + 0.000833 \times (\text{pH})^2 \quad (3)$$

The ANOVA for Eq. (3) was presented in Table 2. In the above model, quadratic and linear parameters were significant with $p < 0.05$. Any p-value smaller than 0.05 confirms the model is significant at the 95% confidence limit [21, 22]. R^2 equals 0.9347 for Eq. (3) confirming a very good fitting between the estimated and experimental values. The observed versus estimated values are shown in Fig. 2 for Cd removal (%). It can be seen that most of the experimental values lie close to the straight line, which is the predicted values.

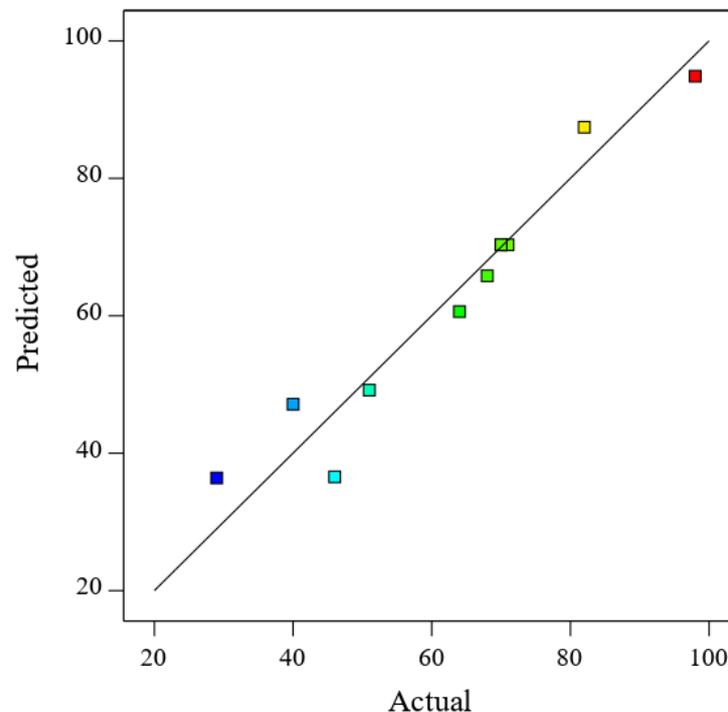


Figure 2. The predicted and actual values of Cd removal

3.3. Contour plots

D/C and pH as two independent parameters were simultaneously analyzed to investigate their effects on the Cd removal. For this, Eq. (3) is performed to export the contour and response surface plots. Fig. 3 (a and b) represents the maximum Cd removal, which was measured at 90% at D/C = 50 and pH = 8.74. Fig. 3 (a and b) confirms that the D/C and pH factors are important parameters that affect the Cd removal. Based on the results, the decrease of removal reaches when D/C and pH decrease, nearly 10 and 5, respectively. The higher amount of D/C and the higher amounts of pH lead to a more reduced percentage of Cd. Following this, further increasing of pH results in more reduction of Cd removal until pH = 8.74. At D/C 10 and pH = 5, the removal percentage of Cd obtains to a minimum amount (46%), while at D/C 50 and pH =

8.74, the maximum removal was shown at about 90%.

In order to validate the model optimization of Cd removal, three more runs were considered. Furthermore, the obtained optimal points were compared with those resulted from experimental data during the same conditions. To investigate the effect of pH on the adsorption mechanism, the equilibrium studies at different pH amounts were carried out, ranging from 3 to 10. It can be concluded from Fig. 3c that the pH of Cd solution has a considerable effect on the removal process. Increasing the pH from 3 to 10 causes that the removal percentage rises from almost 46 to 90% at pH = 8.74. Following that pH value above 8.74 reduces the removal of Cd. Fig. 3c also indicates that with an increment of D/C, the removal of Cd significantly increases up to approximately 90%. Therefore, both pH and D/C values of the wastewater are equally important factors for the removal of Cd.

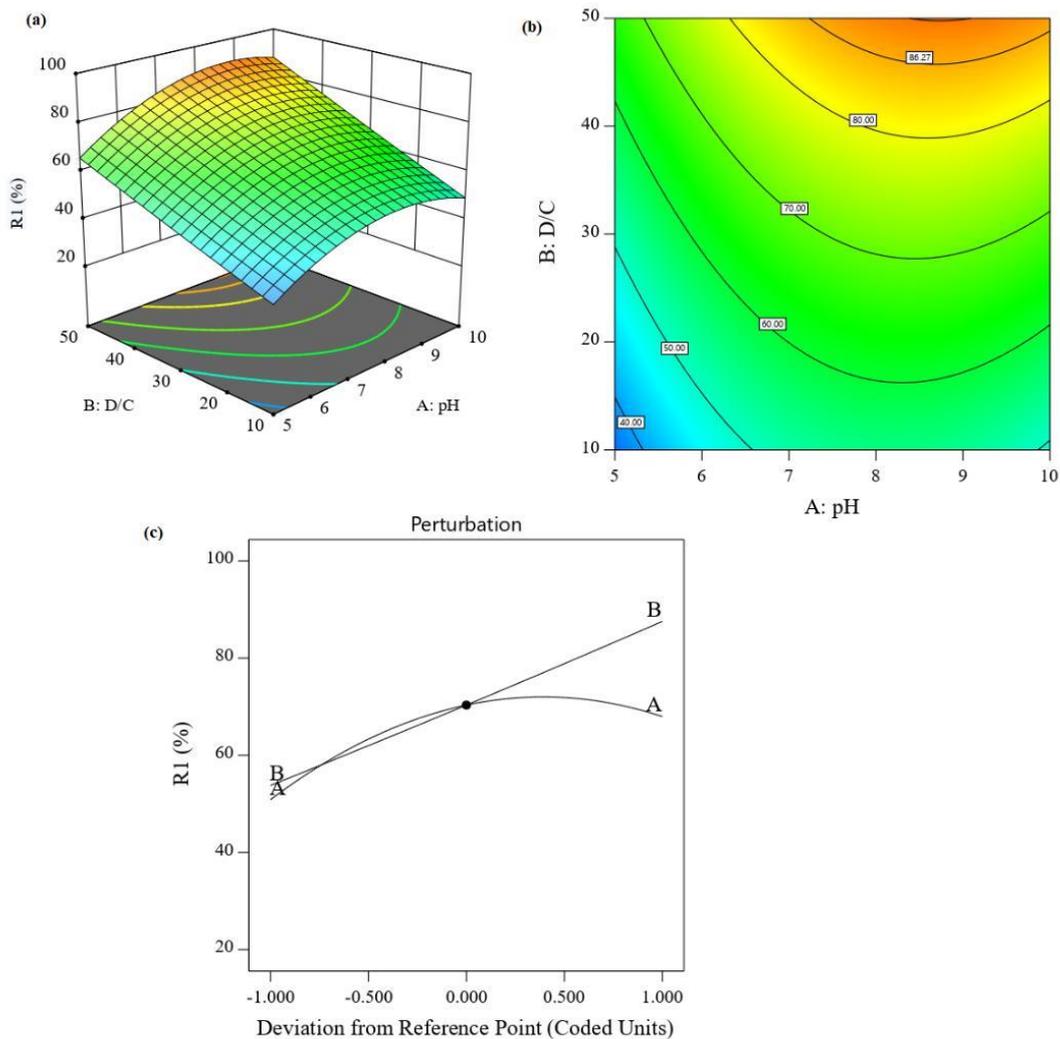


Figure 3. a) 3D plot, b) contour plot and c) perturbation plot describing the response surface of the adsorbent as a function of pH (A) and D/C (B) for Cd removal

4. Financial Feasibility and Investment Strategy

What are the financial and economic evaluation indicators of water treatment projects? Why should water treatment projects be evaluated financially and economically? These are some of the questions that have been investigated in this section.

In this section, the key indicators in the financial feasibility of water treatment projects have been examined. Furthermore, modern investment strategies and efficient financing methods for water treatment projects are provided.

Economic and environmental aspects that previously been studied have not covered the details of the application of WAS in heavy metals removal. Every project, regardless of type and size, should be economical. The economic aspect of a project is to ensure the profitability of its investment and sustainability [23]. The feasibility study is a type of research method, especially in engineering sciences and management, which includes the following:

- Technical studies and estimation of infrastructure facilities of the project
- Determine the planning horizon
- Identify goals, opportunities, and threats
- Identify costs
- Identify revenues
- Identify profit
- Financial forecasting and how to finance the project
- Determining the financial and economic indicators of the project

In the following, the key indicators in the financial and economic evaluation of water treatment projects are presented.

I. Net Present Value (NPV)

NPV is a method for assessing the feasibility of a project or investment plan. It is determined by taking the difference between the PV of cash inflows and the PV of cash outflows over a period of time. For each time span, the aim is to measure the net cash flow. To calculate the NPV, a five-step method can be employed:

- Evaluate the project's cost.
- Evaluate the future cash flows of the project over its expected life.
- Evaluate the project's riskiness and the cost of capital
- Measure the NPV of the project.
- Deciding whether to accept or reject the project

Following is the formula to calculate NPV:

$$B_{PV} = \sum_{t=1}^n \frac{B_t}{(1+i)^{t-1}} \quad (4)$$

$$C_{PV} = \sum_{t=1}^n \frac{C_t}{(1+i)^{t-1}} \quad (5)$$

$$NPV = B_{PV} - C_{PV} \quad (6)$$

projects by which The financial indicators of the projects can be calculated and analyzed and the effect of changes in each of the input parameters of the system on the financial processes of the project can be examined and finally a decision can be made regarding the acceptance or non-acceptance of the project.

Furthermore, it should be noted that methods of financing play an important role in the profitability of industrial projects. Hence, modern investment strategies must be implemented to increase the profitability of industrial projects and select the best financing method in the water & wastewater industry. Given the importance of this issue, the following strategies are suggested:

- Investment banks could operate as the issuer of securities for water treatment projects financing
- Securitization could provide an important role in project financing through economical and low-cost financing via the stock market.
- Forecasting effective indicators in investment projects using new hybrid models [24].
- Applying efficient and modern approaches in the project portfolio management and evaluating their performance based on risk-adjusted methods [25].
- Cooperation of insurance companies to manage the risk of water treatment projects. Reinsurance companies could also play their significant role in the risk transfer.
- Islamic securities can lead to the development of industrial projects. Sukuk are considered as Islamic financial instruments created for middle and long term financing. Depending on the project being financed by the Sukuk, various forms of Sukuk are based on different Islamic contract frameworks (Murabaha, Ijara, Istisna, Musharaka, Istithmar, etc.)
- Due to the type of industry and the nature of different types of Islamic securities, the use of Istisna' is suggested and preferred. Istisna' is generally a long-term contract in Islamic finance whereby a party undertakes to produce or construct assets, with an obligation from the producer to deliver them to the customer upon completion. Istisna' can be widely used in infrastructure and industrial projects including water treatment projects. Its diagram is shown in Fig 4.

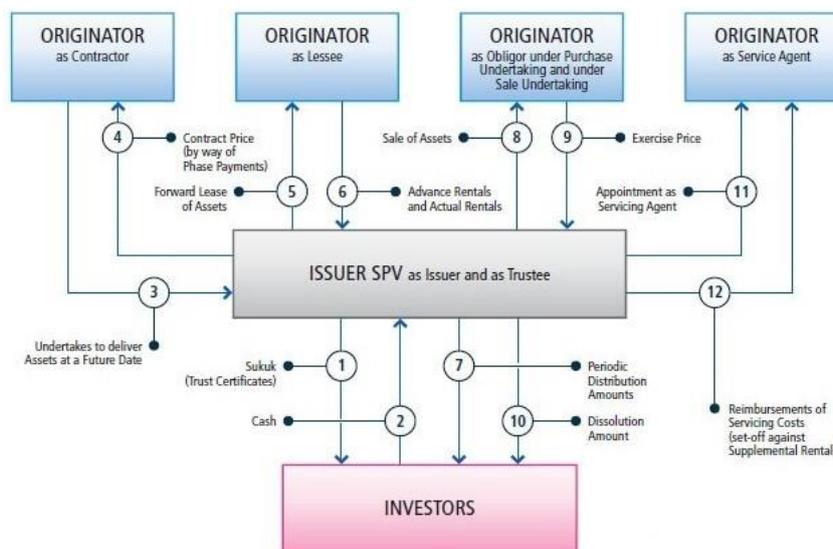


Figure 4. Structure of Sukuk Istisna' (Source: islamicmarkets.com)

5. Conclusions

In the present study, a waste adsorbent (Sludge-based activated carbon) is used to absorb Cd without using highly toxic chemical syntheses. The promising adsorbent has been attracted scientists for environmental protection, since it can be suggested as an effective and economical adsorbent for the removal of Cd from the water on an industrial scale. The optimization and modeling of Cd removal were also studied with the use of surface methodology–central composite design (RSM–CCD). Two common factors, including D/C and pH were considered as the control factors. A quadratic model Cd removal was extracted by ANOVA results, confirmed that there was a good correlation between the experimental data and theoretical models. The obtained results indicate that D/C and pH were the critical factors with a high considerable effect. The optimum points were obtained at (D/C) = 50 and pH = 8.74, resulting in the prediction of removal percentage at 90%, while at D/C 10 and pH = 5, the removal percentage of Cd obtained to a minimum amount (46%). Mathematical parameters including P-value and R² were obtained 0.005 and 0.9347, confirming that the model is significant. Furthermore, the key indicators in the financial feasibility of water treatment projects were evaluated and the modern investment strategies were proposed to increase the profitability of industrial projects and select the best financing method in the water & wastewater industry. The results confirmed that the adsorbent is superior for the removal process of Cd from an aqueous solution.

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