

Research Article

Development of Polymer Based Nanocomposites as a Marker of Cadmium in Complex Matrices

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Poly(propylene carbonate)/ β -cyclodextrin (PPC-BCD) nanocomposites were developed as effective extractor for a specific extraction and separation of cadmium(II) by use of inductively coupled plasma-optical emission spectrometry. The selectivity of nanocomposites with different wt% of BCD (PPC-BCD 0.5, PPC-BCD 1, PPC-BCD 3, PPC-BCD 5, or PPC-BCD 10) was investigated toward Cd(II). Based on selectivity and pH studies, Cd(II) was the most quantitatively adsorbed on PPC-BCD 5 phase at pH 6, indicating that PPC-BCD 5 was the most selective toward Cd(II) among other nanocomposites. On the basis of adsorption isotherm study, the superior adsorption capacity of PPC-BCD 5 phase for Cd(II) was found to be $149.25 \text{ mg}\cdot\text{g}^{-1}$, following the Langmuir adsorption isotherm model. The kinetic of adsorption for Cd(II) has been examined by pseudo-first- and second-order models. The kinetic exploration suggested a pseudo-second-order kinetic model for the adsorption of Cd(II) on the PPC-BCD 5. Additionally, results of thermodynamic investigation demonstrated favorable spontaneous process for the adsorption mechanism of PPC-BCD 5 toward Cd(II).

1. Introduction

Petroleum-derived plastics cause the worldwide environment and earth pollution during their production and disposal. Therefore, the development of biodegradable materials such as starch plastics, cellulose plastics, poly(lactic acid), and soy-based plastics has been receiving considerable research attention [1]. Specifically, poly(propylene carbonate) (PPC) which utilizes carbon dioxide has attracted attention due to its good compatibility, resistance, and innocuousness [2]. These specific characteristics are profitable in adhesives, solid electrolytes, barrier materials, plasticizers, and biomedical and packaging applications. But for vast use of PPC, the refining of its thermal, mechanical, and sensing properties is needed by combining with other polymers [3], adding inorganic fillers [4] or chemically modifying the end groups [5].

To improve the mechanical and gas barrier properties of PPC, it was combined with exfoliated graphite (EG) via a solution blending method, resulting in highly enhanced barrier properties [6]. PPC-silica hybrid films showed proficient aqueous ethanol sensing properties [7].

Meanwhile, β -cyclodextrin (BCD) is a cyclic oligosaccharide containing 7 glucopyranose units, which are linked together by α (1-4) connection creating a torus-shaped ring structure with a hydrophilic exterior and a hydrophobic cavity [8, 9]. BCD is basically nanosized material with outer diameter of 154 nm and cavity diameter of 60-65 nm [10, 11] and the most interesting ability of BCD is to make inclusion complexes with different organic molecules and metal substances into its hydrophobic cavity through host-guest interactions [8]. These fascinating properties make them auspicious for applications in drug carrier systems, nanoreactors,

bioactive supramolecular assemblies, molecular recognition, metal extractors, and so forth [8–12].

In general, it is very important to find appropriate methods that meet a quality control for determination of metal ions. However, direct detection of metal ions using analytical methods is insufficient due to their low concentrations and the high concentration of interfering matrix components in most real samples. Thus, an effective separation technique is generally necessary for accurate and effective extraction of metal ions. A wide range of treatment techniques are there for separation of metal ions, for example, precipitation [13], liquid-liquid extraction [14], ion exchange [15], cloud point extraction [16], and solid phase extraction (SPE) [17, 18]. Among numerous methods, adsorption technique is doubtless the cost-effective and proficient method and has extensive applications in different fields. Different types of adsorbents comprising inorganic oxides [19–21], zeolites [22], silica [23–25], various resins [26–30], biological adsorbents [31], activated carbon [32, 33], and carbon nanotubes [34] are utilized as adsorption materials.

Similarly, this investigation was devoted to studying and evaluating the effectiveness of newly synthesized PPC-BCD 5 as a specific solid phase extractor for Cd(II) by inductively coupled plasma-optical emission spectrometry. The selectivity of PPC (PPC-BCD 0.5, PPC-BCD 1, PPC-BCD 3, PPC-BCD 5, or PPC-BCD 10) toward Cd(II) was studied. In addition, the influence of pH on the selectivity and effectiveness of PPC-BCD 5 for adsorption of Cd(II) was investigated. Other parameters, like concentration and contact time effects, pursuing the supreme uptake of Cd(II) on the PPC-BCD 5 phase were explored under batch techniques. The thermodynamic behavior of Cd(II) adsorption on the PPC-BCD 5 phase was also investigated.

2. Experimental

2.1. Chemicals and Reagents. Poly(propylene carbonate) (PPC) was delivered by SK Innovation Co., Ltd. (Cheonan, Korea). β -cyclodextrin (BCD, purity >97%) was purchased from Sigma-Aldrich (Yongin, Korea). Dimethylformamide (DMF) was bought from Duksan Chemical Co., Ltd. (Ansan, Korea). All other chemicals were bought from Sigma-Aldrich (Milwaukee, WI, USA). In the experiment, double distilled deionized water was used.

2.2. Preparation of the New Solid Phase Extractor. In this study, five different PPC-BCD extractors were prepared via solution method. Firstly, 30 mL of PPC (2 g) solution was prepared by dissolving in DMF at 50°C. A dispersed solution of BCD was prepared in DMF using 20 min ultrasonication. To explore the influence of BCD on the extraction properties, formulations with several different BCD contents were prepared: 0.5, 1, 3, 5, and 10 wt% with respect to the PPC content. These samples depending on the PPC content were coded as PPC-BCD 0.5, PPC-BCD 1, PPC-BCD 3, PPC-BCD 5, and PPC-BCD 10, respectively. The PPC-BCD solutions were gently put onto a glass plate and kept for 2 hr drying at

120°C. The dried extractor films were approximately 35 μm thick by using a digital micrometer (Mitutoyo Co., Japan).

2.3. Adsorption Method Procedure. A standard solution of Cd(II) was made in 18.2 M Ω -cm distilled water and kept at 4°C. The standard solutions of 1 mg L⁻¹ of Cd(II) were made for selectivity and individually mixed with 20 mg PPC (PPC-BCD 0.5, PPC-BCD 1, PPC-BCD 3, PPC-BCD 5, or PPC-BCD 10). In addition, standard solutions of 1 mg L⁻¹ Cd(II) ion were made in the pH values ranging from 1.0 to 9.0 with appropriate buffer solutions, 0.2 mol L⁻¹ HCl/KCl for pH 1.0 and 2.0, 0.1 mol L⁻¹ CH₃COOH/CH₃COONa for pH 3.0–6.0, and 0.1 mol L⁻¹ Na₂HPO₄/HCl for pH 7.0–9.0. Then, all standard solutions were individually mixed with 20 mg PPC-BCD 5 in order to study the effect of pH on the selectivity of PPC-BCD 5 adsorption toward Cd(II). All mixtures were shaken for 1 h using a mechanical shaker at 150 rpm and room temperature. The PPC-BCD 5 phase was then removed by filtration, and the concentration of metal ion of interest in the aqueous solution was checked by inductively coupled plasma-optical emission spectrometer. For investigation of adsorption capacity of Cd(II) under batch conditions, standard solutions of 5, 10, 15, 20, 30, 50, 75, 100, 125, 150, 200, and 250 were made as above, set to the ideal pH value of 6.0, and separately mixed with 20 mg PPC-BCD 5. Additionally, the influence of contact time on Cd(II) uptake capacity was performed at similar batch conditions but at dissimilar equilibrium periods (2.5, 5, 10, 20, 30, 40, 50, and 60 min). For thermodynamic investigation, standard solutions of 5 mg L⁻¹ Cd(II) were made, set to the pH value of 6.0, and separately mixed with 20 mg PPC-BCD 5. Thermodynamic study of the adsorption of PPC-BCD 5 toward Cd(II) was also performed at similar batch circumstances at diverse temperatures (273, 298, 313, 338, and 353 K).

2.4. Instrumentation. The buffer's pH was measured by a pH meter (InoLab pH 7200, IL, USA). Inductively coupled plasma-optical emission spectrometer (ICP-OES) model Optima 4100 DV, USA, was utilized for the determination of Cd(II). The ICP-OES instrument was optimized every day before measurement and used with the following parameters: FR power, 1300 kW; frequency, 27.12 MHz; demountable quartz torch, Ar/Ar/Ar; plasma gas (Ar) flow, 15.0 L min⁻¹; auxiliary gas (Ar) flow, 0.2 L min⁻¹; nebulizer gas (Ar) flow, 0.8 L min⁻¹; nebulizer pressure, 2.4 bar; glass spray chamber according to Scott (Ryton), sample pump flow rate, 1.5 mL min⁻¹; integration time, 3 s; replicates, 3; and wavelength range of monochromator, 165–460 nm. Concentrations of Cd(II) were determined at wavelengths of 228.80 nm for Cd(II).

3. Results and Discussion

3.1. Selectivity Study. Selectivity of PPC (PPC-BCD 0.5, PPC-BCD 1, PPC-BCD 3, PPC-BCD 5, or PPC-BCD 10) toward Cd(II) was studied based on calculation of the distribution

TABLE 1: Selectivity study of different phases (20 mg) of adsorption toward Cd(II) ($N = 3$).

Phase	q_e (mg g^{-1})	K_d (mL g^{-1})
PPC	1.213	4.04×10^4
PPC-BCD 0.5	1.205	3.35×10^4
PPC-BCD 1	1.180	2.11×10^4
PPC-BCD 3	1.158	1.56×10^4
PPC-BCD 5	1.248	7.80×10^5
PPC-BCD 10	1.178	2.03×10^4

coefficient. The distribution coefficient (K_d) can be acquired from the following equation [35]:

$$K_d = \frac{(C_o - C_e)}{C_e} \times \frac{V}{m}, \quad (1)$$

where C_o and C_e are the initial and final concentrations before and after filtration with the adsorbent, respectively, V refers to the volume (mL), and m is the weight of adsorbent (g). Distribution coefficient values examined in current study are illustrated in Table 1. As revealed in Table 1, PPC-BCD 5 phase has the maximum distribution coefficient value ($7.80 \times 10^5 \text{ mL g}^{-1}$) toward Cd(II) among all other phases. The present study results specified that the selectivity of newly prepared PPC-BCD 5 phase toward Cd(II) was highest as compared to other phases investigated in this study.

3.2. Effect of pH. Extraction of metal ions from aqueous media by process of adsorption is usually pH dependent because pH has an effect on the surface charge of adsorbent, the extent of ionization, and species of adsorbate [34]. In the current study, the influence of pH on the adsorption of Cd(II) by newly synthesized PPC-BCD 5 phase was investigated. A concentration of 1 mg L^{-1} Cd(II) was chosen, and pH values were adjusted to a range from 1.0 to 9.0 with corresponding buffer solutions. All standard solutions were individually mixed with 20 mg PPC-BCD 5. The percentage extraction of Cd(II) was calculated based on a difference between the initial (C_o) and final (C_e) concentrations before and after filtration with PPC-BCD 5, respectively, as follows:

$$\% \text{Extraction} = \frac{C_o - C_e}{C_o} \times 100. \quad (2)$$

It can be clearly observed from Figure 1 that the % extraction is strongly reliant on the pH value of solution. Figure 1 depicts that there is an upsurge followed by a succeeding decline in the % extraction of Cd(II) with a rise of the pH value from 1.0 up to 9.0. This behavior is consistent with the saturation of binding sites of PPC-BCD 5 with Cd(II). However, it is motivating to notice that the % extraction of Cd(II) reached the highest percentage (99.80%) at pH 6.0, providing that the PPC-BCD 5 phase was most selective toward Cd(II) at this pH value.

The highest percentage of Cd(II) extraction and selectivity at pH 6.0 with PPC-BCD 5 phase can be possibly due to the electrostatic interaction between positively charged

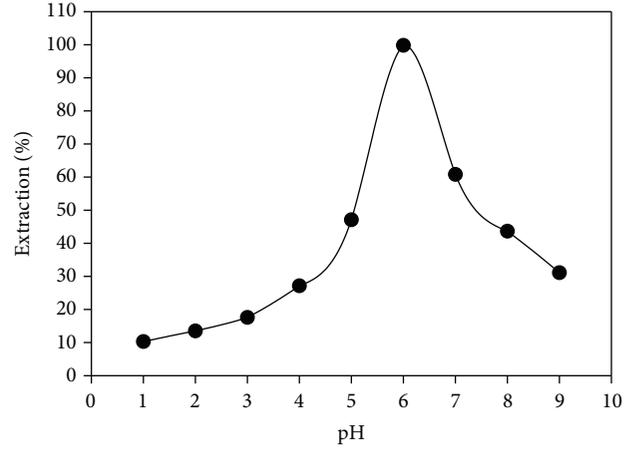


FIGURE 1: Effect of pH on the adsorption of 1 mg L^{-1} Cd(II) on 20 mg PPC-BCD 5 phase at 25°C .

Cd(II) ions and negatively charged sites presented on PPC-BCD 5. Seeing the above results, the optimum pH value of 6.0 was chosen to be the optimum regarding examination of other parameters responsible for its maximum uptake on PPC-BCD 5 under static conditions.

3.3. Determination of Adsorption Capacity. Adsorption capacity represents the utmost metal amount taken up by 1 g of solid phase and presented by mg metal g^{-1} . In this study, the uptake capacity of Cd(II) was investigated by varying amounts of Cd(II) and individually mixing them with 20 mg PPC-BCD 5 at pH 6.0 under batch procedure. Adsorption capacity can be expressed using the following:

$$q_e = \frac{(C_o - C_e)V}{m}, \quad (3)$$

where q_e denotes the adsorbed Cd(II) by PPC-BCD 5 (mg g^{-1}), C_o and C_e refer to the initial and equilibrium concentrations of Cd(II) ion in solution (mg L^{-1}), respectively, V is the volume (L), and m is the weight of PPC-BCD 5 (g). From adsorption isotherm study, the adsorption capability of PPC-BCD 5 for Cd(II) was determined to be 149.25 mg g^{-1} (Figure 2), which is more in quantity as compared to those formerly reporting the adsorption capacity of Cd(II) with other adsorbents (4.92 [36], 9.39 [37], 84.30 [38], 57.90 [39], 97.36 [40], and 123.65 [41] mg g^{-1}).

3.4. Adsorption Isotherm Models. It is very important to study adsorption isotherm models for the development of equation that precisely symbolizes the results. Both Langmuir and Freundlich adsorption isotherm models [42, 43] were utilized to deduce equilibrium isotherm data. In this study, experimental data were well correlated to Langmuir equation. The Langmuir isotherm model represents the monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform energies of adsorption with no transmigration of adsorbate in the plane of the surface.

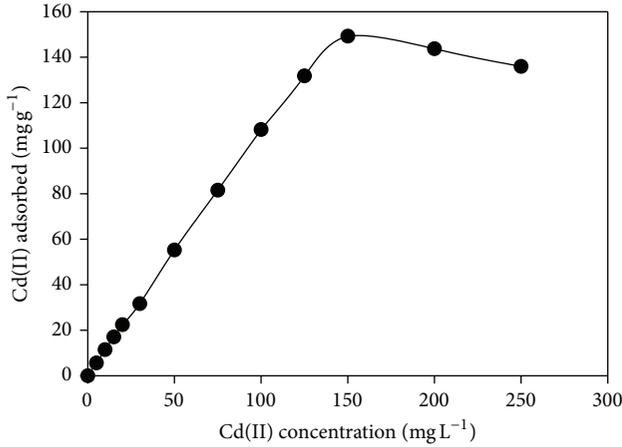


FIGURE 2: Adsorption profile of Cd(II) on 20 mg PPC-BCD 5 in relation to the concentration at pH 6.0 and 25°C.

The Langmuir classical adsorption isotherm can be stated as follows [44]:

$$\frac{C_e}{q_e} = \left(\frac{C_e}{Q_o} \right) + \frac{1}{Q_o b}, \quad (4)$$

where C_e is the concentration of metal ion in solution at equilibrium (mg mL^{-1}) and q_e refers to the amount of metal ion per gram of the adsorbent at equilibrium (mg g^{-1}). The symbols Q_o and b refer to Langmuir constants for PPC-BCD 5 and are related to the maximum Cd(II) adsorption capacity (mg g^{-1}) and affinity parameter (L mg^{-1}) in that order. Langmuir constants Q_o and b can be calculated from a linear plot of C_e/q_e against C_e with a slope and intercept equal to $1/Q_o$ and $1/Q_o b$, respectively. Moreover, vital features of the Langmuir adsorption isotherm model can be obtained in terms of a dimensionless constant separation factor or equilibrium parameter, R_L , which is represented as follows:

$$R_L = \frac{1}{(1 + bC_o)}, \quad (5)$$

where b is the Langmuir constant, demonstrating the nature of adsorption and shape of isotherm and C_o denotes the initial concentration of Cd(II). The value of R_L describes the nature of the adsorption isotherm, and R_L values between 0 and 1 represent a favorable adsorption [45].

A linear plot was obtained from Langmuir isotherm equation based on the least square fit, verifying the validity of Langmuir adsorption isotherm model (Figure 3). Based on the above results, one can conclude that the adsorption method was chiefly monolayer on a homogeneous PPC-BCD 5 surface. Calculated Langmuir constants Q_o and b are determined to be 150.44 mg g^{-1} and 0.11 L mg^{-1} , respectively. The correlation coefficient (R^2) acquired from the Langmuir model is measured to be 0.986 for adsorption of Cd(II) on PPC-BCD 5, further showing that the data were well in accordance considering the Langmuir model. The R_L value of Cd(II) adsorption on PPC-BCD 5 is 0.06, making an extremely favorable adsorption route based on

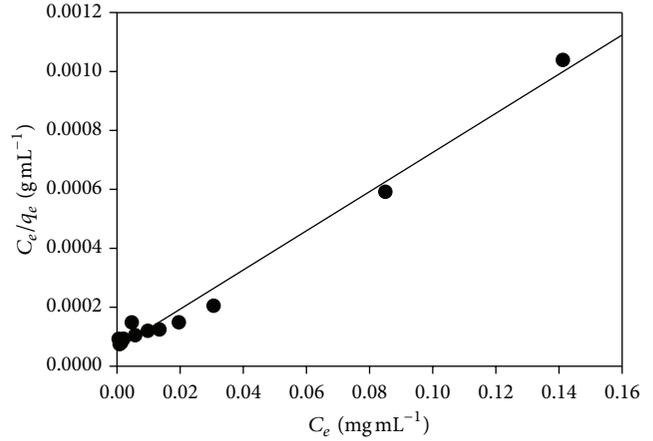


FIGURE 3: Langmuir adsorption isotherm model of Cd(II) adsorption on 20 mg PPC-BCD 5 at pH 6.0 and 25°C. Adsorption experiments were obtained at different concentrations ($5\text{--}250 \text{ mg L}^{-1}$) of Cd(II) under batch conditions.

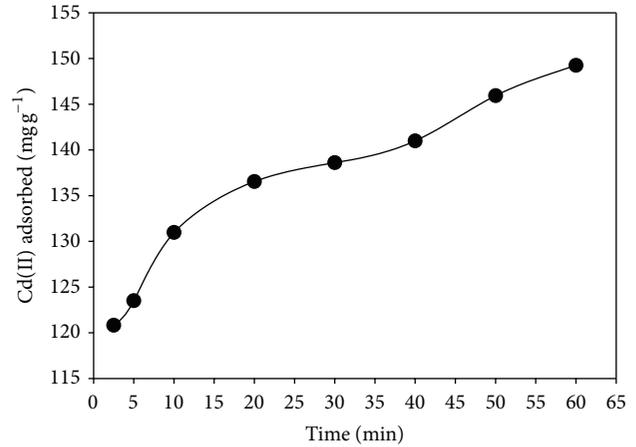


FIGURE 4: Effect of contact time on the adsorption of 150 mg L^{-1} Cd(II) on 20 mg PPC-BCD 5 at pH 6.0 and 25°C.

the Langmuir model possible. One can also observe that the Cd(II) adsorption capacity (150.44 mg g^{-1}) evaluated from Langmuir equation was strongly in concurrence with that (149.25 mg g^{-1}) experimentally measured from the adsorption isotherm study.

3.5. Effect of Contact Time. The effect of shaking time on the % extraction of Cd(II) is a significant factor for calculating the possible prejudice order regarding the behavior of PPC-BCD 5 adsorption toward Cd(II) and finding the approximate time needed to acquire equilibrium. In this study, various contact times varying from 2.5 to 60.0 min were examined at the concentration of 150 mg L^{-1} Cd(II) (Figure 4). As displayed in Figure 4, the amount of Cd(II) adsorbed onto PPC-BCD 5 phase significantly increased with increasing contact time, indicating that PPC-BCD 5 had rapid adsorption kinetics for Cd(II). It can be clearly observed from Figure 4 that over 130 mg g^{-1} Cd(II) was adsorbed on the PPC-BCD 5 phase

TABLE 2: Calculated thermodynamic parameters of 5 mg L⁻¹ Cd(II) adsorption on 20 mg PPC-BCD 0.5 ($N = 3$).

ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)				
		$T = 273$ K	$T = 298$ K	$T = 313$ K	$T = 338$ K	$T = 353$ K
-9.34	46.18	-22.05	-23.01	-23.64	-25.09	-25.66

after only 10 min of the equilibrium periods. The amount of Cd(II) adsorbed was also increased up to more than 138 mg g⁻¹ after 30 min until the maximum adsorption of PPC-BCD 5 for Cd(II) reached 149.25 mg g⁻¹ after 60 min.

3.6. Kinetic Study. The effect of concentration on reaction rates is very essential in understanding the reaction mechanism. The adsorption kinetic data of Cd(II) adsorption on PPC-BCD 5 were investigated in terms of pseudo-first- and second-order kinetic equations [46] for the measurement of changes in adsorption regarding time and calculating kinetic parameters. Kinetic models were utilized for fitting of experimental data having the correlation coefficient (R^2) as assess of agreement between the experimental data. The pseudo-first-order equation can be expressed as follows:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303} \right) t, \quad (6)$$

where k_1 (min⁻¹) refers to the rate constant of the pseudo-first-order adsorption, q_t (mg g⁻¹) represents the amount of adsorption at time t (min), and q_e (mg g⁻¹) denotes the amount of adsorption at equilibrium. The adsorption rate constant (k_1) and adsorption capacity (q_e) for PPC-BCD 5 were calculated from the slope and intercept, respectively, of the plot of $\log(q_e - q_t)$ against t .

The adsorption kinetic data of Cd(II) adsorbed on PPC-BCD 5 were also studied in terms of a pseudo-second-order adsorption. The pseudo-second-order model explains that the rate limiting step is possibly chemical adsorption relating valence forces through sharing or exchanging of electrons between the adsorbent and adsorbate [47]. The pseudo-second-order equation can be written as follows:

$$\frac{t}{q_t} = \frac{1}{v_o} + \left(\frac{1}{q_e} \right) t, \quad (7)$$

where $v_o = k_2 q_e^2$ denotes the initial adsorption rate (mg g⁻¹ min⁻¹), k_2 (g mg⁻¹ min⁻¹) corresponds to the rate constant of adsorption, q_e (mg g⁻¹) refers to the amount of metal ion adsorbed at equilibrium, and q_t (mg g⁻¹) is the amount of metal ion on the surface of adsorbent at any time t (min). The parameters q_e and v_o can be easily attained from the slope and intercept, respectively, of a plot of t/q_t versus t (Figure 5). It is interesting to note that adsorption kinetics data fitted well with the second-order kinetic model. The correlation coefficient (R^2) factor was measured to be 0.99, showing the reliability and accuracy of the pseudo-second-order adsorption. The parameters q_e , v_o , and k_2 were determined to be 149.84 mg g⁻¹, 103.64 mg g⁻¹ min⁻¹, and 0.005 g mg⁻¹ min⁻¹. The adsorption capacity of Cd(II)

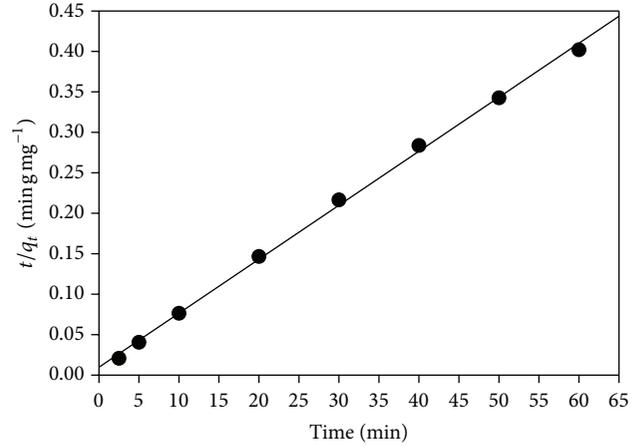


FIGURE 5: Pseudo-second-order adsorption kinetic model of Cd(II) uptake on 20 mg PPC-BCD 5 at pH 6.0 and 25°C.

on PPC-BCD 5 estimated from the pseudo-second-order kinetic model (149.84 mg g⁻¹) was also in good agreement with adsorption capacities obtained from both adsorption isotherm experiments (149.25 mg g⁻¹) and Langmuir isotherm model (150.44 mg g⁻¹), confirming the fact that the pseudo-second-order nature of the adsorption of Cd(II) on PPC-BCD 5 is highly applicable.

3.7. Thermodynamic Study. The study of thermodynamic parameters offers a good understanding of mechanism for the adsorption of Cd(II) on PPC-BCD 5. Therefore, the influence of temperature regarding the adsorption of 20 mg PPC-BCD 5 for 5 mg L⁻¹ Cd(II) was investigated at varied temperatures (273, 298, 313, 338, and 353 K). The distribution adsorption coefficient (K_d) representing the nature of a metal ion adsorbed by an adsorbent (mL g⁻¹) can be acquired from (1). Besides, thermodynamic parameters of the standard enthalpy change (ΔH° , kJ mol⁻¹) and standard entropy change (ΔS° , J mol⁻¹ K⁻¹) were determined, as summarized in Table 2, from the slope and intercept, respectively, of the linear variation of $\ln K_d$ with the reciprocal of temperature ($1/T$) as follows:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \left(\frac{\Delta H^\circ}{RT} \right), \quad (8)$$

where R denotes the universal gas constant (8.314 J mol⁻¹ K⁻¹) and T represents the temperature in Kelvin. The standard Gibbs free energy change (ΔG° , kJ mol⁻¹) summarized in Table 2 was determined from the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ. \quad (9)$$

As shown in Table 2, measured values of standard enthalpy change ΔH° and Gibbs free energy change ΔG° are negative, as the standard entropy change ΔS° is positive. The examined negative ΔH° value proposed an exothermic adsorption of Cd(II) on PPC-BCD 5. Additionally, the adsorption mechanism of PPC-BCD 5 toward Cd(II) is believed to be a common spontaneous method and thermodynamically favorable because of the negative ΔG° along with positive ΔS° . The positive ΔS° value provides some structural changes in PPC-BCD 5 and Cd(II) and indicates the increased haphazardness during the adsorption process of Cd(II) on PPC-BCD 5. These results are in accordance with the data measured from adsorption isotherm experiments and Langmuir and kinetic adsorption isotherm models.

4. Conclusion

To investigate the feasibility of PPC to apply for the selective detection of toxic metal ion in complex matrices, a series of PPC-BCD extractors were newly prepared by solution blending of biodegradable PPC and BCD. The proposed method based on the newly synthesized PPC-BCD 5 phase not only had the efficiency toward a selective adsorption of Cd(II) but also provided high uptake capacity of Cd(II). Results obtained from adsorption isotherm models displayed that Langmuir adsorption isotherm model has best described the Cd(II) adsorption on PPC-BCD 5. Kinetic isotherm results demonstrated that the adsorption of PPC-BCD 5 toward Cd(II) followed a pseudo-second-order kinetic reaction. Thermodynamic study reveals that the adsorption mechanism of Cd(II) adsorption on PPC-BCD 5 was a common spontaneous method and thermodynamically favorable. Additionally, the adsorption procedure is found to be exothermic in nature. This method can be an useful approach in providing a selective separation and calculation of Cd(II) from the complex matrices.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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