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Adsorption of Cd^{2+} Ions Using Cassava Peel Activated Carbon: Study of Adsorption Kinetics, Isotherms and Thermodynamics

Tri Ariyanto Nugroho, Cucun Alep Riyanto*, November Rianto Aminu

Department of Chemistry, Faculty of Science and Mathematics, Satya Wacana Christian University, Salatiga, Central Java, Indonesia
* corresponding author: cucun.riyanto@uksw.edu

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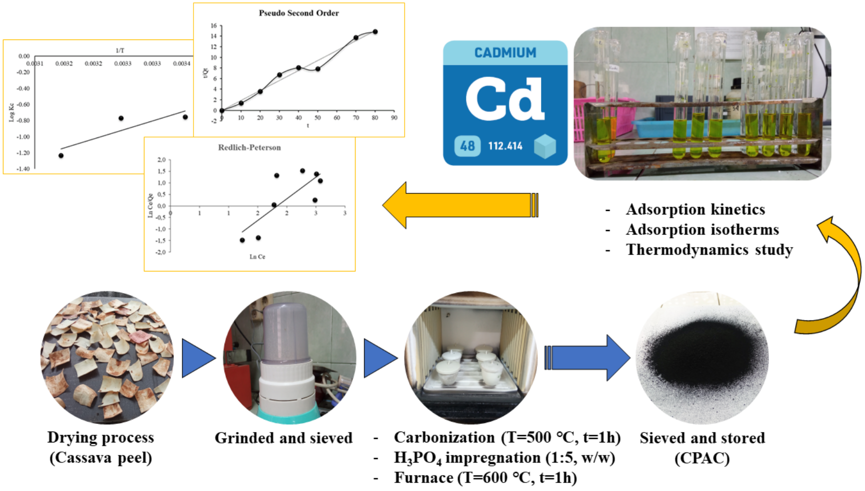
GRAPHICAL ABSTRACT



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ABSTRACT

Heavy metal Cd^{2+} ions are dangerous pollutants in water and ecological systems if they exceed the quality standard threshold. Cassava peel has a reasonably high carbon element content, 59.31% (w/w), so it can be used as an activated carbon to break down Cd^{2+} metal ions in water. This research aims to determine the kinetic model and adsorption isotherms of Cd^{2+} ions using Cassava Peel Activated Carbon (CPAC), which was chemically activated with H_3PO_4, determine the optimum pH and temperature conditions for Cd^{2+} ions adsorption and select the adsorption capacity of Cd^{2+} ions using CPAC activated by H_3PO_4. CPAC is made through a carbonization process at a temperature of 500 °C for 1 hour. Next, it was impregnated with H_3PO_4 at a concentration of 30 % with a ratio of 1:5 (w/w) for 24 hours and physically activated at 600 °C for 1 hour. Based on research, kinetic model and adsorption isotherms of Cd^{2+} ions using CPAC started by H_3PO_4 following Pseudo-Second-Order (PSO) kinetic model and Freundlich isotherm, the optimum pH and temperature conditions for Cd^{2+} ion adsorption were obtained at pH five and temperature 25 °C. Thermodynamic parameters, such as Gibbs energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), have been evaluated and indicate physical, spontaneous, and exothermic adsorption processes. The adsorption capacity of Cd^{2+} ions using CPAC activated by H_3PO_4 is 5.2219 mg/g.

1. INTRODUCTION

The presence of heavy metals in the environment is a significant concern due to their toxicity to many forms of life. Heavy metals will not degrade into harmless end products, unlike organic pollutants, which are mainly susceptible to biological degradation [1]. Cd^{2+} ions are a transition metal exhibiting "teratogenic, carcinogenic, and mutagenic" biological toxicity [2]. If the Cd^{2+} ions enter the body from the food chain, they can cause damage to the lungs, liver, kidneys, bones, reproductive organs, immune and cardiovascular systems, and various other diseases [3]. One example of cadmium pollution occurred in the upper reaches of the Jinzu River in Japan, which came from mining waste. This cadmium pollution causes a disease known as "Itai-itai disease". It was reported that 132 residents died as an impact of this pollution [4]. Several methods to reduce pollution from heavy metals in aqueous solutions are chemical precipitation, conventional coagulation, osmosis, ion exchange, ultrafiltration, and adsorption [5]. Compared to other methods, the adsorption method has advantages, including relatively high efficiency and effectiveness, relatively simple management, and does not cause negative impacts on the environment [6]. In previous research, Suprabawati *et al.* (2018) [7], used cassava peel as active carbon, which was chemically activated with KOH 0.4 M and had an adsorption efficiency of Pb^{2+} metal ions of 98%. Research by Darmawati *et al.* (2019) [8] studied the effect of differences in the mass of activated carbon from cassava peel, which was activated using 2% NaOH for the adsorption of Mn^{2+} metal ions, resulting in data that the addition of 4 grams of activated carbon had the highest adsorption percentage until 92.33%.

Activated carbon is an adsorbent that can be used for adsorption, primarily metal ions. Using natural materials to make activated carbon is recommended because it is relatively safe for the environment, and the costs are cheap. An alternative activated carbon from raw materials that can be used to overcome water pollution caused by cadmium metal ions (Cd^{2+}) is activated carbon from cassava peel. Research by Schwantes *et al.* (2016) [9] used cassava peel as active carbon, which was chemically activated with NaOH for the adsorption of Cd^{2+} metal ions, resulting in an adsorption capacity of 19.54 mg/g. In addition, a research compared the effect of activators H_3PO_4, $ZnCl_2$, NaCl, Na_2CO_3, and KOH, as well as the effect of particle size on the quality of cassava peel-activated carbon [10]. The H_3PO_4 activator (2.44%) and 100 mesh particle size produce the best quality cassava peel activated carbon with a water content of 3.5%, ash content of 7.5%, and the iodine number was 2537.71 mg/g. According to analysis, this cassava peel-activated carbon meets the active carbon quality standards according to SNI No.06-3730-1995.

The degree of acidity or pH is one of the factors that influences the adsorption process using activated carbon. The pH value effects the metal ion adsorption mechanism [11]. Research by Hasrianti (2015) [12] carried out the adsorption of Cd^{2+} ions using cassava peel adsorbent at various pH conditions, obtaining an optimum pH of 6.1 with the highest adsorption of Cd^{2+} ions at 68.58%. Another parameter that can influence the adsorption process is temperature. Based on adsorption theory, the adsorption process decreases with increasing temperature, and the first adsorbed molecules on the surface tend to be desorbed from the surface at high temperatures [13]. Research by Kumar *et al.* (2010) [14] compared the effect of temperature on the adsorption of Cd^{2+} metal ions using rice husk adsorbent; the results showed that adsorption decreased with increasing adsorption temperature. Based on previous studies, the research about adsorption kinetics, isotherms, or thermodynamics of adsorption of Cd^{2+} metal ions with cassava peel activated carbon activated by H_3PO_4 with variations in temperature and pH has never been done. This research aims to determine kinetic model and adsorption isotherms of Cd^{2+} ions using cassava peel activated carbon, which was chemically activated with H_3PO_4, determine the optimum pH and temperature conditions for Cd^{2+} ion adsorption and select the adsorption capacity of Cd^{2+} ions using CPAC activated by H_3PO_4.

2. EXPERIMENTAL METHODS

2.1. Tools and Materials

The equipment used includes an analytical balance with an accuracy of 0.1 mg (Ohaus PA214), a balance with an accuracy of 0.01 g (Ohaus TAJ601), pH meter (Hanna HI 9812), furnace (vulcan A-550), grinder (Philips), UV-Vis Spectrophotometer (PG Instruments T60), sieve (60 mesh), volumetric flask, filter paper, beaker. The instruments used for sample characterization were an

Infrared Spectrophotometer (FT-IR, Shimadzu Prestige 21, Gadjah Mada University) and Brunauer Emmett Teller (BET, Quantachrome NOVA Instruments, Semarang State University).

The raw material in this research is cassava peel obtained from one of the food processing industries in Salatiga. The chemicals used are H_3PO_4 (85%), NaOH, buffer pH of 7, $C_{76}H_{52}O_{46}$, $Cd(CH_3COO)_2 \cdot 2H_2O$, NH_4Cl, NH_4OH (25%), CH_3COOH (100%), CH_3COONa, each of which has a pro-analysis grade that were purchased from Merck, Germany. Then, the distilled water was obtained from the Chemistry Laboratory of Satya Wacana Christian University, Salatiga.

2.2. Research Procedures

2.2.1. Sample Preparation

The white cassava peel is separated from the dirt attached, washed with water, and cut into small pieces (~ 4x4 cm). After that, the cassava peel was dried in the sun for two days. The cassava peel was dried again in a dry cabinet at 60 °C for 24 hours. The dried cassava skin is ground using a grinder and sifted (30 mesh) [15, 16].

2.2.2. Carbonization and Sample Activation

Cassava peel was carbonized using a furnace at a temperature of 500 °C for 1 hour. The resulting carbon was impregnated using H_3PO_4 at a concentration of 30% with a ratio of 1:5 (w/w) for 24 hours. The results of the impregnation process are filtered and placed in an oven at 110 °C for 24 hours. The activated carbon obtained was then physically started using a furnace at a temperature of 600 °C for 1 hour; after that, the activated carbon was neutralized with 1 M NaOH and rinsed with distilled water until pH 7. The final activated carbon was dried in an oven at 110 °C for 24 hours, then sieved with a sieve (60 mesh) and stored [16].

2.2.3. Adsorption Kinetics

A weight of 10 mg of cassava peel activated carbon (CPAC) was added to 25 mL of a standard Cd^{2+} 5 mg/L solution and stirred with a magnetic stirrer at room temperature for 10, 20, 30, 40, 50, 60, and 70 minutes [14]. Data plotting in kinetic model includes:

Pseudo-Second Order Kinetics:

$$\frac{t}{q_t} = \frac{1}{q_e} t + \left(\frac{1}{kq_e^2}\right) \tag{1}$$

The q_t value is the amount of adsorbate adsorbed in unit time, and k is the equilibrium rate. The plot used is t vs t/q_t [17].

Elovich Kinetics:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{2}$$

The q_t value is the amount of adsorbate adsorbed at time t, α is the desorption constant, and β is the initial adsorption rate. The plot used is ln t vs q_t [18].

Intra-Particle Model Kinetics:

$$q_t = K_p\sqrt{t} + C \tag{3}$$

K_p is the diffusion rate constant ($mg/g.min^{1/2}$), q_t is the adsorption capacity at time t, and C is the intercept which shows the thickness of the boundary layer. The plot used is $\sqrt{t}$ vs q_t [19].

Bangham Kinetics:

$$\ln q_t = \vartheta \ln t + \ln k \tag{4}$$

The q_t value is amount of adsorbate at time t, and k is the Bangham constant. The plot used is ln t vs ln q_t [20].

2.2.4. Adsorption Isotherm

The adsorption isotherm study was carried out on 25 mL of standard Cd^{2+} solution concentrations of 6, 7, 8, 9, 10, 11, 12, and 13 mg/L added with 10 mg of CPAC and stirred with a magnetic stirrer at room temperature. Plotting data in adsorption isotherm model, among others:

Langmuir Isotherm:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{5}$$

The C_e value is the adsorbate concentration (mg/g), and K_L is the Langmuir constant related to the adsorption capacity (mg/g). The plot used is C_e vs C_e/q_e [21].

Redlich-Peterson Isotherm:

$$\ln\frac{C_e}{q_e} = \beta \ln C_e - \ln A \tag{6}$$

The q_e value is the equilibrium adsorbate loading on the adsorbent (mg/g), C_e is the equilibrium liquid phase concentration of the adsorbent (mg/L), A is Redlich-Peterson constant (L/g), and β is exponent. The plot used is ln C_e vs ln C_e/q_e [21, 22].

Temkin Isotherm:

$$q_e = \frac{RT}{b}\ln K_T + \frac{RT}{b}\ln C_e \tag{7}$$

The K_T value is the Temkin isotherm constant (L/g), and b is the Temkin constant related to heat absorption (J/mol). The plot used is ln C_e vs q_e [23, 24].

Elovich Isotherm:

$$\ln\frac{q_e}{C_e} = \ln K_E q_m - \frac{q_e}{q_m} \tag{8}$$

The Elovich isotherm is constant, and maximum adsorption capacity is obtained from the slope and intercept of the ln q_e/C_e vs q_e [23, 24].

2.2.5. Determination of Optimum pH

The Cd^{2+} standard solution (25 mL) with optimum concentration was prepared at pH of 5, 7, and 9. After that, 10 mg of CPAC was added to each and stirred with a magnetic stirrer at room temperature for the optimum time [14].

2.2.6. Determination of Optimum Temperature

25 mL of Cd^{2+} standard solution with optimum concentration was prepared at temperature of 25, 35, and 45 °C. Each solution added with 10 mg of CPAC and stirred with a magnetic stirred at the optimum pH for the optimum time [14].

2.2.7. Determination of Cd^{2+} Concentration

A standard Cd^{2+} solution was prepared with a concentration of 0.5, 1.0, 2.0, 4.0, 5.0, 10, 15, and 20 mg/L of stock solution in a 25 mL volumetric flask. A ratio of tannic acid: Cd^{2+} was made with a concentration of 4:1 and volume 2:1 with conditions of pH 10. Leave it for 20 minutes and measure the complex solution using a UV-Vis Spectrophotometer at the optimum wavelength. Next, a relationship curve was created between standard concentration (x-axis) and absorbance (y-axis). The slope, intercept, and correlation coefficient (r) were calculated [25, 26].

3. RESULT AND DISCUSSIONS

3.1. Characterization of Cassava Peel Activated Carbon (CPAC) using FTIR

The functional groups analysis was performed on standard activated carbon and CPAC using Fourier Transform Infrared (FTIR). Functional groups on the surface of common activated carbon and CPAC can determine the properties of the activated carbon surface [27]. The results of the FTIR analysis are presented in Figure 1. FTIR analysis results show that the absorption pattern and wavenumber of CPAC functional groups (Figure 1b) are close to standard activated carbon (Figure 1a). CPAC has several absorption peaks detected, namely 3448.72 cm^{-1}, which indicates the presence of O-H bond absorption. A rise appears at wave number 2924.09 cm^{-1}, indicating the C-H stretching group. There is a peak wave number of 671.23 cm^{-1}, which is an out-of-plane C-H group. Also, an absorption band appears at wavenumber 2337.72 cm^{-1}, indicating the C≡C functional group. The C=C active group is observed at a wavenumber of 1620.21 cm^{-1}. The C=C bonds formed mean the purer C element produced by activated carbon [16, 28]. The peak wave number of 1188.15 cm^{-1} indicates the stretching vibration of P=O from the aromatic group P-O-C [16, 29]. In general, activated carbon only has oxygen-based functional groups on the carbon surface. However, through the activation process of phosphoric acid, P-O-C bonds can be connected to the carbon surface. This absorption peak can be characteristic of activated carbon containing phosphate due to the influence of chemical activation using phosphoric acid [16, 30].

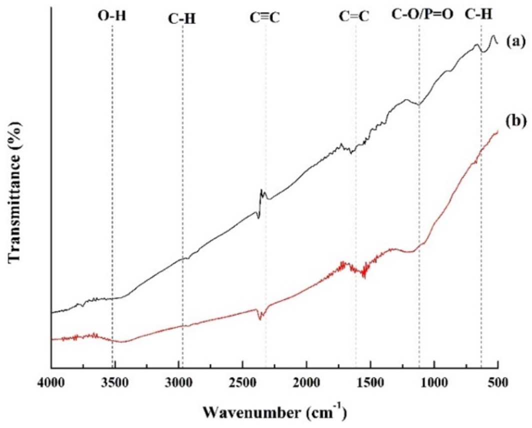

Figure 1. FTIR spectra: (a) standard activated carbon; (b) CPAC.

3.2. CPAC Surface Area and Pore Distribution (BET) Analysis

Brunauer Emmett Teller (BET) was used to determine the surface area and pore distribution of CPAC. The results of CPAC analysis using BET are presented in Figure 2.

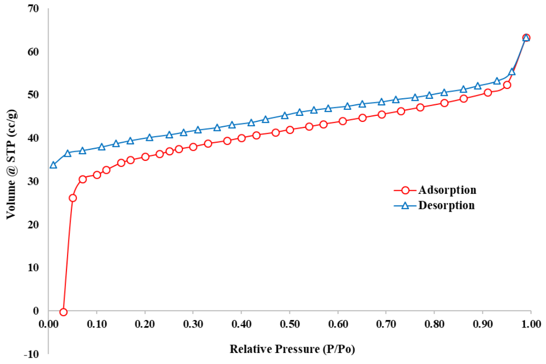

Figure 2. N_2 adsorption-desorption isotherms on CPAC

The results of BET analysis show that the surface area and pore size of CPAC were 126.182 m^2/g and 1.552 nm. Figure 2 shows a type 1 isothermal curve according to the IUPAC classification, which indicates that activated carbon has a microporous structure [31]. At P/Po = 0, the adsorbed gas is quite large, so the curve rises sharply to reach 25 cc/g. That result shows that CPAC has a reasonably high surface area. These results align with research [32], which states that chemically activated cassava peel activated carbon produced through a carbonization process at a temperature of 450-650 °C has a microporous structure and a BET surface area of 1154 m^2/g.

3.3. Adsorption Kinetics

The kinetic data obtained were analyzed using four kinetic models: Pseudo-Second Order (PSO), Elovich, Intra-Particle (IP) Model, and Bangham. The results of plotting data on the adsorption kinetics of Cd^{2+} ions using CPAC are presented in Table 1 and Figure 3.

TABLE I. Kinetic parameters of Cd^{2+} ion adsorption using CPAC

Model	Parameter		Equation	R^2
Elovich	**β (g/mg)**	**α (mg/g.min)**	y = 0.9613x + 1.8612	0.4704
	1.0402	6.6631		
Bangham	**K**	**ϑ**	y = 0.5567x – 0.3764	0.6927
	0.6863	0.5567		
IP Model	**K_p**	**C**	y = 0.3808x + 2.7714	0.3094
	0.3808	2.7714		

Pseudo Second Order	**q_e (mg/g)**	**k (g/mg min)**	y = 0.1915x – 0.0391	**0.9775**
	5.2219	-0.9379		

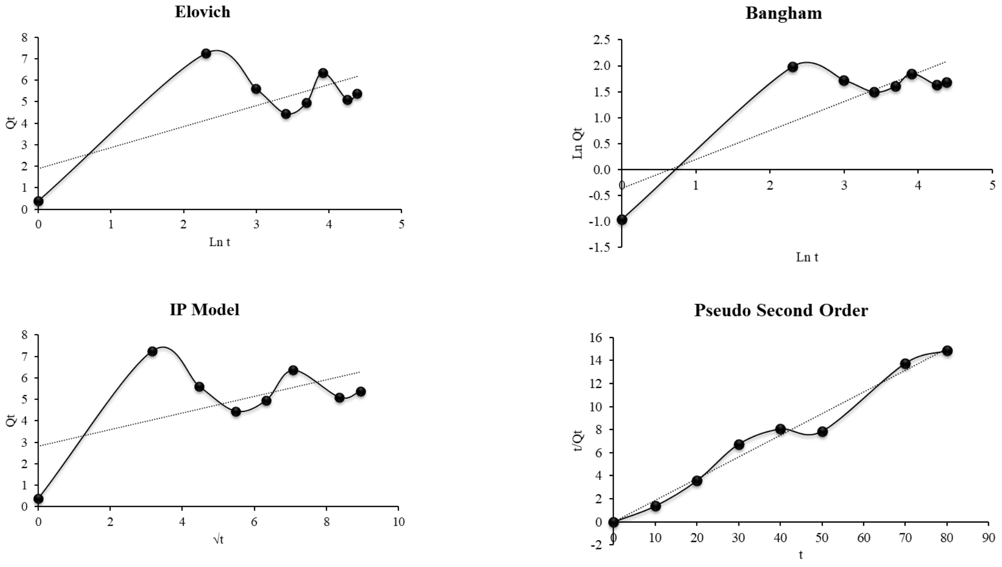

Figure 3. Plotting of Cd^{2+} ion adsorption kinetics data using CPAC.

The model of Cd^{2+} adsorption kinetics using CPAC tends to follow Pseudo Second Order (PSO) kinetics with an R^2 value of 0.9775. This model assumes that the adsorption process occurs by chemisorption, which forms a monolayer [33]. In Table 1, the q_e parameter value is 5.2219 mg/g, which shows the CPAC adsorption capacity and rate constant is -0.9379 (mg/g.min). The negative k value is because CPAC has reached the saturation point in adsorbing metal ions [34]. The kinetic model in this research is in line with research [14], which carried out adsorption kinetics of Cd^{2+} metal ions using rice husks following a Pseudo Second Order. A study from Hasrianti (2015) [12] states that the adsorption kinetics of Cd^{2+} metal ions using cassava peel biosorbent without carbonization and chemical activation have a maximum adsorption capacity of 0.90 mg/g. This research showed that CPAC activated using H_3PO_4 could increase the adsorption capacity to 5.2219 mg/g.

3.4. Adsorption Isotherm

The isotherm data obtained was analyzed using 4 adsorption isotherm models, including Langmuir, Temkin, Elovich, and Redlich-Peterson. The results of plotting Cd^{2+} ion adsorption isotherm data using CPAC are presented in Table 2 and Figure 4.

TABLE II. Cd^{2+} ion adsorption isotherm parameters using CPAC

Model	Parameter		Equation	R^2
Langmuir	**K_L (mg/g)**	**q_m (mg/g)**	y = 0.2729x + 0.0281	0.3334
	9.7182	3.6643		
Temkin	**B**	**K_T (L mol^{-1})**	y = -7.6651x + 22.622	0.4154
	-323.2276	0.0523		
Elovich	**q_m (mg/g)**	**K_E (L/mg)**	y = 0.1942x – 1.7581	**0.9223**
	-5.1493	1.4069		
Redlich-Peterson	**A**	**β**	y = 1.8761x – 3.4132	**0.6083**
	30.3623	1.8761		

The Cd^{2+} adsorption isotherm model with CPAC follows Elovich model with an R^2 value of 0.9223. However, in the Elovich isotherm model, some parameters have negative values, so this model cannot be used because the maximum capacity with a negative value in the Elovich isotherm parameters is not possible [35]. So, the second highest R^2 model was chosen after the Elovich isotherm, namely the Redlich-Peterson isotherm model with an R^2 value of 0.6083.

The Redlich-Peterson isotherm is a mixed isotherm of three parameters, including Henry, Freundlich, and Langmuir, which can represent adsorption equilibrium over a wide concentration range [21]. Parameter A in Redlich-Peterson model indicates the Redlich-Peterson constant (L/g) and β is a heterogeneity index between 1 and 0. The Redlich-Peterson isotherm model has a linear dependence on concentration and an exponential function that simplifies to a linear isotherm. If the value of $\beta = 0$, it will be simplified to the Henry isotherm, $\beta = 1$ will become the Langmuir isotherm equation, and $\beta > 1$ will become the Freundlich isotherm equation [21], [36].

Based on the parameter data contained in Table 2, it is found that the value of the β parameter in the Redlich-Peterson isotherm is 1.8761 (>1), so the Cd^{2+} adsorption isotherm model with CPAC is simplified to the Freundlich isotherm. Freundlich model applies to adsorption processes that occur on heterogeneous surfaces. This model describes surface heterogeneity, active sites' exponential distribution, and their energies [21]. In this research, the K_F dan 1/n value obtained was 30.3599 $mg.g^{-1}$ and -1.414, respectively. Because the value of 1/n is less than 1, this indicates that the chemical adsorption process is running [37]. Research by Hasrianti (2015) [12] carried out Cd^{2+} adsorption using cassava peel biosorbent following Freundlich isotherm model. This result also aligns with research [14], which stated that the Cd^{2+} adsorption isotherm with rice husk adsorbent followed Freundlich isotherm model with an R^2 value of 0.995.

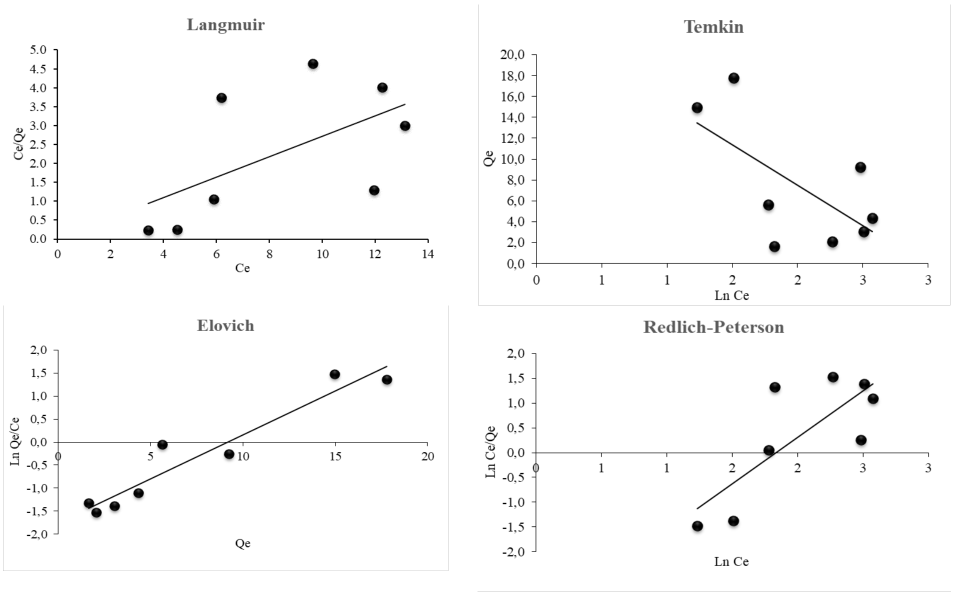

Figure 4. Plotting of Cd^{2+} ion adsorption isotherm data using CPAC.

3.5. Determination of Optimum pH

The adsorption process is carried out at different pH for optimizing pH condition. The optimum pH value was obtained through the highest amount of Cd^{2+} metal ions adsorbed using CPAC. In this research, the adsorption process was carried out at pH conditions of 5, 7, and 9.

TABLE III. Effect of pH on adsorption of Cd^{2+} ions using CPAC.

pH	Adsorption of Cd^{2+} Ions		
	C_0(mg/L)	C_e (mg/L)	q_e (mg/g)
5	9.97	8.17	4.49
7	9.75	8.29	3.64
9	9.90	8.53	3.43

Table 3 shows that increasing the pH value causes a decrease in the adsorption of Cd^{2+} ions. The optimum pH value for adsorption of Cd^{2+} ions using CPAC was obtained at pH 5 conditions with the amount of Cd^{2+} ions adsorbed at 1.80 mg/L. According to the literature on Cd^{2+} speciation diagrams, it shows that the dominant Cd^{2+} species at pH > 8.0 is $Cd(OH)_2$, while at pH < 8.0, it is Cd^{2+} and $Cd(OH)^+$. The carboxyl and hydroxyl groups on the surface of CPAC play a role in the adsorption of Cd^{2+} ions. At pH < 8.0, the positively charged Cd^{2+} and $Cd(OH)^+$ species present in the solution can exchange with H^+ from the –COOH or hydroxyl carbon group [38]. Based on the results obtained, CPAC was more effective in adsorbing Cd^{2+} metal ions compared to research [39] using rice husk biosorbent, which resulted in the adsorption of Cd^{2+} ions in multicomponent waste at pH 5 conditions of 0.4868 mg/g. In addition, research [40] conducted adsorption of Cd^{2+} ions under optimum pH conditions using HNO_3-activated sugarcane bagasse cellulose adsorbent, obtaining a maximum adsorption capacity of 2.215 mg/g.

3.6. Determination of Optimum Temperature

The effect of temperature shows that when the temperature is increased, there is a decrease in adsorption capacity. Based on Table 4, the optimum temperature was obtained when adsorption was carried out at 25 °C, and there was a decrease in the adsorption of Cd^{2+} metal ions when the temperature increased at 35 °C and 45 °C. This is due to the weakening of the bond energy between the adsorbate and the adsorbent [41, 42].

TABLE IV. Effect of temperature on adsorption of Cd^{2+} ions using CPAC

pH	**Temperature (°C)**	**Adsorption of Cd^{2+} Ions**		
		C_0 (mg/L)	**C_e (mg/L)**	**q_e (mg/g)**
5	25	8.29	7.05	3.09
5	35	8.29	7.08	3.01
5	45	8.29	7.83	1.14

Adsorption can occur through an ion exchange mechanism because the ions on the active groups on the surface of the adsorbent can exchange places with the adsorbate ions. The ion exchange mechanism combines chemical and physical agents because it will bind the adsorbate ions through chemical bonds. Still, these bonds are quickly rereleased so ion exchange can occur [43]. Thermodynamic parameters such as Gibbs energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) during adsorption can be evaluated via Equation 9-11 [44, 45].

$$K_c = \frac{C_{Ae}}{C_e} \quad (9)$$

$$\Delta G^\circ = -RTLnK_c \quad (10)$$

$$\text{Log } K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (11)$$

The values of ΔH° and ΔS° are determined through the slope and intercept of the plot of log K_c versus 1/T (Figure 4). The ΔG° value is calculated using Equation (10). The values of changes in Gibbs free energy (kJ/mol), enthalpy (kJ/mol), and entropy (J/mol.K) of Cd^{2+} ion adsorption using CPAC are presented in Table 5.

TABLE V. Thermodynamic parameters of Cd^{2+} ions adsorption using CPAC.

Cd^{2+} Concentration (mg/L)	**ΔH° (kJ/mol)**	**ΔS° (J/mol.K)**	**ΔG° (kJ/mol)**		
			25 °C	**35 °C**	**45 °C**
8	-42.8647	-156.8783	-3806.56	-4066.32	-4343.65

Based on Table 5, the enthalpy change (ΔH°) and entropy change (ΔS°) values obtained in this study were -42.8647 kJ/mol and -156.8783 J/mol.K. Negative ΔH° values indicate an exothermic adsorption process [45]. According to [46], an adsorption process with a bond strength < 84 kJ/mol indicates a physical adsorption process. Negative entropy change (ΔS°) values indicate a decrease in the disorder at the solid/liquid interface during adsorption [47]. Negative ΔG° values of adsorption validate a spontaneous process, while positive ΔG° values indicate a non-spontaneous process [45]. The resulting negative ΔG° value indicates a spontaneous adsorption process of Cd^{2+} ions on the surface of the CPAC adsorbent. This aligns with research from Ho et al. (2006) [48] on Cd^{2+} adsorption because ΔG° was negative [45].

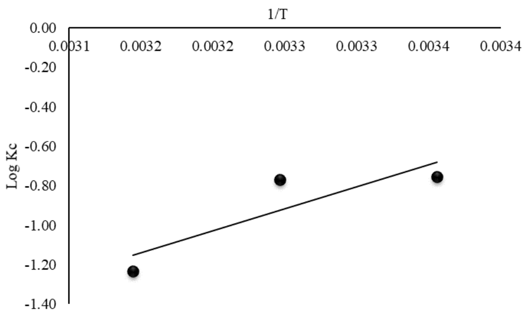

Figure 5. Thermodynamic study of Cd^{2+} ions adsorption using CPAC.

Table 5 shows the change in Gibbs free energy (ΔG°), which obtained a negative value under a temperature of 45 °C in the adsorption of metal ions Cd^{2+} using CPAC, which shows the feasibility and spontaneity of the adsorption process under a temperature of 45 °C. The increase in the negative value of ΔG° with increasing adsorption temperature indicates that lower temperatures make the adsorption process easier [47]. These results align with research from Kumar et al. (2015) [14], which shows that the feasibility and spontaneity of adsorption of Cd^{2+} metal ions using rice husk adsorbent is below a temperature of 45 °C.

4. CONCLUSIONS

Based on the research that has been carried out, model the adsorption kinetics of Cd^{2+} ions using cassava peel activated carbon (CPAC) started by H_3PO_4 follows Pseudo Second Order (PSO) kinetic model with an R^2 value of 0.9775 and the Redlich-Peterson isotherm with an R^2 value of 0.6083 and has a β parameter value of 1.8761 (>1) so that Cd^{2+} adsorption isotherm model with CPAC is simplified to the Freundlich isotherm. The optimum pH and temperature conditions for the adsorption of Cd^{2+} ions using CPAC activated by H_3PO_4 were obtained at pH 5 and a temperature of 25 °C. Thermodynamic parameters such as Gibbs energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) have been evaluated and indicate physical, spontaneous, and exothermic adsorption processes. The adsorption capacity of Cd^{2+} ions using CPAC activated by H_3PO_4 was 5.2219 mg/g.

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References

[1] M. R. Matsumoto, “Modeling Cadmium Adsorption by Activated Carbon Using The Langmuir and Freundlich Isotherm Expressions,” *Sep. Sci. Technol.*, vol. 28, no. 13–14, pp. 2179–2195, Oct. 1993, doi: 10.1080/01496399308016742.

[2] K. Cai, Y. Yu, M. Zhang, and K. Kim, “Concentration, Source, and Total Health Risks of Cadmium in Multiple Media in Densely Populated Areas, China,” 2019, doi: 10.3390/ijerph16132269.

[3] L. Luo, Y. Ma, S. Zhang, D. Wei, and Y. G. Zhu, “An Inventory of Trace Element Inputs to Agricultural Soils in China,” *J. Environ. Manage.*, vol. 90, no. 8, pp. 2524–2530, Jun. 2009, doi: 10.1016/J.JENVMAN.2009.01.011.

[4] S. Kawano, H. Nakagawa, Y. O.-E. Research, and U. 1986, “A Mortality Study of Patients With Itai-Itai Disease,” *Elsevier*, 1986, Accessed: Aug. 09, 2022. [Online]. Available: https://www.sciencedirect.com/science/article/abs/pii/S0013935186800858

[5] F. Fu and Q. Wang, “Removal of Heavy Metal Ions From Wastewaters: A Review,” *J. Environ. Manage.*, vol. 92, no. 3, pp. 407–418, 2011, doi: 10.1016/j.jenvman.2010.11.011.

[6] M. A. Hossain, H. H. Ngo, W. S. Guo, and T. Setiadi, “Adsorption and Desorption Of Copper (II) Ions Onto Garden Grass,” *Bioresour. Technol.*, vol. 121, pp. 386–395, 2012.

[7] A. Suprabawati, N. W. Holiyah, and J. Jasmansyah, “Activated Carbon from Cassava Peel as

Adsorbent of Lead Metal (Pb2+) in the Water," *J. Kartika Kim.*, vol. 1, no. 1, pp. 21–28, 2018.

[8] Darmawati, S. Maulidar, and K. Nisa, "Pengaruh Penambahan Karbon Aktif Dari Kulit Singkong Terhadap Penurunan Kadar Mangan (Mn) Dalam Air Dengan Beberapa Variasi Konsentrasi," *Biot. J. Ilm. Biol. Teknol. dan Kependidikan*, vol. 7, no. 2, p. 96, 2019, doi: 10.22373/biotik.v7i2.5656.

[9] D. Schwantes *et al.*, "Chemical Modifications Of Cassava Peel As Adsorbent Material For Metals Ions From Wastewater," *J. Chem.*, vol. 2016, 2016, doi: 10.1155/2016/3694174.

[10] D. Ocktafiani, I. Aziza, P. Utami, D. Cahya, and H. Budiastuti, "Cassava Peel Waste Becomes Activated Carbon – A Literature Review," pp. 92–97, 2020.

[11] J. Oscik, *Adsorption*, Copper. New York: John Wiley and Sons, 1991.

[12] H. Hasrianti, "Adsorpsi Ion Cd2+ pada Limbah Cair Menggunakan Kulit singkong," *Dinamika*, vol. 4, no. 2, 2015.

[13] M. H. Jnr and A. I. Spiff, "Effects of Temperature On The Sorption of Pb2+ and Cd2+ From Aqueous Solution by Caladium Bicolor (Wild Cocoyam) Biomass," *Electron. J. Biotechnol.*, vol. 8, no. 2, pp. 43–50, 2005.

[14] P. S. Kumar, K. Ramakrishnan, S. D. Kirupha, and S. Sivanesan, "Thermodynamic and Kinetic Studies Of Cadmium Adsorption From Aqueous Solution Onto Rice Husk," *Brazilian J. Chem. Eng.*, vol. 27, no. 2, pp. 347–355, 2010, doi: 10.1590/s0104-66322010000200013.

[15] C. A. Maghfirana, "Kemampuan Adsorpsi Karbon Aktif dari Limbah Kulit Singkong Terhadap Logam Timbal (Pb) Menggunakan Sistem Kontinyu." UIN Sunan Ampel Surabaya, Surabaya, 2019.

[16] F. P. Perdani, C. A. Riyanto, and Y. Martono, "Karakterisasi Karbon Aktif Kulit Singkong (Manihot esculenta Crantz) Berdasarkan Variasi Konsentrasi H3PO4 dan Lama Waktu Aktivasi," vol. 04, no. 02, pp. 72–81, 2021, doi: 10.20885/ijca.vol4.iss2.art4.

[17] I. O. Oboh, E. O. Aluyor, and T. O. K. Audu, "Second-Order Kinetic Model For The Adsorption of Divalent Metal Ions on Sida Acuta Leaves," *Int. J. Phys. Sci.*, vol. 8, no. 34, pp. 1722–1728, 2013.

[18] R. B. Holle, A. D. Wuntu, and M. S. Sangi, "Kinetika Adsorpsi Gas Benzena Pada Karbon Aktif Tempurung Kelapa," *J. MIPA*, vol. 2, no. 2, pp. 100–104, 2013.

[19] M. A. Zulfikar, T. Widiansyah, H. Setiyanto, and K. K. K. Analitik, "Studi Kinetika Adsorpsi Asam Humus dari Air Gambut Menggunakan Selulosa Jerami Padi," *Pros. SNSTL I*, 2014.

[20] L. Largitte and R. Pasquier, "A Review Of The Kinetics Adsorption Models and Their Application to The Adsorption Of Lead by An Activated Carbon," *Chem. Eng. Res. Des.*, vol. 109, pp. 495–504, 2016.

[21] N. Ayawei, A. N. Ebelegi, and D. Wankasi, "Modelling and Interpretation of Adsorption Isotherms," *Hindawi J. Chem.*, 2017.

[22] B. Felita, C. A. Riyanto, and Y. Martono, "Activated Carbon From Plantain Stems as NO2^- and Mn2+ Adsorbent on Well Water," *EduChemia (Jurnal Kim. dan Pendidikan)*, vol. 6, no. 1, p. 38, 2021, doi: 10.30870/educhemia.v6i1.8887.

[23] C. A. Riyanto, E. Prabalaras, and Y. Martono, "Karakterisasi Nanopartikel Karbon Aktif Dari Daun Eceng Gondok (Eichhornia Crassipes) Berdasarkan Variasi Suhu dan Waktu Aktivasi," *J. Kim. dan Kemasan*, 2019.

[24] K. Vijayaraghavan, T. V. N. Padmesh, K. Palanivelu, and M. Velan, "Biosorption of Nickel(II) Ions Onto Sargassum wightii: Application of Two-Parameter and Three-Parameter Isotherm Models," *J. Hazard. Mater.*, vol. 133, no. 1–3, pp. 304–308, 2006, doi: 10.1016/j.jhazmat.2005.10.016.

[25] N. Ariska, R. Supriyanto, and A. A. Kiswandono, "Studi Analisis Ion Logam Cd (II) Dengan Asam Tanat Menggunakan Spektrofotometer Ultraungu-Tampak," vol. 3, no. 02, pp. 79–90, 2018.

[26] A. Heri and S. Sutanto, "Validasi Metode Uji Kadmium Dalam Air Sumur Secara Spektrofotometri Serapan Atom," *EKOLOGIA*, vol. 16, no. 1, pp. 31–37, Apr. 2016, doi: 10.33751/EKOL.V16I1.60.

[27] A. B. D. Nandiyanto, R. Oktiani, and R. Ragadhita, "Indonesian Journal of Science & Technology How to Read and Interpret FTIR Spectroscope of Organic Material," *Indones. J. Sci. Technol.*, vol. 4, no. 1, pp. 97–118, 2019.

[28] Z. A. Nasution and S. M. Rambe, "Karakterisasi dan Identifikasi Gugus Fungsi Dari Karbon Cangkang

Kelapa Sawit Dengan Metode Methano-Pyrolysis," *J. Din. Penelit. Ind.*, vol. 24, no. 2, pp. 108–113, 2013.

[29] E. A. Khan and T. A. Khan, "Adsorption Of Methyl Red On Activated Carbon Derived From Custard Apple (Annona Squamosa) Fruit Shell: Equilibrium Isotherm and Kinetic Studies," *J. Mol. Liq.*, vol. 249, pp. 1195–1211, 2018, doi: 10.1016/j.molliq.2017.11.125.

[30] L. Efiyanti, S. A. Wati, and M. Maslahat, "Pembuatan dan Analisis Karbon Aktif Dari Cangkang Buah Karet Dengan Proses Kimia dan Fisika," *J. Ilmu Kehutan.*, vol. 14, no. 1, pp. 94–108, 2020.

[31] M. Thommes *et al.*, "Physisorption Of Gases, With Special Reference to The Evaluation Of Surface Area and Pore Size Distribution (IUPAC Technical Report)," *Pure Appl. Chem.*, vol. 87, no. 9–10, pp. 1051–1069, 2015, doi: 10.1515/pac-2014-1117.

[32] Y. Sudaryanto, S. B. Hartono, W. Irawaty, H. Hindarso, and S. Ismadji, "High Surface Area Activated Carbon Prepared From Cassava Peel By Chemical Activation," *Bioresour. Technol.*, vol. 97, no. 5, pp. 734–739, Mar. 2006, doi: 10.1016/J.BIORTECH.2005.04.029.

[33] G. W. Kajjumba, S. Emik, A. Öngen, H. Kurtulus Özcan, and S. Aydın, "Modelling of Adsorption Kinetic Processes—Errors, Theory and Application," in *Advanced Sorption Process Applications*, IntechOpen, 2018. doi: 10.5772/intechopen.80495.

[34] N. Nurhasni, F. Firdiyono, and Q. Sya'ban, "Penyerapan Ion Aluminium dan Besi dalam Larutan Sodium Silikat Menggunakan Karbon aktif," *J. Kim. Val.*, vol. 2, no. 4, 2012, doi: 10.15408/jkv.v2i4.269.

[35] Y. S. Halomoan, C. A. Riyanto, and N. R. Aminu, "Adsorpsi Ion logam Ca2+ dan Mg2+Dalam Air Sumur Menggunakan Karbon Sekam Padi," 2022.

[36] C. A. Riyanto, B. M. Raharjianti, and N. R. Aminu, "Studi Kinetika dan Isoterm Adsorpsi Ion Fe (III) dan Mn (II) pada Karbon Aktif Batang Eceng Gondok," *J. Ris. Teknol. Ind.*, vol. 15, no. 1, p. 44, 2021, doi: 10.26578/jrti.v15i1.6633.

[37] S. Yenti, A. Fadli, R. Fifiyana, and M. Sari, "Model Kesetimbangan Freundlich Pada Adsorpsi Ion Kadmium Menggunakan Hidroksiapatit," *Pros. Semin. Nas. Fis. Univ. Riauke-3*, no. September, pp. 106–113, 2018.

[38] K. A. Krishnan and T. S. Anirudhan, "Removal of Cadmium(II) From Aqueous Solutions by Steam-Activated Sulphurised Carbon Prepared From Sugar-Cane Bagasse Pith: Kinetics and Equilibrium Studies," *Water SA*, vol. 29, no. 2, pp. 147–156, 2003, doi: 10.4314/wsa.v29i2.4849.

[39] N. Nurhasni, H. Hendrawati, and N. Saniyyah, "Penyerapan Ion Logam Cd dan Cr Dalam Air Limbah Menggunakan Sekam Padi," *J. Kim. Val.*, vol. 1, no. 6, 2010.

[40] R. Kusumawardani, T. Anita, and L. Destiarti, "Adsorpsi Kadmium Menggunakan Adsorben Selulosa Ampas Tebu," *J. progaram Stud. Kim. Fak. MIPA Univ. tanjungpura*, vol. 7, no. 3, pp. 75–83, 2018.

[41] L. Zhao *et al.*, "Synthesis, Characterization and Adsorptive Performance of MgFe2O4 Nanospheres For SO2 Removal," *J. Hazard. Mater.*, vol. 184, no. 1–3, pp. 704–709, 2010.

[42] F. A. Nurdila, N. S. Asri, and D. E. Suharyadi, "Adsorpsi Logam Tembaga (Cu), Besi (Fe) dan Nikel (Ni) dalam Limbah Cair Buatan Menggunakan Nanopartikel Cobalt Ferrite (CoFe2O4)," *J. Fis. Indones.*, vol. 19, no. 55, pp. 23–27, 2015.

[43] P. W. Atkins, "Kimia Fisika Edisi ke IV," *Erlangga, Jakarta*, 1990.

[44] P. W. Atkins and J. de Paula, *Atkins' Physical Chemistry*. Oxford university press, 2014.

[45] A. N. Ebelegi, N. Ayawei, and D. Wankasi, "Interpretation of Adsorption Thermodynamics and Kinetics," *Open J. Phys. Chem.*, vol. 10, no. 03, pp. 166–182, 2020, doi: 10.4236/ojpc.2020.103010.

[46] Y. S. Al-Degs, M. I. El-Barghouthi, A. H. El-Sheikh, and G. M. Walker, "Effect of Solution pH, Ionic Strength, and Temperature on Adsorption Behavior of Reactive Dyes on Activated Carbon," *Dye. Pigment.*, vol. 77, no. 1, pp. 16–23, 2008, doi: 10.1016/j.dyepig.2007.03.001.

[47] P. Saha and S. Chowdhury, *Insight Into Adsorption Thermodynamics*. 2011. doi: 10.5772/13474.

[48] Y. S. Ho and A. E. Ofomaja, "Biosorption Thermodynamics of Cadmium On Coconut Copra Meal As Biosorbent," *Biochem. Eng. J.*, vol. 30, no. 2, pp. 117–123, 2006, doi: 10.1016/j.bej.2006.02.012.