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Removal of Cd(II) from aqueous solution using H_2SO_4-modified pine cone powder

Loại bỏ Cd(II) trong dung dịch nước bằng bột quả thông hoạt hóa với H_2SO_4

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Abstract

In this study, H_2SO_4 modified pine cone powders (PC) were tested to remove Cd(II) ions from aqueous water. The results showed the Cd(II) adsorption capacities of the PC powder and H_2SO_4 modified PC powder were 14.96 and 74.94 mg/g, respectively. The modified PC powder had higher adsorption capacities than raw PC powder, which can be attributed to the surface structural changes by the acid treatment. The equilibrium adsorption data are more consistent with the Langmuir isotherm equation than with the Freundlich equation. The Cd(II) adsorption on the two adsorbents tends to increase with increasing solution pH under acidic conditions (pH 2.0 - 6.5). The optimum pH for Cd(II) adsorption is 6.0. The desorption ability of Cd(II) by 0.1 M HCl solution was found around 96.7- 99.1%. The results indicated that H_2SO_4 modified PC powder could be utilized as promising adsorbent for Cd(II) removal from water.

Keywords: Removal of Cd(II); H_2SO_4 modified; pine cone powder; adsorption isotherm.

Tóm tắt

Trong nghiên cứu này, H_2SO_4 đã được sử dụng để hoạt hóa bột quả thông và áp dụng cho việc loại bỏ Cd(II) trong dung dịch nước. Kết quả thu được cho thấy khả năng hấp phụ Cd(II) của bột quả thông trước và sau khi hoạt hóa bởi H_2SO_4 lần lượt là 14,96 và 74,94 mg/g. Bột quả thông sau khi hoạt hóa bởi H_2SO_4 có khả năng hấp phụ cao hơn do sự thay đổi cấu trúc bề mặt vật liệu. Quá trình hấp phụ phù hợp hơn với phương trình đẳng nhiệt Langmuir so với phương trình Freundlich. Khả năng hấp phụ Cd(II) lên bề mặt vật liệu hấp phụ có xu hướng tăng khi tăng độ pH từ 2.0 – 6.0. Giá trị pH tối ưu cho sự hấp phụ Cd(II) là 6.0. Khả năng giải hấp của Cd(II) bằng dung dịch HCl 0,1 M dao động trong khoảng từ 96,7 đến 99,1%. Dựa vào kết quả thu được, có thể kết luận rằng, bột quả thông sau khi hoạt hóa bởi H_2SO_4 có thể sử dụng như vật liệu tiềm năng để loại bỏ Cd(II) trong dung dịch nước.

Từ khóa: Loại bỏ Cd(II); hoạt hóa bởi H_2SO_4; bột quả thông; hấp phụ đẳng nhiệt.

1. Introduction

Heavy metal remediation of aqueous streams is of special concern due to persistency of heavy metals in environment [1-2]. Conventional treatments technologies for the removal of these toxic heavy metals such as

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chemical precipitation and biological are not economical further resulting in generating huge quantity of toxic chemical sludge. Adsorption is a potential alternative to the existing conventional technologies for the removal and/or recovery of metal ions from aqueous solutions [3]. The major advantages of adsorption over conventional treatment methods include: low cost, high efficiency, minimization of chemical or sludge, regeneration of adsorbents and possibility of metal recovery [4]. Cadmium is a highly toxic element affecting the environment and considered to be carcinogenic. The discharged effluent will be absorbed and accumulated by microorganisms. Also, cadmium will be transferred to humans via the food chain and then cause serious damage to kidney and bones. That is why we need consider cadmium pollution. The most representative forest in Korea is the coniferous forest. Coniferous forests account for 52% of the total forest land, the majority of the tree species of Korea's forests are the red pine and white pine. In the recent years, pine cone (PC) has been tried with varying success for heavy metal removal [5-7] and dye [8]. Large quantities of cones in Korea were regarded as Forestry waste and thus there is a potential to be used as adsorbent for removing heavy metals. The objective of the present work was to investigate the feasibility of producing adsorbent from the PC powder of Korea by H_2SO_4 modification and their ability to remove Cd(II) ions from aqueous solution.

2. Materials and Methods

2.1. Materials

The used raw pine cones in the present experiments were collected around University of Ulsan located in an urban residential area in Ulsan, Korea. The collected pine cones were washed to remove impurities such as sand, leaves and soils. Pine cones were dried at 90°C for 12 hours. The dried pine cones were grinded and then the resultant PC powder was sieved. The sieved particles about 150μm to 200μm were collected, preserved at room temperature in an airtight plastic container and used for analysis as well as adsorption experiments. The chemical composition of the PC powder is presented in Table 1 [11]. The modified PC powder sample was prepared by mixing 10 g of raw PC powder with 100 mL of 0.5 M H_2SO_4 solution. The whole reaction mixture was stirred in a magnetic stirrer at 25^{o}C for a period of 12 hours and then the powder was filtered and repeatedly washed with distilled water. The washed powder was then oven dried overnight at 50°C and used for adsorption and characterization.

Table 1. Chemical composition of raw pine cone powder

Species	Composition (%)
Cellulose	46.7
Lignin	24.9
Hemicelluloses	23.6
Extractives	4.8

2.2. Chemicals and analytical instruments

The Cd(II) stock solution containing 1000 mg Cd/L was prepared by dissolving cadmium nitrate ($Cd(NO_3)_2$) powder (analytical reagent grade from Sigma-Aldrich Germany) in distilled water. Cd(II) working solutions in different concentrations were prepared by diluting the Cd(II) stock solution with distilled water. The pH measurements were done with a Digital pH meter Orion 5Star and pHs of solutions were adjusted to the required value by using 0.1M NaOH and 0.1 M HNO_3. Concentrations of Cd(II) were measured using atomic absorption spectrophotometer VARIAN

AA240. The scanning electron micrographs (SEM) were obtained on Hitachi 4700 microscope to identify morphology information on the PC and H_2SO_4 modified PC powder.

2.3. Effect of solution pH on Cd(II) adsorption

Batch experiments of adsorption were performed in 250 mL Erlenmeyer flasks. Flasks were being agitated on Shaking water bath HST -205SW at 120 rpm for specified time intervals. The effect of pH on Cd(II) adsorption was examined maintaining pHs at different values between 2 and 6.5. Concentration of Cd(II) solution for the study of solution pH effect was 100 mg/L and adsorbent dose was 0.1 g at 25ºC.

2.4. Study of adsorption isotherms

The Cd(II) adsorption isotherm study was carried out with different initial concentrations of Cd(II) and a fixed concentration of the adsorbents at room temperature (25°C). Six levels of initial Cd(II) concentrations (50, 100, 200, 300, 400 and 500 mg/L) were used. The pH of the solution was maintained at an optimum pH and reaction time was 60 minutes. At the end of the adsorption period, the solution was filtered through a 0.45 μm membrane filter and then analyzed for Cd(II). The quantity of adsorbed Cd(II) (adsorption capacity) was calculated from the decrease in the Cd(II) concentration of interest solution. The isotherm data on Cd(II) adsorption were fitted to Langmuir and Freundlich equations.

2.5. Desorption studies

To evaluate Cd(II) desorption from the samples, the residual solids retained on the filter paper were collected in a 250-mL Erlenmeyer flask after filtration of the suspension from an adsorption test solution. To each flask 100 mL of 0.1M HCl solution was added. The flask was covered during magnetic stirring at 120 rpm for 12 h while pH was maintained at the same value as in the desorption experiment. The suspension solution was filtered and then analyzed for Cd(II) concentration in a similar way to described previously. The quantity of desorbed Cd(II) was determined by the amount of Cd(II) in solution after the desorption experiment.

3. Results and discusion

3.1. Scanning electron microscope (SEM)

The microstructures of PC powder before and after the acid treatment were observed by scanning electron micrographs. The SEM shown in Figure 1 enables the direct observation of the surface microstructures of PC powder and H_2SO_4 modified PC powder.

Micrographs show considerable changes in morphology of the PC powder after the acid treatment with increased number of pores on adsorbent surface which can be utilized for more sorption potential of Cd(II) ions in aqueous solution.

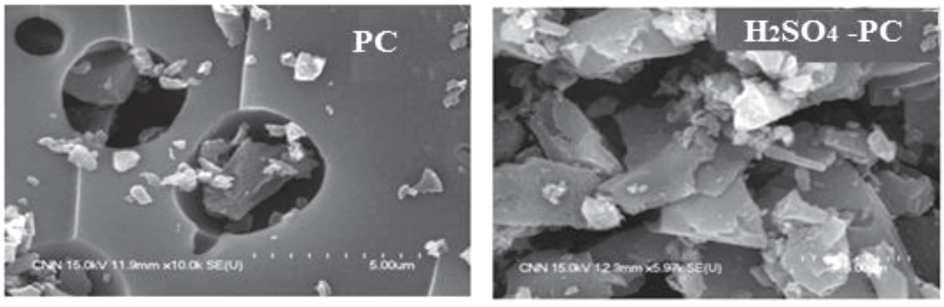


Figure 1. Scanning electron microscope of PC and H_2SO_4 modified PC powders

3.2. Effect of pH on Cd(II) adsorption

The effect of initial pH on the Cd(II) adsorption by PC powder and H_2SO_4 modified PC powder was shown in Figure 2. The initial pH effect at strong acidic condition, pH 2.0 - 3.0, was much lower than at weak acidic conditions, pH 5.0-6.0. This is because there is more competition between H^+ ions and Cd(II) ions for adsorption sites of the PC and H_2SO_4 modified PC powders at lower pH conditions. The maximum adsorption of Cd(II) was observed at pH 6.0. The pH above 6.5 for Cd(II) was not used in order to avoid the precipitation of metal ions in the form of their hydroxides [9]. This phenomenon can be explained by the surface charge of the adsorbent and the H^+ ions present in solution. At high pH values, presence of H^+ ion in solution decreased and the surface of the adsorbent has a higher negative charge which results in a higher attraction of Cd(II) ions.

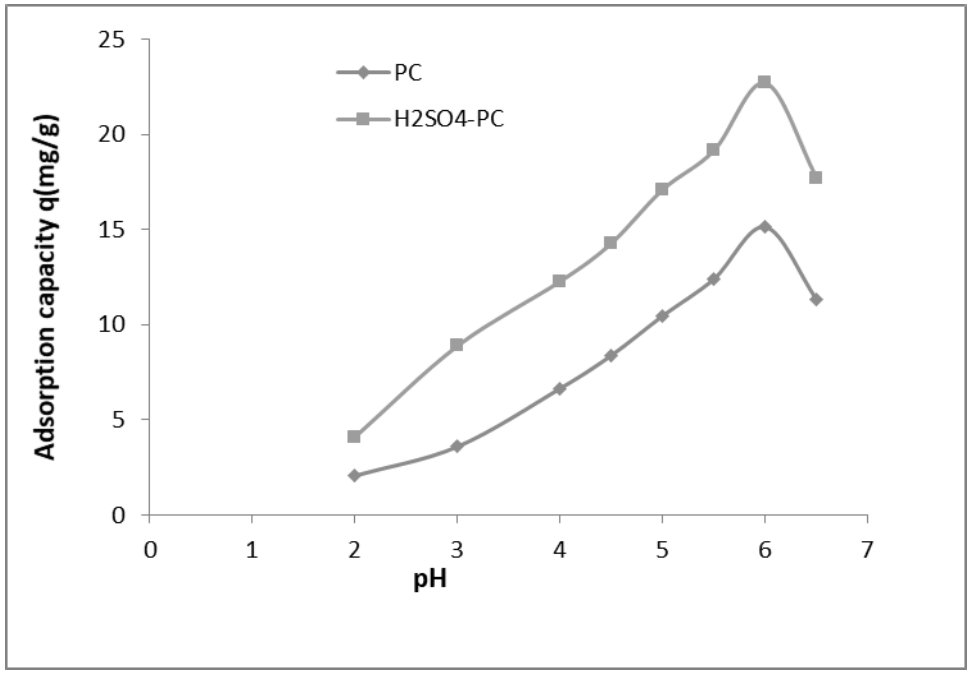


Figure 2. Effect of solution pH

3.3. Cd(II) adsorption isotherms

Figure 3 shows the equilibrium adsorption uptake of Cd(II) ions by the adsorbents at different initial concentration Cd(II). The increase initial concentration of Cd(II) greatly increases the equilibrium adsorption uptake of Cd(II). The adsorption capacities of Cd(II) tend to get a constant value. This means that there is a maximum or limit value available for active adsorption of Cd(II), due to the saturation of the sorbent sites by Cd(II) ions. The maximum adsorption of the PC powder and H_2SO_4 modified PC powder based on Langmuir model were 14.96 and 74.94 mg/g, respectively.

Two typical isotherms, as described below:

Langmuir model stands for monolayer adsorption, assuming that adsorption takes place at a specific number of adsorption sites, each site is occupied by one adsorbate molecule, all sites are the same, and there is no interaction between adsorbed molecules.

The Langmuir model is presented by equation (1):

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L.q_{max}} \quad (1)$$

where q_e (mg g^{-1}) is amount of adsorbed at the equilibrium, q_{max} (mg g^{-1}) is maximum adsorption capacity, K_L (L mg^{-1}) is Langmuir constant and C_e (mg L^{-1}) is equilibrium concentration.

The Freundlich model represents non-ideal adsorption, with multi adsorption sites and heterogeneous surfaces. It is based on the assumption that active binding sites are occupied first, and the binding ability declines with an increase in the site occupation.

The Freundlich empirical model is given by the equation (2):

$$q_e = K_f C_e^{1/n} \quad (2)$$

and its linear form is expressed as:

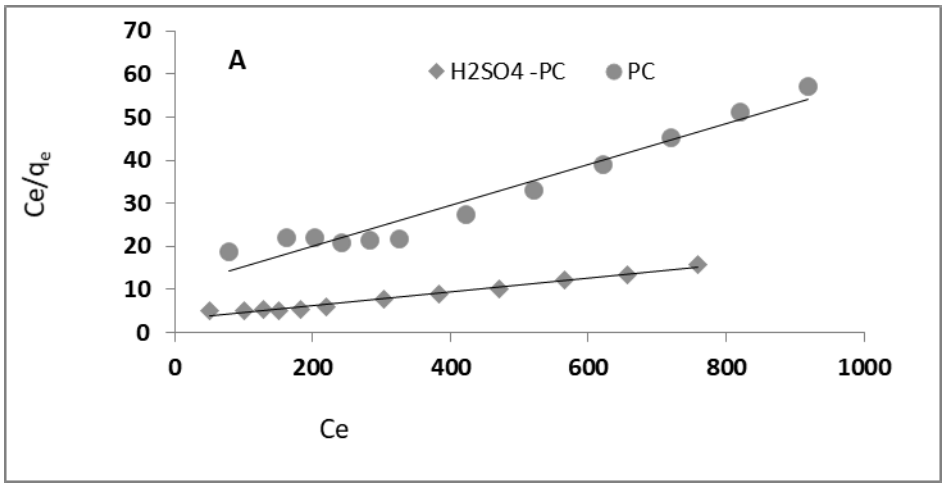
$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e$$

where C_e (mg L^{-1}) is the equilibrium concentration, q_e (mg g^{-1}) is amount of adsorbed at equilibrium, K_F (mg g^{-1}) and n are the Freundlich constants for the capacity and intensity of adsorption, respectively.

The other isotherm parameters can be determined by regression of the experimental data using each isotherm equations shown in Fig. 3(A) and (B). The isotherm data showed Figure (3A) and (3B) were fitted with two models. Table 2 shows adsorption model parameters, including correlation coefficients (R^2) estimated from each isotherm.

Table 2. Langmuir and Freundlich isotherm constants

	Langmuir isotherm			Freundlich isotherm		
Adsorbent	q_{max} (mg/g)	b	R^2	K_f	1/n	R^2
PC powder	14.96	0.0141	0.961	10.69	0.3239	0.894
Modified PC powder	74.94	0.0095	0.990	11.96	0.3083	0.871



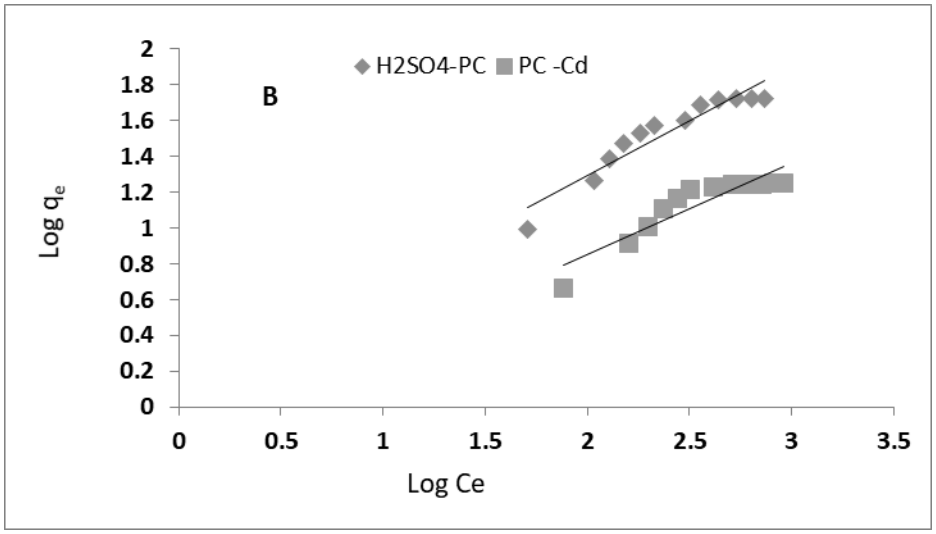


Figure 3 (A). Langmuir isotherm and 3(B): Freundlich isotherm

3.4. Desorption studies

The adsorption of Cd(II) on PC powder and H_2SO_4 modified PC powder is highly pH dependent, hence its desorption may also be controlled by adjusting the pH of the interest solution. Hydrogen ions may replace the Cd(II) ions on the metal loaded adsorbent thus functioning as cation exchanger [10]. The tests of Cd (II) desorption were conducted with three initial concentrations of Cd(II) (50, 100, and 500 mg/L) (pH = 4). Table 3 shows desorption data of Cd(II) adsorbed by the PC and H_2SO_4 modified PC powders.

Table 3. Desorption of Cd(II) ions

Initial Conc. (mg/L)	Sample	Adsorbed Cd(II) (mg/g)	Desorbed Cd(II) (mg/g)	Desorbability (%)
50	PC	6.21	6.11	98.4
	H_2SO_4 - PC	14.23	13.84	97.3
100	PC	9.96	9.87	99.1
	H_2SO_4 - PC	23.39	22.61	96.7
500	PC	14.58	14.17	97.2
	H_2SO_4 -	74.41	73.36	98.6

The identified desorbability of Cd(II) ranged from 96.7 to 99.1%. The elution of the adsorbed Cd(II) solution allows collection of Cd(II) ions and concentrating solution which could be suitable for recovery of the cadmium. Also the adsorbents used for Cd(II) removal can be regenerated through proper procedures and then the regenerated adsorbent may be reused for Cd(II) removal again.

4. Conclusions

In the adsorption and desorption study of Cd(II) ions in aqueous solution using PC and H_2SO_4 modified PC powders, the followings can be concluded:

(1) The identified adsorption capacities of Cd(II) ions by the PC and H_2SO_4 modified PC powders were 14.96 and 74.94 mg/g, respectively.

(2) The adsorption of Cd(II) by both adsorbents well fitted with Langmuir isotherm equation ($R^2 \geq 0.961$, 0.990) rather than Freundlich isotherm equation.

(3) The adsorbed Cd(II) easily desorbed by 0.1M HCl solution with desorption efficiency of 96.7 - 99.1%. Therefore, this absorbent can be utilized for Cd(II) wastewater treatment.

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