Jurnal Serambi Engineering JSE Volume IX, No.3, Juli 2024 Hal 10042 - 10047 p-ISSN : 2528-3561 e-ISSN : 2541-1934

Kinetic Adsorption Study of Cd(II) Metal Ions Using Glutaraldehyde-Crosslinked Thiosemicarbazide-Modified Poly (vinyl alcohol)

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Received: July 3, 2024 Approved: July 8, 2024

Abstract

Cd(II) metal ions are commonly found in water bodies and are non-essential and carcinogenic, leading to lung cancer. Thus, it is crucial to remove Cd(II) metal ions from water. Adsorption is one effective separation method due to its relative simplicity and cost-effectiveness. In this work, the adsorption kinetics study of Cd(II) metal ions using PVA.cl.GA-TSC were examined. Polyvinyl alcohol (PVA) was cross-linked with glutaraldehyde and subsequently modified with thiosemicarbazide (TSC). The resulting PVA.cl.GA-TSC was characterized using FTIR. The adsorption process was carried out in a batch system at room temperature. The study revealed that the adsorption kinetics of Cd(II) metal ions with PVA.cl.GA-TSC followed a pseudo-second-order kinetic model, with a rate constant of 0.4×10^{-3} $g.mg^{-1}.min^{-1}$. In the kinetics data, an intra-particle diffusion model was also performed to understand the adsorption reaction mechanism. The intra-particle diffusion model indicated that the rate-determining step was governed by the intra-particle diffusion stage, with a rate constant of 0.387 $mg.g^{-1}min^{-1/2}$.

Keywords: *Adsorption, Cd(II), polyvinyl alcohol (PVA), thiosemicarbazide (TSC)*

Abstrak

Ion logam Cd(II) banyak ditemukan di perairan. Ion logam tersebut merupakan ion logam non-esensial dan bersifat karsinogenik. Penting untuk memisahkan ion logam Cd(II) dari perairan. Salah satu metode pemisahan yang dapat dilakukan adalah adsorpsi karena pengoperasiannya yang relatif mudah dan murah. Pada penelitian ini, dilakukan studi kinetika adsorpsi ion logam Cd(II) menggunakan PVA.cl.GA-TSC. Polivinil alkohol (PVA) diikat-silang dengan glutaraldehid kemudian dilanjutkan dengan modifikasi menggunakan tiosemikarbazida (TSC). PVA.cl.GA-TSC yang telah terbentuk dikarakterisasi menggunakan FTIR. Metode adsorpsi dilakukan menggunakan sistem batch pada suhu ruang. Studi kinetika adsorpsi ion logam Cd(II) menggunakan PVA.cl.GA-TSC mengikuti model kinetika pseudo orde-2 dengan tetapan laju sebesar $0{,}4 \times 10^{-3}$ $g.mg^{-1}.min^{-1}$. Pada data kinetika dilakukan juga pemodelan difusi intra-partikel untuk mengetahui mekanisme reaksi adsorpsi yang terjadi. Berdasarkan pemodelan difusi intra-partikel pada data kinetika adsorpsi, diketahui bahwa tahap penentu laju ditentukan oleh tahap difusi intra-partikel dengan nilai tetapan laju sebesar 0,387 $mg.g^{-1}menit^{-1/2}$.

Kata Kunci: *Adsorpsi, Cd(II), polivinil alkohol (PVA), tiosemikarbazida (TSC).*

1. Introduction

Heavy metal ions are often found in water bodies both naturally and because of human activities [1]. Industrial waste that is not properly treated can increase the concentration of metal ions in aquatic environments, posing a danger to living organisms. One of the heavy metal ions is Cd(II), which can be toxic to living organisms and the environment even at low concentrations [2], [3]. Cd exposure can increase the risk of lung cancer [4] and induce kidney damage [5].

Various methods can be utilized to separate heavy metal ions from the environment, including adsorption, membrane-based filtration, precipitation, coagulation-flocculation, and electrochemical methods [6]. Among these methods, adsorption is extensively studied due to its simplicity, cost-effectiveness, and the wide range of adsorbents that can be developed for metal ion separation [7]. One type of adsorbent that is extensively researched is polymer-based adsorbents because they are relatively inexpensive and readily available, such as polyvinyl alcohol (PVA) [8]. However, PVA is not very active as an adsorbent and is soluble in water. Therefore, in this work, PVA was cross-linked with glutaraldehyde to reduce its solubility in water [8], [9], [10].

Furthermore, the cross-linked PVA with glutaraldehyde, referred to as PVA.cl.GA was further modified with thiosemicarbazide (TSC). TSC is a compound that contains a thiourea group consisting of nitrogen and sulphur atoms, which can easily bind to heavy metal ions. The modified adsorbent has an increased number of active sites, thereby enhancing its adsorption capacity for heavy metal ions [9].

2. Material and Methods

Material

The materials used in this work include PVA powder from PT. Asahimas Chemical (ASC), thiosemicarbazide (TSC) (Merck), glutaraldehyde from (Merck), $CdCl_2.H_2O$ (Merck), HCl, phosphate buffer with a pH of 4.1, ethanol, and distilled water.

Preparing PVA.cl.GA

The preparation of the PVA.cl.GA-TSC adsorbent followed the research conducted by Zhang *et al*. in 2021 [9], with slight modifications. Initially, a 3.5% w/v PVA solution was created by dissolving 0.7250 g of PVA in 20 mL of distilled water at 90°C until fully dissolved. After cooling, the surface foam was removed. The solution was then added to 25% v/v glutaraldehyde at pH 1 and stirred with a magnetic stirrer at room temperature for 2 hours. A white solid formed, which was washed with ethanol and distilled water until the filtrate became neutral. The resulting solid was dried, yielding 0.7846 g of cross-linked PVA with GA, designated as PVA.cl.GA.

Preparing PVA.cl.GA-TSC

1.5752 g of TSC was dissolved in 90 mL of phosphate buffer at pH 4.1. Once fully dissolved, 0.5418 g of PVA.cl.GA was added to the mixture and stirred with a magnetic stirrer for 3 hours at a temperature of around 48-55°C. The final product was rinsed with distilled water until the filtrate became neutral. After drying, PVA.cl.GA-TSC, amounting to 0.7806 g.

Characterization and analysis

PVA, PVA.cl.GA, and PVA.cl.GA-TSC were characterized using an FTIR spectrometer (Shimadzu IR Prestige-21) in the wavenumber range of 4000-400 cm^{-1}. The concentration of metal ions before and after the adsorption process was measured using an Atomic Absorption Spectrometer (Agilent).

Batch adsorption experiments

The adsorption of metal ions was conducted using a batch system at room temperature on an SHA-C shaker at a speed of 130 rpm. A total of 0.05 g of PVA.cl.GA-TSC was added to 100 mL of 100 mg/L Cd(II) solution at pH 5.2 in a 250 mL Erlenmeyer flask. The contact time for adsorption was varied at 15, 30, 45, 60, 90, 120, 150, and 240 minutes. The adsorption capacity of each sample, q_e (mg/g), was calculated using the equation 1.

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad \text{(equation 1)}$$

where C_0 and C_e represent the initial and equilibrium concentrations of the adsorbate in the solution (mg/L), respectively, V is the volume of the solution (L), and m is the mass of the adsorbent (g).

3. Results and Discussion

FTIR analysis

The FTIR spectra are displayed in Figure 1, illustrating the changes in functional groups on PVA, PVA.cl.GA, and PVA.cl.GA-TSC. In PVA.cl.GA, a decrease in the intensity of the -OH group is observed, along with the formation of an absorption band at a wavenumber of 1724 cm^{-1}, corresponding to the aldehyde group from glutaraldehyde. Additionally, the intensity of the C-O bond increased. The spectrum of PVA.cl.GA-TSC in the wavenumber range of 3750-3000 cm^{-1} became broader due to the presence of -NH_2 groups, which produce N-H vibrations in this range. In the spectrum of PVA.cl.GA-TSC, two new absorption bands were also formed, corresponding to the C=N absorption band (1527 cm^{-1}) and the –(C=S)-N absorption band (821 cm^{-1}) [9], [10]. The FTIR characterization results indicate that the PVA.cl.GA and PVA.cl.GA-TSC adsorbents were successfully obtained.

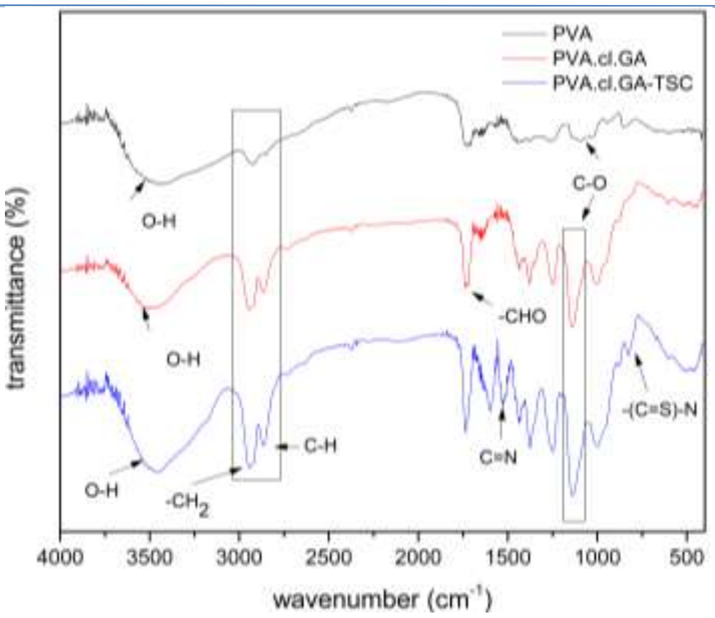


Figure 1. FTIR spectra of PVA, PVA.cl.GA, and PVA.cl.GA-TSC.

Effect of Contact Time

In this study, the initial pH of the Cd(II) solution was adjusted to pH 5.2. At this pH, the active sites capable of binding metal ions (such as hydroxyl, carboxyl, and amino groups) are negatively charged, facilitating electrostatic interactions between the negatively charged adsorbent and the positively charged metal ions [9]. At highly acidic pH levels, metal ions compete with hydrogen ions in water to bind with the active sites of the adsorbent. This competition can reduce the adsorption capacity of the adsorbent for metal ions [11]. Conversely, at highly base pH, the adsorbent becomes deprotonated and negatively charged. Moreover, at highly base pH, metal ions begin to precipitate as hydroxides [12]. Therefore, the use of extreme pH conditions is avoided.

Figure 1 illustrates the impact of contact time on the adsorption of Cd(II) metal ions. According to the figure, prolonged contact between the adsorbent and the analyte solution results in increased adsorption capacity. This phenomenon occurs because more analytes can bind to the active sites of the adsorbent over time. After 120 minutes of contact time, the adsorption capacity reaches a plateau, suggesting that the adsorbent surface becomes saturated [13]. Therefore, the optimal contact time for the adsorption of Cd(II) metal ions using PVA.cl.GA-TSC is 120 minutes.

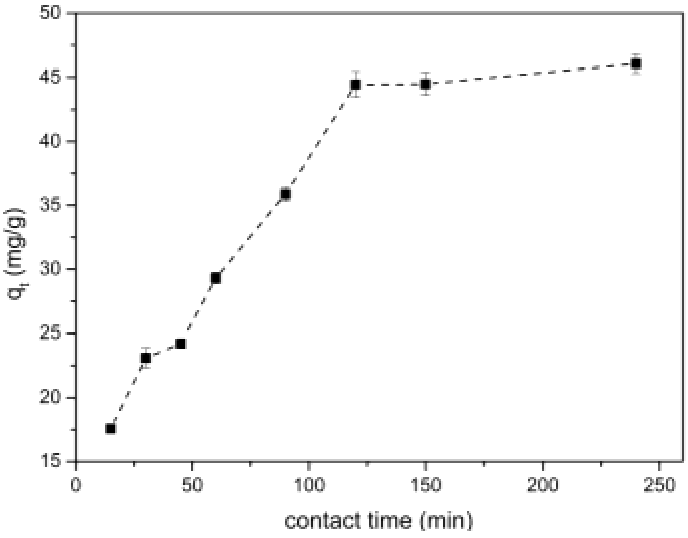


Figure 2. The influence of contact time on Cd(II) metal ion adsorption using PVA.cl.GA-TSC.

Adsorption kinetics

In this study, kinetic adsorption studies were conducted to investigate the adsorption mechanisms. The adsorption kinetics of Cd(II) metal ions using PVA.cl.GA-TSC were analyzed using pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models. The linear form of the pseudo-first-order kinetic model is expressed by Equation 3 [14].

$$\log(q_e - q_t) = \frac{k_1}{2{,}303} t + \log q_e \qquad (3)$$

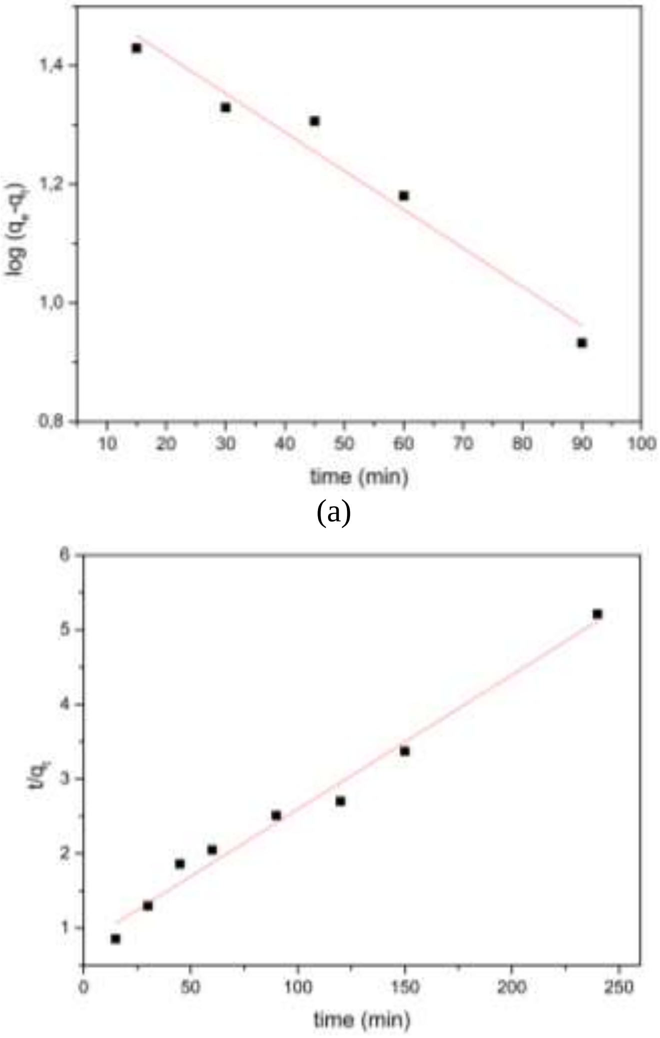
with q_e and q_t represent the amount of adsorbate adsorbed by the adsorbent at equilibrium (mg/g) and at contact time t (minutes), respectively, k_1 (min^{-1}) denotes the PFO kinetic rate constant, which is obtained from the slope of the plot of $\log(q_e - q_t)$ versus t. To accurately estimate kinetic parameters in the PFO equation, trial-and-error approach can be use to determine the optimal q_e value [15] or employ nonlinear optimization techniques [16].

Another commonly used adsorption kinetic model is the PSO model, first reported by Ho (1995). PSO can be described in linear form type 1 as shown in Equation 4 [15], [16].

$$\frac{t}{q_t} = \left(\frac{1}{q_e}\right) t + \frac{1}{k_2 q_e^2} \qquad (4)$$

with k_2 representing the pseudo-second-order kinetic rate constant (g mg^{-1} min^{-1}).

The plot curves from both models are shown in Figure 3, and the kinetic adsorption parameters can be seen in **Table 1**. The PSO model exhibits better fitting of the adsorption kinetics, indicated by a higher R² value. Therefore, the adsorption kinetics of Cd(II) from water by PVA.cl.GA-TSC follows the PSO model.



(a)

(b)

Figure 3. Adsorption kinetics model (a) Pseudo-first-order (PFO) and (b) Pseudo-second-order (PSO) for Cd(II) metal ion adsorption using PVA.cl.GA-TSC.

Table 1. Parameters of the adsorption kinetics model for Cd(II) metal ion adsorption using PVA.cl.GA-TSC

Adsorption kinetics model	k	$q_{e,cal}$ mg/g	R^2	$q_{e,xp}$ (mg/g)
PFO	$14{,}99 \times 10^{-3}$ min^{-1}	35,33	0,966	46,07
PSO	$0{,}41 \times 10^{-3}$ $g.mg^{-1}.min^{-1}$	55,52	0,982	

The PSO model does not provide insights into the detailed reaction mechanism. Therefore, kinetic study data is employed to investigate the intra-particle diffusion model. This model describes the adsorption process in three stages. Firstly, in the film diffusion stage, the adsorbate diffuses from the bulk phase or solution body to the outer surface of the adsorbent. Secondly, intra-particle diffusion occurs as the adsorbate moves into the pores of the adsorbent and towards its active sites. Finally, in the third stage, adsorption happens within the adsorbent itself, a process that typically occurs rapidly [17]. The Weber-Morris intra-particle diffusion model, 1963, is modelled with equation 5 [16], [18].

$$q_t = K_d\sqrt{t} + C \qquad (5)$$

with q_t (mg g^{-1}) representing the amount of adsorbate adsorbed at time t (minute) and K_d (mg (g $min^{1/2})^{-1}$) being the intra-particle diffusion rate constant. A higher value of C indicates a greater influence on the boundary layer [19].

Based on the intra-particle diffusion model, the results for Cd(II) metal ion adsorption using PVA.cl.GA-TSC can be observed in **Figure 4**. The model suggests that the adsorption process involves two stages, as indicated by the presence of two linear curve segments. The first stage has a rate constant, $\boldsymbol{K_{d,1}}$, shown with a slope of 3.18 $mg.g^{-1}.min^{-1/2}$. Meanwhile, the second stage has a rate constant, $\boldsymbol{K_{d,2}}$, of 0.387 $mg.g^{-1}.min^{-1/2}$. The rate-determining stage of the adsorption process is determined by the stage with the smaller rate constant. Therefore, the adsorption of Cd(II) metal ions using PVA.cl.GA-TSC is controlled by the intra-particle diffusion stage.

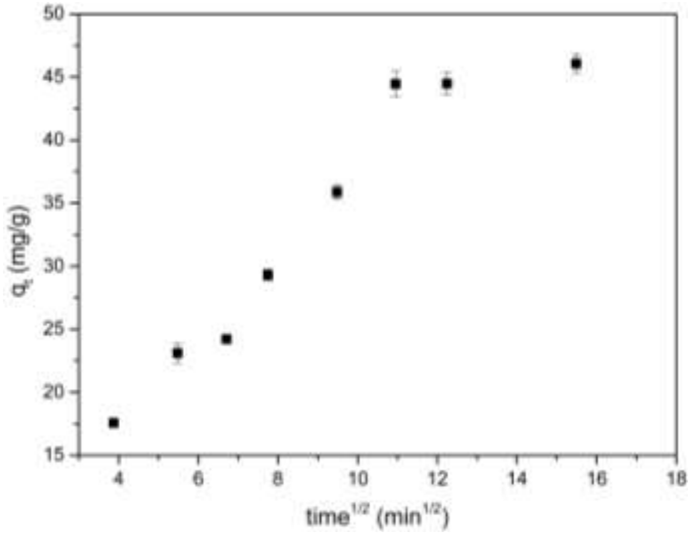


Figure 4. Intra-particle diffusion model for Cd(II) metal ion adsorption using PVA.cl.GA-TSC.

4. Conclusion

In this study, FTIR characterization confirmed the successful cross-linking of PVA using glutaraldehyde and modification with TSC. The adsorption of Cd(II) metal ions using PVA.cl.GA-TSC exhibited an optimal contact time of 120 minutes. Kinetic adsorption studies revealed that the process followed the pseudo-second-order (PSO) kinetic model, with a rate constant of 0.41×10^{-3} $g.mg^{-1}.min^{-1}$ and an adsorption capacity of 46.07 mg/g. The adsorption mechanism was primarily governed by the intra-particle diffusion stage, characterized by a rate constant of 0.387 $mg.g^{-1}.min^{-1/2}$.

5. Acknowledgment

Research facility support for this work was provided by Bandung of Technology, Faculty of Mathematics and Natural Sciences, Department of Chemistry.

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