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RESEARCH PAPER

Kinetic and Thermodynamic Parameters of Cadmium Ion Removal by using the Orange Wood-Synthesized Activated Carbon Nanoparticles Modified with Cysteine

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Abstract
Activated carbon is known an as appropriate adsorbent due to its high adsorption capacity for most pollutants, especially heavy metals. In the present study, activated carbon was synthesized from orange wood by employing the chemical activation method. Additionally, cysteine amino acid was used to modify the activated carbon surface, leading to an enhancement in adsorption ability because of having a nitrogen group. Based on the results, the adsorption capacity of the modified activated carbon was obtained at 120 mg g^{-1} adsorbent. The parameters affecting adsorption such as the amount of used adsorbent, as well as solution pH, primary concentration, and contact time were optimized, followed by performing the adsorption process under optimal conditions. The optimal adsorption conditions included the pH of 6, contact time of 60 min, adsorbent amount of 50 mg, and primary cadmium concentration of 80 ppm. Further, kinetic and thermodynamic parameters were assessed and optimized. The results of which represented the best fit between adsorption with Langmuir isotherm and the pseudo-second-order kinetic model. The results represented that the quasi-second-order model with a higher regression coefficient (R^2 = 0.97) described the experimental data better than the quasi-first-order one (R^2 = 0.83). The adherence of adsorption kinetics to the pseudo-second-order model suggested a chemical interaction as the rate-determining step. Regarding adsorption thermodynamics, the effect of temperature was examined on adsorption by using Van't Hoff's equations, which reflect the endothermicity of the process.

Keywords: Adsorption, Cadmium, Kinetic model, Modified activated carbon, Thermodynamic model

INTRODUCTION

During the past decades, the growth of industries and the use of metal materials have resulted in producing and disposal of a large number of heavy metals in industrial effluents. Heavy metals are inclined to dissolve in aqueous solutions. These metal ions are indestructible and accumulate in living organisms, which ultimately cause various diseases and disorders (Yang et al.,2021). Wastewater pollution by heavy metal ions is considered a global environmental problem. An increase in urbanization and industrial progress has promoted water pollution, along with elevating water consumption. In the United States, thousands of tons of plant wastewater containing heavy metals are annually left in the environment, leading to the release of cadmium, lead, zinc, arsenic, nickel, and the like, as well as their transmission to humans through the food chain. Generally, heavy metals are systemic toxins, which can cause death by affecting nerves, kidneys, and fetuses (Patwa & Flora, 2021).

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Cadmium (Cd) is among the most widely used metals, which has recently been highlighted by many environmental researchers due to its durability and damage to the environment and living organisms. In addition, it is known as one of the toxic metals to humans and the environment (Deng et al.,2020). This element is distributed in the Earth's crust abundantly and uniformly, while its inorganic compounds exist only in the special regions of the world. Further, zinc ore contains a large value of cadmium. In the late 19th century, cadmium production began as a by-product of zinc mining, whereas it has been increasingly utilized over the recent century. This element is known as one of the important environmental pollutants found in all ecosystems such as water, air, food, and plants (HOCAOĞLU-ÖZYİĞİT & GENÇ, 2020). Due to the presence of heavy metals in industrial effluents, as well as the environmental problems caused by their improper disposal, such effluents should be treated before discharging into the environment or entering into an effluent collection system. The surface and groundwater resources contaminated with heavy metals need to be treated. So far, different methods such as settlement (Ayyanar & Thatikonda, 2021), coagulation (Liao et al., 2021), sedimentation (Ye et al., 2021), floating (Ma et al., 2021), membrane process (Alshahrani et al., 2021), electrochemical cell (Delil et al., 2020), precipitation (Ali Redha, 2020), ion exchange (Bashir et al., 2019), and adsorption have been applied to remove heavy metals (Duan et al., 2020), each of which represents specific advantages and limitations. Among the techniques, the adsorption using activated carbon (AC) has attracted the attention of many researchers due to its success in eliminating the low levels of heavy metals with proper efficiency. Adsorption is considered one of the economic methods for separating heavy metals from effluent. In this regard, AC has been well known as an adsorbent with high adsorption capacity and low cost. The extensive applications in separation, purification, recovery and environment-related processes reveal the importance of this substance (Reza et al., 2020).

Given that an appropriate adsorbent is the most critical parameter in adsorption, the selection of an adsorbent that can be used purposefully is considered important. Cost-effectiveness and technical usability are the two key factors highly affecting the selection of such adsorbents for treating heavy metals. The features of an ideal adsorbent involve wide surface area (great adsorption capacity), mechanical stability, adaptability, easy regeneration, availability, cost-effectiveness, eco-friendliness, feasible performance, high adsorption rate, and selectivity, as well as the proper distribution of pore size and volume. Adsorption and selectivity increase in regular molecular structure. Today, nanomaterials can be separated by using the adsorption process (Yang et al., 2021).

This adsorbent is synthesized by using cellulosic and polymeric raw materials such as wood, fruit peel and pit, tree bark, and other agricultural wastes (cellulosic ones), coal, petroleum coke, and polymeric raw substances (carbon raw ones) (Blachnio et al., 2020). Several studies have been conducted in this regard. For example, Amini et al. (2019) and Ghasemi et al. (2013), focused on removing cadmium and nickel ions from aqueous solutions by date-palm leaf ash and grape biochar, respectively. Additionally, Ma et al. (2016) determined the maximum cadmium adsorption capacity of wheat straw. Park et al. (2016) used sesame straw to eliminate cadmium, copper, lead, zinc, and chromium. Dai et al. (2018) assessed the use of agricultural effluent as an adsorbent to remove pollutants.

Thus, the present study assessed the product obtained from the chemical activation of orange wood by using the adsorption method as a raw material to produce activated carbon. Furthermore, it examined the cadmium removal percentage from synthetic samples. Activation temperature and time, chemical activating agents, and initial particle size were recognized as the factors affecting activated carbon synthesis. All of the adsorption tests were implemented in a non-continuous system at room temperature. Further, an atomic absorption spectrometer was utilized to obtain cadmium concentrations. The effect of pH, adsorbent amount, contact time, and primary cadmium concentration was first considered in the specific ranges based on the results of the previous research on cadmium elimination by using adsorbents, followed by

evaluation and optimization. Then, Langmuir and Freundlich's isotherms were compared, and the pseudo-first- and pseudo-second-order kinetic models for adsorption were examined. The thermodynamic parameters of adsorption were calculated by using Van't Hoff's equations. This study primarily aimed to provide a method for cadmium ion adsorption from samples based on the wastes of orange wood as activated carbon, as well as obtain the optimal parameters of the technique.

MATERIALS AND METHOD

Most of the main used substances like potassium hydroxide, sulfuric and phosphoric acid, piperidine, cadmium nitrate, and L-cysteine were provided from Merck (Germany) in high purity (99.90%). Therefore, they were applied without concentration. Additionally, glutaraldehyde and absolute ethanol were obtained from Sigma Aldrich. The deionized water was purchased from Morvarid Pars Co. to prepare solutions.

The sample concentration was determined on a flame atomic absorption spectrometer (AA800) equipped with a hollow cathode lamp for cadmium ions by using the standard curve. Further, a pH meter (Knick 765, Germany), laboratory mill (M20 Universal mill, IKA), laboratory furnace with the timer (eFL2626, L&L), and sieve shaker (M 20 Universal mill, IKA) were utilized for dispersing solution, and creating and modifying AC.

Nano adsorbent preparation

In this study, a carbon nanostructure synthesized from orange wood was applied, the surface of which was modified during two steps to optimize the adsorption of cadmium heavy metal. In this respect, AC particles were first produced based on the chemical activation technique reported in the previous studies with slight changes (Karimpour et al.,2020; Baloji et al.,2019). To this end, raw materials (orange wood) were powdered by using a laboratory mill and sized by passing through a laboratory sieve shaker, followed by washing with absolute ethanol and hot deionized water several times. Then, activating agents (potassium hydroxide, and phosphoric and nitric acid) were added to the raw sample and heated for an appropriate time. After compression, the impregnated plant was calcified in a high-temperature furnace for the carbonization process. It is worth noting that the simultaneous implementation of activation and carbonization steps at proper temperature results in preparing AC with desired porous structure. Finally, the resultant particles were rinsed, dried, powdered, and modified through crosslinking with L-cysteine amino acids (Qiao et al.,2022).

Study design

The parameters influencing the synthesis of AC from orange wood were evaluated in Minitab 2018 software by employing a screening method. Activation temperature (400-600 ℃) and time (30-90 min), chemical activating agents (potassium hydroxide, and phosphoric and nitric acid), and initial particle size (200-400 μm) were identified as the effective factors. Taguchi's signal-to-noise analysis, a strong analytical tool of Minitab software, was utilized to optimize the parameters, followed by using AC with optimal parameters (Table 1) for adsorption tests. Fig. 1 displays the effectiveness of each factor on particle porosity.

Primary solution preparation

The primary cadmium solution (stock, 1000 mg L^{-1}) was prepared by pouring 2.103 g of cadmium nitrate ($Cd(NO_3)_2$) into a 1000-mL volumetric flask and making to volume with the gradual addition of deionized water while stirring for uniformity. This solution was utilized to create the other solutions with different levels required for assessing the adsorption process.

Table 1. Optimal conditions for AC synthesis

Parameter	Optimal Level	
	Orange	
$\mathbf{X_1}$(°C)	2	500
$\mathbf{X_2}$(min)	2	60
$\mathbf{X_3}$	2	H_3PO_4
$\mathbf{X_4}$(µm)	3	200

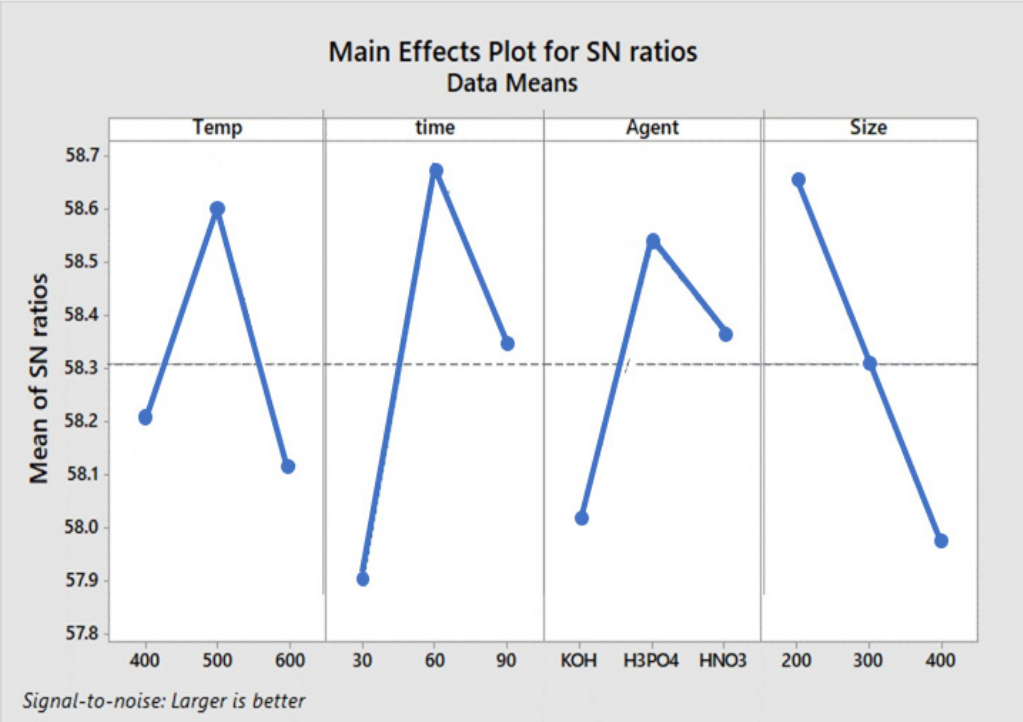

Fig 1. Effect of each parameter on the signal-to-noise ratio of the specific surface of AC from orange wood

Adsorption tests

In this experimental study, all adsorption tests were performed in a non-continuous system at ambient temperature. The pH, adsorbent amount, contact time, and primary cadmium concentration were determined in a specific range based on the previous research on cadmium elimination using adsorbent and evaluated. Briefly, a certain amount of the intended AC was added into 80 ppm cadmium solution, the temperature of which was set after adjusting pH at the desired level. The solution was laid on a stirrer heater for a certain time and transferred into a falcon tube for centrifuging. The solution was separated from the adsorbent in 10-15 min, filtered, and used to record absorbance by using an atomic absorption spectrometer.

To examine the effect of modifying surface on heavy metal adsorption, a certain value of sample was taken after the synthesis step and subjected to adsorption tests. In this regard, 80 $mg.L^{-1}$ cadmium solutions was created, and poured into 50 mL of cadmium solution, into each of which 50 mg of adsorbent was added. Then, the mixture was placed under the ultrasonic bath (100 W) for 30 min, followed by separating adsorbents by using a centrifuge and measuring solution concentration on an atomic absorption spectrometer. The efficiency and adsorption capacity was calculated based on equation 1.

Calculation of efficiency and adsorbent capacity

In the present study, the effect of the AC surface modification on the adsorption ability of adsorbent and modified adsorbent was assessed. Then, the amount of used adsorbent, as well as solution pH, primary concentration, and contact time were optimized. The data were stored in Excel software and analyzed.

Equations 1 and 2 were respectively applied to obtain cadmium removal percentage (adsorption efficiency) and equilibrium adsorption capacity (Sharma & Naushad,2020).

$$R(\%) = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

$$q_e = (C_0 - C_e) \times \frac{V}{m} \quad (2)$$

where C_o indicates the primary level of metal ions in solution (mg L^{-1}) and C_e illustrates equilibrium or cadmium ion value in solution after the adsorption process (mg L^{-1}). The mass of the used adsorbent is demonstrated with m (mg). In addition, V, q_e, and R denote solution volume (mL), adsorption capacity (adsorbed metal ions/sorbent mass unit) (mg g^{-1}), and adsorption efficiency (%), respectively.

Adsorption isotherm evaluation

Regarding the adsorption process in a solid-liquid system, a component or some components of solution accumulates and concentrate on the solid surface until reaching equilibrium. The equilibrium is described by using the parameters of sorbate concentration per sorbent mass unit in equilibrium time (q_e) and remaining sorbate level in solution at the same time (C_e). Further, sorption isotherm is an equation representing the changes in q_e relative to C_e. Langmuir and Freundlich's isotherms are known as two classic and widely-used isotherms with proper precision for fitting adsorption test data, which were utilized in the present study.

Langmuir isotherms

The equilibrium Langmuir equation reflects the monolayer and homogeneous adsorption of adsorbate, the adsorption process follows which is called ideal. The linear form of the Langmuir model is as follows (Chang et al., 2020).

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad (3)$$

where C_e denotes equilibrium metal concentration in solution (mg L^{-1}), which is determined through experimenting. Furthermore, q_e reveals the amount of adsorbed cadmium per adsorbent mass unit (mg g^{-1}), calculated based on equation 2. The q_{max} and K_L are Langmuir isotherm constants. Fig. 2 plots $\frac{C_e}{q_e}$ versus C_e for the cadmium ion adsorption process.

Freundlich isotherms

The Freundlich isotherm is based on the assumption that the adsorbent possesses a non-uniform surface with different levels of adsorption sites, the linear form of which is expressed as equation 4 (Budhiary & Sumantri,2021).

$$\log(q_e) = \log(K_F) + \frac{1}{n}\log(C_e) \quad (4)$$

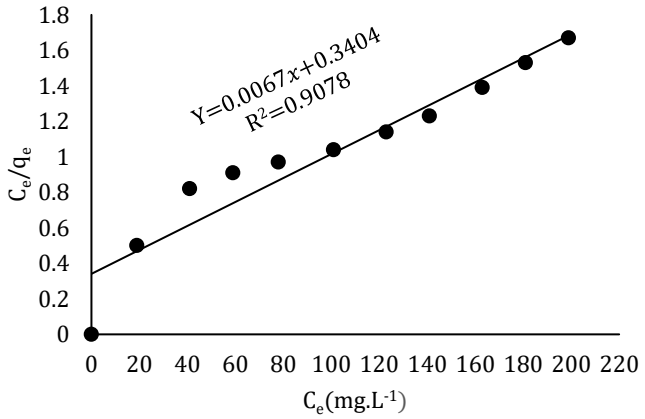

Fig 2. Langmuir isotherm of cadmium ions by the modified AC (AC@CYs) (50 mL of 80 ppm cadmium solution; pH: 6; adsorbent amount: 50 mg; contact time: 60 min)

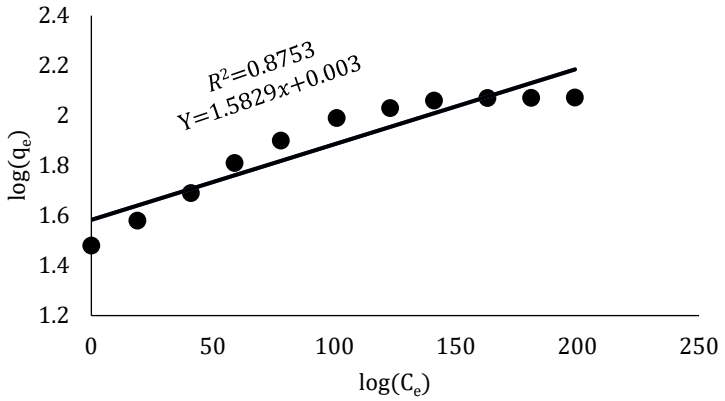

Fig 3. Freundlich isotherm of cadmium ions by AC@CYs (50 mL of 80 ppm cadmium solution; pH: 6; adsorbent amount: 50 mg; contact time: 60 min)

where K_F reveals relative adsorption capacity and n indicates the distribution of adsorbate particles on the adsorbent surface. The Freundlich model parameters can be calculated by linearizing and plotting $\log(q_e)$ relative to $\log(C_e)$ (Fig. 3).

The results of the present study exhibited the adherence of the adsorption equilibrium understudy to the Langmuir model due to the high precision of fitting the data to this model. Accordingly, there are a fixed number of available sites with equal energy on the adsorbent surface. The adsorption process is reversible so desorption occurs when the experiment process changes. The maximum theoretical adsorption capacity was equal to 125 mg Cd g adsorbent, which is close to that of the real one (120 mg Cd g adsorbent).

According to Han et al. (2013) and Chand et al. (2014), 34 and 76 mg Cd/g are respectively adsorbed by rice straw in the solution system and modified apple pomace. Regarding heavy metal removal from aqueous solutions, Ali et al. evaluated the potential of using the green adsorbent of peanut hull and referred to 14.13 mg g^{-1} adsorbent as the maximum adsorption capacity (Ali et al.,2016). Furthermore, Bhardwaj et al. assessed cadmium adsorption by Aesculus Indica seed shell and found the maximum adsorption capacity of 34.36 mg g^{-1} adsorbent (Bhardwaj et al.,2019). The results of the present study represented the optimum cadmium adsorption by the intended adsorbent compared to the similar ones.

The constants of adsorption isotherms can be determined by linearizing and using the slope and intercept of their diagram.

Table 2. Adsorption isotherm parameters in the present stud

Isotherm Model	Parameters	Values
Langmuir	K_L	0.16
	q_{max}	125
	R^2	0.9078
Freundlich	K_F	38.27
	n	33
	R^2	0.8753

Table 3. Adsorption kinetic equations applied in the present study

Model	Exponential form	Linear form	References
pseudo-first-order	$q_t = q_e[1 - \exp(-K_1 t)]$	$\ln(q_e - q_t) = \ln q_e - \frac{K_1}{2.303} t$	(Bavel et al., 2020)
pseudo-second-order	$q_t = \frac{K_2 {q_e}^2 t}{1 + q_e K_2 t}$	$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{1}{q_e} t$	(Afolabi et al., 2020)

Table 4. Parameters utilized in the intended kinetic models

Coefficient	Defined
q_t	The amount of adsorbent in the solid phase at time t (mg L^{-1})
q_e	The amount of adsorbent in the solid phase at equilibrium (mg g^{-1})
K_1	Quasi-first-order adsorption constant (min^{-1})
K_2	Quasi-second-order adsorption constant (g mg^{-1} min^{-1})
t	adsorption time(min)

Assessment of adsorption kinetics

The determination of the time required for optimal sorption in a solid-liquid system is considered one of the important objectives of sorption studies. Additionally, examining the effect of contact time on sorption level is known as a kinetic study. Sorption kinetics includes assessing the chemical reaction rate to understand the effective factors of the sorption process and equilibrium time. The kinetic study provides useful information on experiment conditions and chemical reaction rate, and consequently the time needed to establish equilibrium. During the recent decades, several mathematical models have been presented for describing sorption data, among which pseudo-first- and pseudo-second-order rate equations, and intra-particle diffusion are the most widely used to explain sorption process rate (Alakhras et al., 2019).

Thus, the parameters affecting the process (solution pH, contact time, and the amount of used adsorbent) were optimized, followed by fitting pseudo-first- and pseudo-second-order rate models to the resultant data for the kinetic study. The kinetic models used in this study are explained in Tables 3 and 4.

Adsorption thermodynamic evaluation

The endothermicity or exothermicity of reaction can be specified by examining the changes in sorption versus temperature. Further, the optimal temperature required for maximizing sorption and recovery can be obtained by assessing the effects of temperature. The Van't Hoff's equations is used to calculate the thermodynamic parameters of adsorption (Lima et al.,2020).

Table 5. Adsorption thermodynamic parameters

coefficient	defined
$\mathbf{K_d}$	Distribution coefficient at temperature T (L mol^{-1})
K	Adsorption equilibrium constant (dimensionless)
T	Temperature (K)
R	Global gas constant (8.314 J mol^{-1} k^{-1})
$\mathbf{\Delta S_{ads}}$	Adsorption entropy (J mol^{-1} k^{-1})
$\mathbf{\Delta H_{ads}}$	Enthalpy of adsorption (KJ mol^{-1})
$\mathbf{\Delta G_{ads}}$	Gibbs free energy in the adsorption process (KJ mol^{-1})

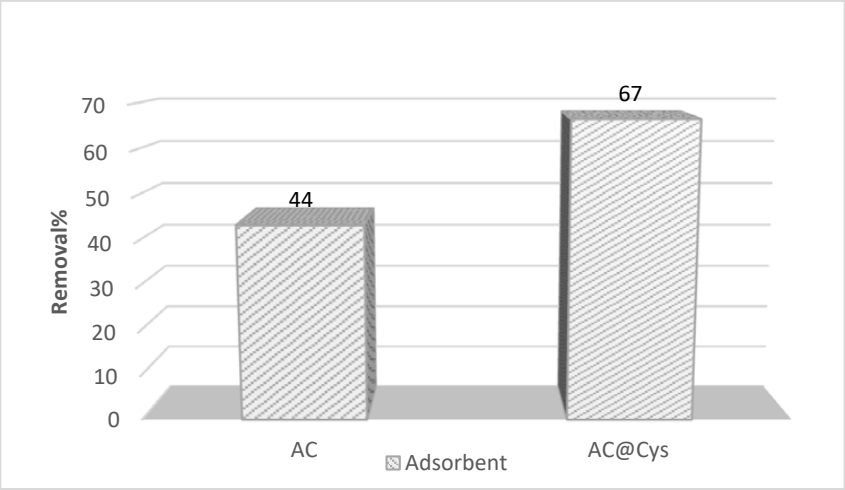

Fig 4. Diagram of the effect of surface modification on cadmium ion removal percentage (50 mL of 80 mg L^{-1}cadmium solution; pH: 6; adsorbent amount: 50 mg; contact time: 60 min; ambient temperature: 20 ℃)

$$ln\, K_d = \frac{\Delta S_{ads}}{R} - \frac{\Delta H_{ads}}{RT} \quad (5)$$

$$\Delta G_{ads} = \Delta H_{ads} - T.\Delta S_{ads} \quad (6)$$

The distribution coefficient, which is temperature-dependent, is defined as the ratio of the value of solid sorbate to sorbate concentration in the equilibrium time ($K_d = \frac{q_e}{C_e}$). ΔG_{ads} was obtained according to equation 6. After linearizing and plotting $\ln K_d$ relative to $\frac{1}{T}$, the slope ($\frac{-\Delta H_{ads}}{R}$) and intercept ($\frac{\Delta S_{ads}}{R}$) of the line were respectively considered as sorption entropy and enthalpy. Due to the temperature-dependency of ΔG_{ads}, its values were determined parametrically.

RESULTS AND DISCUSSION

Surface modification

A surface is modified when substance surface properties are insufficient for a specific application or should be improved to increase process efficiency. The surface of AC nanoparticles is modified with the materials having desired adsorption ability since they can adsorb an insignificant level of heavy metals due to great interior area, porous structure, high adsorption capacity, and surface reactivation capability (Anjum et al.,2017).

Fig. 4 depicts the adsorption amount by the adsorbent. As shown, adsorption capacity

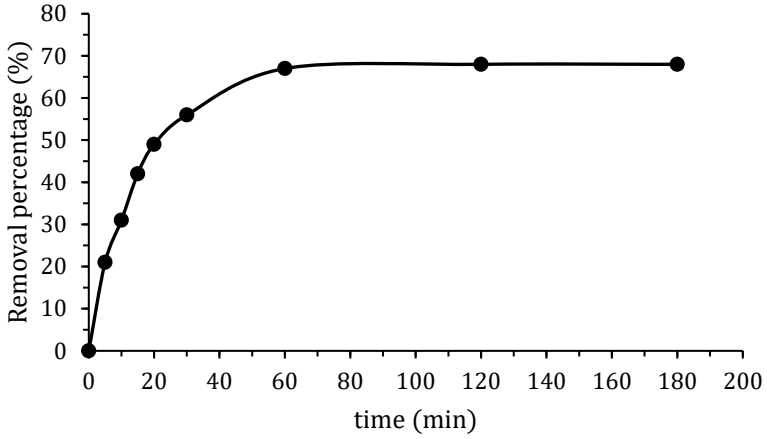

Fig 5. Diagram of the effect of contact time on cadmium ion removal percentage (50 mL of 80 mg L^{-1} cadmium solution; pH: 6; adsorbent amount: 50 mg; ambient temperature: 20 ^{O}C)

enhances following surface modification and the final adsorbent is surface-modified correctly. The surface modification mechanism by AC includes adsorption through entrapping metal ions in adsorbent pores. Physisorption is weaker than chemisorption (Fig. 4).

Optimal contact time

Equilibria time is considered as one of the critical factors in the adsorption process by the sorbent. Kinetic information is practically valuable, represents the sorption rate of sorbate on the sorbent, and controls equilibrium time. To evaluate the effect of time, all adsorption conditions were considered constant except its time. The results indicated an elevation in the AC specific area and a maximum removal percentage (70%) by raising activation time from 30 to 60 min, followed by a strong decrease in removal rate. In fact, the adsorption process is equilibrated so that no substance is eliminated over time. This behavior is related to the fact that a limited increase in activation time provides an opportunity needed to complete carbonization, and exert gases and volatiles from carbon structure. Furthermore, an enhancement in time results in improving the number of the ions competing to react with adsorbent surface functional groups, and subsequently saturating adsorption sites and promoting the contact of cadmium ions with AC, leading to the acceleration of the adsorption process. However, a further rise in heating time destroys the wall between micro-pores and declines surface area. In other words, the adsorption sites of AC are filled with cadmium metal. Accordingly, the curve becomes descending and is then fixed when equilibrium is established by increasing time.

Adsorption kinetic studies

The pseudo-first- and pseudo-second-order rate equations were applied to examine the kinetics of cadmium metal adsorption. Adsorption kinetics was analyzed to understand the adsorption dynamics of cadmium ions on adsorbent surfaces better and determine a model for estimating adsorption value with time. After matching the experimental data with those obtained from adsorption kinetic equations in Table 3 and validating, the proper kinetic model was reported for each case.

The fitness of quasi-first-order and quasi-second-order kinetic equations in the cadmium adsorption process by AC@Cys under optimal adsorption conditions is illustrated in Figs. 3 and 4, respectively. Table 6 summarizes the parameters of the intended models. The results demonstrated that a quasi-second-order model with a higher coefficient of determination (R^2 = 0.9664) and less root-mean-square-error (RMSE = 0.0712) described the experimental data

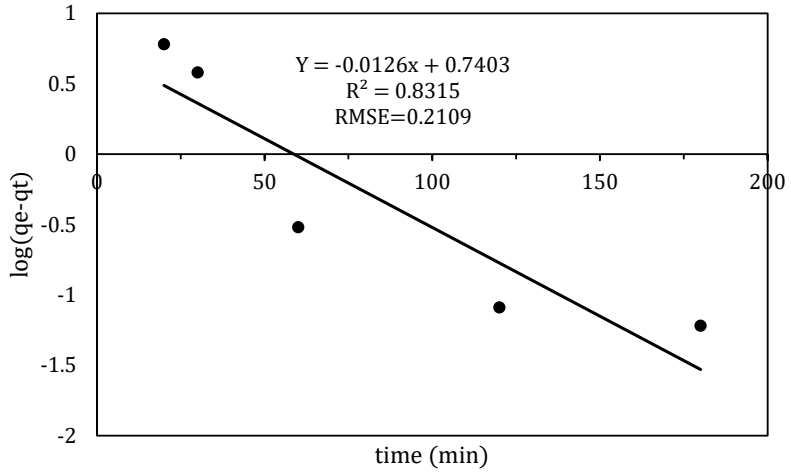

Fig 6. Diagram of quasi-first-order kinetic model for cadmium ion adsorption by C@Cys (50 mL of 80 mg L^{-1}cadmium solution; pH: 6; adsorbent amount: 50 mg; ambient temperature: 20^{O}C)

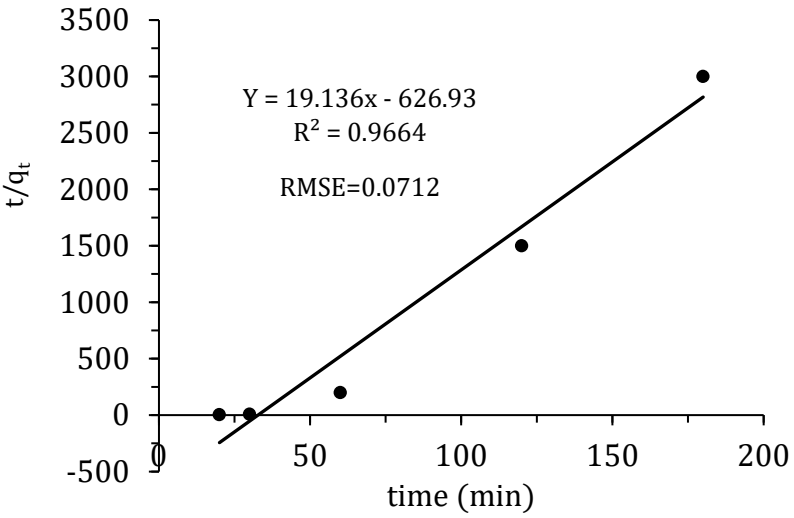

Fig 7. Diagram of quasi-second-order kinetic model for cadmium ion adsorption by AC@Cys 50 mL of 80 mg L^{-1}cadmium solution; pH: 6; adsorbent amount: 50 mg; ambient temperature: 20^{O}C)

better than another (R^2 = 0.8315, RMSE = 0.2109).

Takmil et al. focused on fluoride ion adsorption from synthetic effluent by using AC-modified magnetic nanocomposite (AC/Fe_3O_4) and determined 454.54 mg g^{-1} as the maximum ion adsorption, which is in good agreement with Freundlich isotherm and quasi-second-order kinetic models (Takmil et al., 2020). Regarding chromium removal from aqueous solution, Tamjidi and Esmaeili utilized sodium dodecyl sulfate (SDS)-modified nanocomposite and found 6.4 mg g^{-1} as the highest adsorption capacity. Their results are consistent with Langmuir isotherm and quasi-second-order kinetic models, and the process was exothermic based on its thermodynamic assessment (Tamjidi & Esmaeili, 2019). The application of Fe_3O_4/graphene oxide (GO)/clay composite to eliminate chromium from such solution led to the greatest efficiency (98.84%) and adsorption level (71.47 mg g^{-1}). Kinetic and thermodynamic studies revealed an improvement in metal adsorption behavior by the quasi-second-order kinetic and Langmuir isotherm models (Tamjidi & Esmaeili, 2022).

Table 6. Kinetic parameters of this study

Kinetic model	Parameters	Values	Unit
Pseudo-first-order	K_1	0.3	(min^{-1})
	R^2	0.8315	
	q_1		($mg\ g^{-1}$)
Pseudo-second-order	K_2	9×10^{-5}	($g\ mg^{-1}\ min^{-1}$)
	q_e	19	($mg\ g^{-1}$)
	R^2	0.9664	

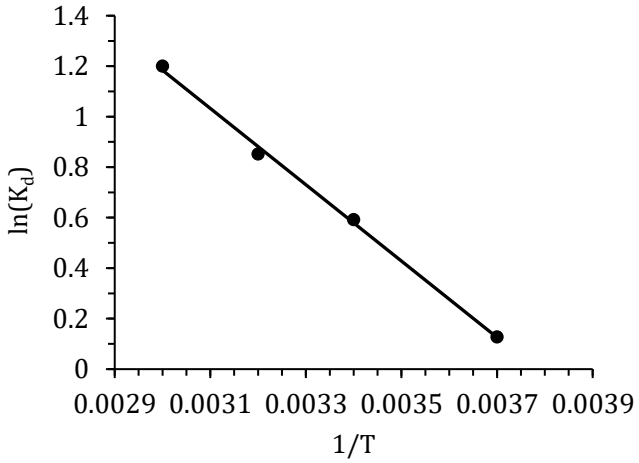

Fig 8. Thermodynamic model of Van't Hoff for cadmium ion adsorption by AC@Cys (50 mL of 80 ppm cadmium solution; pH: 6; adsorbent amount: 50 mg; contact time: 60 min)

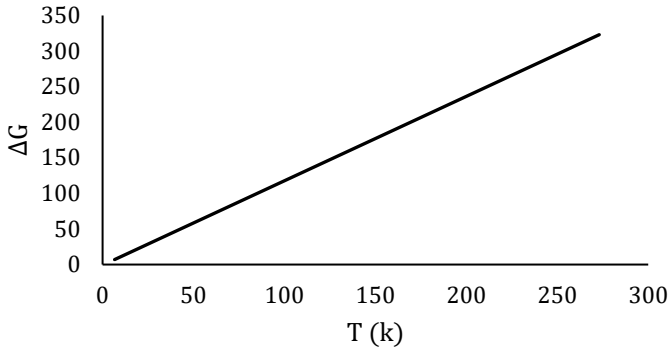

Fig 9. ΔG for cadmium ion adsorption by AC@Cys (50 mL of 80 ppm cadmium solution; pH: 6; adsorbent amount: 50 mg; contact time: 60 min)

Adsorption thermodynamic studies

Thermodynamic parameters such as Gibbs free energy, entropy, and enthalpy changes were obtained by using the Langmuir isotherm equilibrium constant at various temperatures and equations 5 and 6 (Dirbaz & Roosta, 2018). Adsorption thermodynamic functions can be calculated by drawing a thermodynamic model. As already mentioned, we have (Figs. 8 and 9):

The values of ΔS_{ads}, ΔH_{ads}, and ΔG_{ads} are presented in Table 7.

Due to the positive and relatively high level of ΔH_{ads}, the tendency of adsorbent to adsorb

Table 7. Thermodynamic parameters of the intended adsorption process

	parameters	amount
Van't Hoff's Equation	ΔH_{ads} (kJ mol^{-1})	21.43
	ΔG_{ads} (KJ mol^{-1})	ΔG_{ads}= 21.425×T+80
	ΔS_{ads} (J mol^{-1} k^{-1})	80.00

Table 8. Cadmium removal percentage in real sample

sample	Initial concentration of (ppm) cadmium	Removal percentage (%)
Contains only cadmium	80	65
Contains cadmium, cations, and electrolytes	80	48

cadmium was appropriate. In addition, the positive sign of ΔH_{ads} reflected an enhancement in entropy during the adsorption process. Based on the results in Fig. 9, as well as the ascendance of ΔG_{ads} curve versus temperature, the adsorption process was not spontaneous.

Adsorption process in the presence of other ions

In the previous steps, all samples were prepared with deionized water (a synthetic solution). Regarding adsorption in real conditions, two samples were used to determine adsorption efficiency by using the mentioned technique after eliminating cadmium and reading the remaining solution concentration. The first sample contained 80 ppm cadmium and real water solution, while another involved cadmium, lead, copper, and sodium chloride (each with 80 ppm level) to evaluate the adsorbent selectivity. Table 8 outlines the results related to removal. Further, the removal percentage was determined by using equation 1.

As shown in Table 8, the cadmium removal percentage from real samples is close to that from synthetic ones (65%), indicating the generalizability of the adsorption results to real samples. Considering the results of removal percentage in the presence of cations and electrolytes, the adsorbent had some selectivity in the real samples.

Comparison between the maximum adsorption capacities of different adsorbents

Parlayıcı et al. evaluated chromium adsorption on nano ZrO_2/TiO_2-impregnated orange wood sawdust and peach, and reported the pH of 2 and contact time of 120 min as the optimal conditions. The equilibrium adsorption data match the Langmuir and second-order kinetic models (R^2 = 0.99). Additionally, the estimated thermodynamic parameters indicated the spontaneity of the process (Parlayıcı et al., 2020). Ghaedi et al. used the AC synthesized from orange wood to remove sunset yellow, and referred to compliance with the Langmuir isotherm and quasi-second-order kinetic models with an optimal time of 10 min and an optimal removal level of 98% (Ghaedi et al., 2015). According to Reljic et al. (2022), the AC functionalized with sulfur-containing ligands has a significantly higher porosity than non-functionalized ones. They found a direct relationship between increased cadmium adsorption with the presence of the ligands, as well as an enhancement in adsorption kinetics.

The results of a study on eliminating cadmium from an aqueous environment by using cysteine-functionalized carbon nanotubes represented more cadmium removal per unit mass after elevating primary cadmium concentration (Fronczak et al., 2019). Further, the pH of 6.8, as well as compliance with the quasi-second order kinetic and Langmuir isotherm models (R^2 = 0.997) is among the important results of their study. Table 9 summarizes the results of

Table 9. Comparison between the maximum cadmium adsorption by various adsorbents

Type of adsorbent	Heavy metals	Maximum adsorption capacity(mg g^{-1})	Absorption conditions	References
Sunflower straw	Cadmium	8.905	pH=4 C_0=11 mg L^{-1}	(Sepehr & Tosan,2016)
Grape pruning residues	Cadmium	7.895	pH=8 C_0=11 mg L^{-1}	(Sepehr & Tosan,2016)
Magnetite/carbon nanocomposites	Cadmium	76.67	pH=6 C_0=10 mg L^{-1} t=25 ℃	(Andelescu et al.,2018)
Lotus seedpod-derived biochar	Cadmium	51.18	C_0=100	(Chen et al.,2018)
Chitosan-based hydrogel **Polyacrylic acid-based hydrogel**	Cadmium	234.11 192.23	pH=6 C_0=20 mg L^{-1} t=25 ℃	(Vilela et al.,2019)
Washed sunflower residue	Cadmium	8.69	pH=5 C_0=15 mg L^{-1} t=25 ℃	(Jalali & Aboulghazi,2013)
Mesoporous Cobalt-Ferrite Nanocomposite	Cadmium Cr (III)	303 217	pH=6, 7 C_0=20 mg L^{-1} t=25 ℃	(Khoshkerdar, I. and H. Esmaeili, 2019)
bentonite/Fe_3O_4 nanocomposite	Cadmium lead Nickel	9.4339 108.659 5.9808		(Ahmadi & Esmaeili 2018)
Callinectes sapidus	Cadmium lead Nickel	29.23 31.44 29.15	pH=6 C_0=10 mg L^{-1} time=60 min t=25 ℃	(Foroutan, et al 2019)
sugarcane bagasse-activated carbon	Mercury Lead Cadmium	107.75 0.625 2.425	pH=8 C_0=5 mg L^{-1} t=25 ℃	(Javidi Alsadi. & and Esfandiari 2019)
Present study	Cadmium	120	pH=6 C_0=80 mg L^{-1} time=60 min t=20 ℃	———

other similar studies. As shown, the removal percentage in the present study was desirable and acceptable compared to the other research, which is somewhat similar to the results of Fronczak et al. (2019). Furthermore, the functionalization of AC significantly affected the removal level and increase in adsorption kinetics.

CONCLUSION

AC nanocarbons are known as suitable adsorbents for eliminating metal cations from aqueous solutions, the surface modification of which is an important technique for developing

their efficiency. In the present study, AC as an expensive adsorbent was produced from orange wood by using Minitab software, followed by optimization. The factors influencing the synthesis included activation temperature and time, activating agents, and particle size. Additionally, relatively good adsorption capacity and 30 min equilibrium time, reflecting a high adsorption rate, can be a proper option for eliminating metal ions from samples.

In this study, the maximum adsorption capacity was equal to 120 mg g^{-1} adsorbent. In addition, the best cadmium adsorption efficiency was observed in the pH of 6, contact time of 30 min, primary cadmium concentration of 80 ppm, and initial adsorbent amount of 50 mg at 20 ˚C. Based on the results of the thermodynamic evaluation, entropy increased during the adsorption process. The ascendance of curve ΔG_{ads} versus temperature indicated the non-spontaneousness of the process. The adsorption kinetic studies were performed by using pseudo-first- and pseudo-second-order models. The results represented a better description of the experiment data by the quasi-second-order model with a greater regression coefficient (R^2=0.9664) compared to the quasi-first-order one (R^2=0.8315). This adsorbent exhibited good fitness with the quasi-second-order kinetic model, by suggesting chemisorption or activated surface as the adsorption mechanism of adsorbate on the adsorbate surface. The adsorption process was not spontaneous due to the entropy changes of 80 kJ mol^{-1} k^{-1}, enthalpy variations of 21.43 kJ mol^{-1}, the positivity of Gibbs free energy changes, and the ascendance of the curve of ΔG_{ads} relative to temperature. This model revealed that the process rate is determined by a chemical interaction leading to a strong binding between adsorbate and adsorbent surfaces.

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interest regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy have been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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