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Heavy metals removal from synthetic and shipyard wastewater using *Phoenix dactylifera* activated carbon

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ABSTRACT

In this study, an activated carbon was derived from *Phoenix dactylifera* (ACPD) by a newly introduced method of oil submerging and was applied to eliminate Pb(II), Cd(II), and Ni(II) from aqueous solution. At initial pH of 6, temperature of 25°C, metal ions concentration of 10 mg/L, contact time of 100 min, and biosorbent dosage of 5 g/L, the maximum removal of 94.5, 92.4, and 90.3% were attained for Pb(II), Cd(II), and Ni(II), respectively. The Freundlich model was the best model for describing the data among other studied models. A pseudo- second order model showed a better description of the results than the pseudo-first order and intra-particle diffusion models. The enthalpy, entropy, and Gibb's free energy confirmed that the biosorption processes were spontaneous and exothermic. The reusability of ACPD was repeated six times and the reduction in biosorption capacity at the 6th cycle was 3% less than the fresh ACPD. A real sample of shipyard wastewater was successfully treated using ACPD. Therefore, ACPD can be used as a suitable and affordable biosorbent for Pb(II), Cd(II), and Ni(II) ions removal from wastewaters.

Keywords: Activated carbon; Biosorption; *Phoenix dactylifera*; Kinetics study; Shipyard wastewater

1. Introduction

Heavy metals such as Pb(II), Cd(II), and Ni(II) are not degradable in the environment and can be accumulated in the ecosystems and in animal organs. Even very low concentrations of these metals are toxic and carcinogenic; therefore, they can be assumed to be a serious threat for the environment and public health [1–3]. Heavy metal ions of Pb(II), Ni(II), and Cd(II) are generally found in industrial wastewaters and considered as hazardous environmental pollutants. Ni(II) is one of the toxic and heavy metals that is usually used in the production of stainless steel, metal alloys, production of coins, paint, plating, and battery [3]. Ni(II) ions are toxic and non-degradable, causing dermatitis and allergies [4], lung cancer, pulmonary fibrosis and inflammation of the kidneys, chronic bronchitis and sinus, damage to the heart and liver, skin irritation, headaches, and respiratory tract cancer [3]. Cd(II) can cause liver and lung damage, blood pressure defects, fetal defects (teratogenic), cancer, and mutagenesis [4]. Learning and behavior disorders in children, damage to liver, kidney, heart and immune system disorders, changes in the structure of hemoglobin (anemia), infertility, blood pressure diseases, abortion, mental retardation, hepatitis, swelling of the brain (encephalopathy), lung inability, and bone damages are consequences of Pb(II) ion contamination [5]. The World Health Organization (WHO) set a maximum permissible level for Ni(II), Pb(II), and Cd(II) ions in drinking water at 0.07 mg/L, 0.05 mg/L, and 0.003 mg/L, respectively [6]. Therefore, considering the hazards of these heavy metals, they must be removed from wastewaters before entering to the environment and water bodies.

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The removal of heavy metals ions from aqueous solutions and wastewaters is performed through different physical and chemical methods such as flocculation, filtration, evaporation, chemical precipitation, oxidation/reduction, electrochemical methods, ion change, reverse osmosis, biosorption, electrolyte or extraction with liquid, and electron dialysis [7,8]. In most of these techniques, if the concentration of metal ions in aqueous solution is less than 100 mg/L, the removal of heavy metals will be costly, ineffective, and with low efficiency [9,10]. Among the above mentioned methods, the biosorption method is favorable as it is economical, simple, effective, efficient, and reversible, is cost-effective with high efficiency and high operating speed [7,8]. Biosorption immobilizes the contaminants separated from the liquid phase, whereupon the biosorbent can be removed and managed without any environment risk or contaminant; the biosorbent can then be restored using a suitable desorbent method [4].

Activated carbon is widely and successfully used to remove various heavy metals ions from an aqueous solution due to its absorptive capacity. However, this adsorbent poses many restrictions, such as non-renewability of initial materials and high product costs. In the last decade, activated carbons derived from wastes have been applied for adsorbing heavy metals ions [6]. For instance, Zhou et al. [11] have produced an adsorbent from wasted activated sludge for the purpose of removing of Pb(II) and Zn(II), while Tounsadi et al. [12] recently assessed the heavy metal removal ability of an activated carbon from *Glebioniscoronaria*. Ahmed [13] reviewed the application of the palm tree for treating many types of pollutants, such as heavy metals. He pointed out that the preparation techniques of the adsorbent from the date stone still needs to be developed for enhancement purposes of the biosorption process. Many researchers applied different techniques and activators during the production of activated carbon from the date stone, such as steam [14], CO_2 [15], acid [16,17], and alkali [18] applications. Most of the amendment methods are expensive or unpractical. Thus, finding a new amendment method with low or no cost, as well as being efficient, will lead to further application of activated carbon derived from date stone wastes. The activation of carbon usually occurred due to the escaping of volatile matter from the carbon mass. Based on this, if the volatile matter of a carbon source increases, this could lead to an increase in the surface of the resulting activated carbon and, thus, result in an efficient pollutant removal.

In the present study, the date stone of *Phoenix dactylifera* was used as a raw material for activated carbon production. The *P. dactylifera*tree is a native tree in many areas of the world, such as the Middle East and Africa; thus, its date stone can be utilized in activated carbon production as a cheap and abundant source. Many researchers have used the date stone for pollutant removal [19,20]; however, to the best of the author's knowledge, this is the first report that describes the production of activated carbon using the oil submerged method. In this research, activated carbon derived from *P. dactylifera* (ACPD) was submerged in kitchen oil wastes and used as the biosorbent for the removal Pb(II), Cd(II), and Ni(II), while the effect of different parameters, such as initial solution pH, temperature, metal ions concentrations, contact time, and biosorbent dosage on biosorption efficiency, was investigated. The kinetic, isotherm, thermodynamic study, and also field application of ACPD were also performed.

2. Experimental

2.1. Stock solution preparation

A stock solution of Pb(II), Cd(II), and Ni(II) with 1000 mg/L concentration was prepared by dissolving the amount of 1.1158 g $Pb(NO_3)_2$, 2.7442 g $Cd(NO_3)_2{\cdot}4H_2O$, and 3.4197 g $Ni(NO_3)_2{\cdot}4H_2O$ in 1 L double distilled water, respectively. In order to prepare a solution with a certain initial concentration of metal ions, the stock solution was diluted with double distilled water. The initial pH of the solution was regulated with diluted solutions of HCl or NaOH 0.1 M. All the chemicals used in this study were of analytical grade and purchased from Merck Company.

2.2. Preparation and surface analyzing of ACPD

In this study, the activated carbon was derived from the *Phoenix dactylifera* tree (ACPD). The data stones of *P. dactylifera* were prepared from a local date packaging company in Dashtestan region, Iran. The date stones were washed several times with tap water to ensure they were clean. The date stones were then soaked in sulfuric acid (100 mL, 20%) for 24 h and then rinsed with double distilled water several times to neutralize the acidity environment. In order to prepare the activated carbon, the date stones were first placed in aluminum foil in the furnace at 350°C for 2 h (which was used in the test as an unmodified biosorbent). In the next step, approximately 20 g of the nonmodified biosorbent were soaked in 100 mL kitchen oil for 6 h. After that, the oil-soaked date stones were again placed in the furnace at 500°C for 2 h. The final products were removed from the furnace and cooled down to room temperature. After cooling, the obtained materials, including the unmodified biosorbent and modified biosorbent (ACPD), were powdered with the mill and graded with a sieve No. 25 (ASTM E11) and stored at room temperature for further use.

The surface of the fresh and used ACPD was analyzed using a scanning electron microscope (SEM, Hitachi S4160 type). The surface of the biosorbent was scanned after covering the surface with a thin layer of gold and then investigated with the SEM.

The specific surface area of ACPD was measured by methylene blue. For this purpose, different concentrations of methylene blue (1–40 mg/L) were prepared for the calibration plot and concentrations were measured with a Spectrophotometer with 600 nm wavelength. Then, 1 g of prepared biosorbent was added to the methylene blue solution with 20 mg/L concentration and stirred with 200 rpm for 60 min. After that, the mixture was filtered with Whatman filter paper and the final concentration of residual methylene blue was measured. The biosorbent specific surface area was determined using the following equation [21,22]:

$$S_{MB} = \frac{C_{opt} \times A_{MB} \times A_V}{MV_{MB}} \tag{1}$$

where S_{MB} (m^2/g) is the specific surface area of the prepared biosorbent, C_{opt} (mg/mg) is the amount of methylene blue molecules adsorbed by the biosorbent, A_{MB} is the area occupied by a molecule of methylene blue, A_v is Avogadro's number (= 6.02×10^{23} molecules per mole) and MV_{MB} is the molecular weight of methylene blue (= 319.87 g/mol).

2.3. Biosorption tests design

Biosorption tests of Ni(II), Pb(II), and Cd(II) ions from aqueous solution using ACPD were performed in 200 ml Erlenmeyer flasks containing 100 mL of Ni(II), Pb(II), and Cd(II) solutions. The effects of various parameters, such as initial pH (2–10), solution temperature (25, 35, and 45°C), contact time (5–180 min), initial contaminant concentration (10–100 mg/L), and ACPD dosage (1–7 g/L) on biosorption percentage of metals ions, were investigated. In each experimental run, one of the parameters was considered as a variable, while the others were assumed to be constant. To adjust the initial pH of the samples, 0.1 M solutions of HCl and NaOH were utilized and the pH of the samples was measured with a digital pH-meter (Metrohm 744). The measurement of residual metal ions in the solution was done by a Flame Atomic Absorption Spectrometry (FAAS, Plus SpectrAA-10- Varian) equipped with acetylene-air fuel. The biosorption percentage of metal ions and biosorption capacity were calculated using Eqs. (2) and (3):

$$R(\%) = \left(\frac{C_i - C_o}{C_i}\right) \times 100 \tag{2}$$

$$q_e = \left(\frac{C_i - C_o}{W}\right) \times V \tag{3}$$

where C_i and C_o (mg/L) are initial and equilibrium concentrations of metal ions, V (L) is the volume of used solution, M (g) is the weight of the dried biosorbent, R is the biosorption percentage of heavy metals, and q_e (mg/g) is the biosorption capacity.

A wastewater sample was collected from a shipyard factory in Bushehr city, Iran. About 5 L of the wastewater was transferred within 1 h to the laboratory in a polyethylene bottle. The biosorption test was performed on this wastewater at optimal conditions.

2.4. Desorption and reuse study

A desorption study was carried out with 5 g/L ACPD and 100 mL solution containing 10 mg/L of Pb(II), Cd(II), and Ni(II) ions (each having been individually measured) at conditions of initial pH 6, mixing rate of 200 rpm, solution temperature of 25°C, and contact time of 100 min. Upon completion of the experiments, the ACPD was filtered using 42 µm-Whatman filter paper and double distilled water in order to remove extra ions deposited on the surface of biosorbent. A given amount of ACPD was mixed with 10 mL of HNO_3 solution with different concentrations (0.25–1.5 M) for 2 h. After that, the solution was filtered and the concentration of metal ions was measured using the above mentioned method. A desorption study was completed through six stages and the percentage of metal ions was determined using the following equation:

$$\%\text{ of desorption} = \left(\frac{\text{Amount of metal ions desorbed}}{\text{Amount of metal ions adsorbed}}\right) \times 100 \tag{4}$$

3. Results and discussion

3.1. Surface characteristics of ACPD

The structure and texture of ACPD, before and after the biosorption process, was measured and determined using the SEM test (Fig. 1). According to the results, surface of the ACPD before the biosorption process had many layers with limited pores, which were necessary for the process (Fig. 1a). The pores and surfaces structure of the fresh ACPD were changed after the process of Pb(II), Ni(II), and Cd(II) ions biosorption (see Fig. 1 b–d). The active surface area of the ACPD obtained was 386.2 m^2/g by the methylene blue method.

3.2. Effect of pH

The initial pH of a solution is an important factor in the biosorption process, because the hydrogen ions (H^+) content of the solution are competing to relocate on the surface of the biosorbent [23]. The initial pH of solution is effective in charge changes on the surface of the biosorbent and the ionization degree of the adsorbed material (metal ions) during the biosorption process. Fig. 2 shows the metal ions biosorption using ACPD at 25°C, initial contaminants concentration of 10 mg/L , ACPD dosage of 4 g/L, contact time of 100 min and solution pH of 2–10. This figure confirms that metal ions biosorption is low in the acidic medium and, as the initial pH increases, biosorption removal also increases. In all cases, increasing the solution pH led to an increase of metal ions biosorption. Maximum biosorption percentage of 94.55, 90.37, and 92.41% for Pb(II), Ni(II), and Cd(II), respectively was attained at solution pH of 6. At an acidic environment ($pH < 4$), the hydrogen ions content (H^+) is high and the surface of the biosorbent is surrounded by hydrogen ions. As the hydrogen ions and metal ions have similar charges, a repulsive force is formed between them and this formation prevents interplay between the adsorbent surface active sites and metal ions. Therefore, in an acidic environment, the biosorption of metal ions with ACPD is reduced and the hydrogen ion competes with metal ions to relocate the active sites.

As the initial pH increased, the biosorption percentage of metal ions using ACPD was raised. This was because negative charges on the surface of the sorbent increased and the competitive effect of H^+ decreased, therefore groups like hydroxyl, phosphate and amine on the surface of the absorbent would be carriers of the negative charge [9]. It should be mentioned that an increase in the initial pH of the solution results in the creation of various hydrolysis, which can change the relationship between active sites on the activated carbon surface [24]. At a high pH ($pH > 6$), the biosorption percentage decreased again; this was because a complex mixture of metal ions and hydroxide was formed

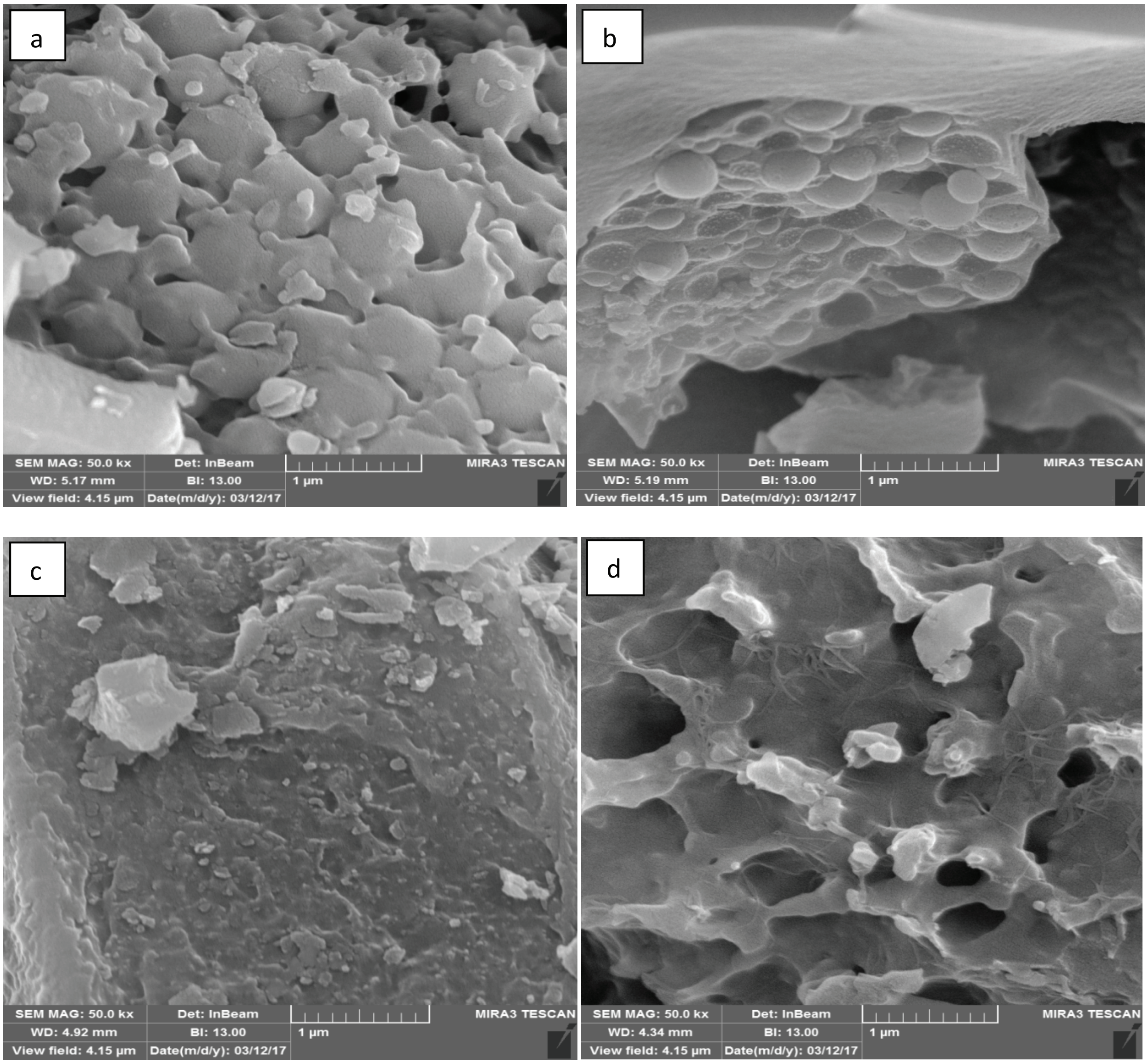

Fig. 1. SEM images of (a) fresh ACPD and ACPD after biosorption of (b) Ni (c) Pb (d) Cd.

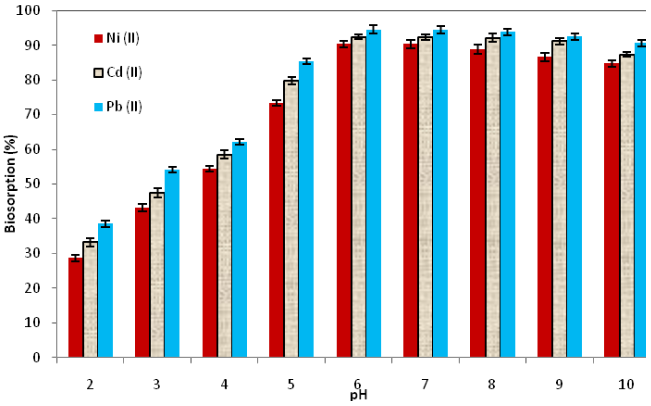

Fig. 2. pH effect on biosorption of heavy metals ions (ACPD dosage: 4 g/L, contact time: 100 min, metal ion concentration: 10 mg/L, temperature: 25 °C).

and deposited on the surface of the biosorbent, leading to a decrease in their solubility inside the solution. As a result, OH^- competes with the active site for biosorption of metal ions [23]. Most of the previous studies [25–27] for biosorption of Pb(II), Ni(II), and Cd(II) have reported that the maximum metal biosorption occurred in a solution with a pH of 5–6.5, which is similar to our study.

3.3. Effect of contact time and metal ions concentration

The biosorption rate is a significant parameter in the design of batch biosorption systems. Therefore, the contact time would be important during the process and, thus, its effect was fully investigated herein. The effect of contact time on biosorption using ACPD is shown in Fig. 3. The biosorption rate increased as the time of contact increased; this trend was observed up to a period of 100 min, which was

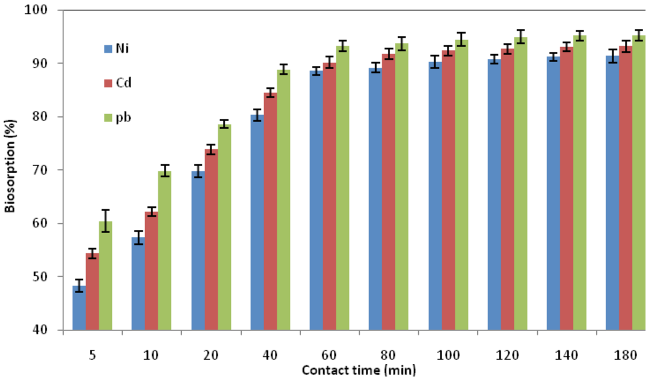

Fig. 3. Effect of time on biosorption of heavy metals ions using ACPD (ACPD dosage: 4 g/L, pH = 6, metal ion concentration: 10 mg/L, temperature: 25 °C).

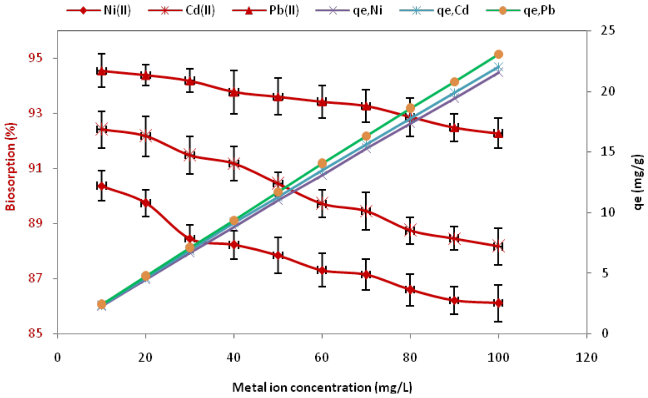

Fig. 4. Effect of initial concentration of heavy metal ions on biosorption capacity of ions (ACPD dosage: 4 g/L, pH = 6, contact time: 100 min, temperature: 25°C).

dedicated to unsaturated active sites and the availability of enough surfaces for metal ions biosorption. Accordingly, 100 min was selected as the optimum and equilibrium time of ions biosorption, and the percentage of metal ions biosorption during this time was 94.55, 92.41, and 90.37% for Pb(II), Cd(II), and Ni(II), respectively.

In batch systems, the initial concentration of metal ions in aqueous solution played an important role as the driving force of mass transfer between the solution and solid phase (ACPD) [28]. The effects of initial concentration of metal ions on the biosorption capacity are shown in Fig. 4. According to these results, the biosorption percentage of Pb(II), Cd(II), and Ni(II) ions increased as the initial concentration of metal ions increased. At low concentrations, the ratio of active sites to available ions in the solution was high; all of the metal ions interacted with the biosorbent and could be removed from the aqueous solution [29]. Remarkably, by increasing the initial concentration of metal ions, the biosorption capacity (q_m) increased and maximum biosorption capacity was determined at 23.07 mg/g, 22.04 mg/g, and 21.52 mg/g for Pb(II), Cd(II), and Ni(II), respectively (Fig. 4). Such an increase in biosorption capacity can be justified by the mass transfer driving force between the aqueous solution and solid phase, as well as the probability of collision between metal ions and biosorbent [30]. Our results have been supported by many studies [31–33].

3.4. Effect of ACPD dose and temperature

The biosorbent dosage is an important parameter from a practical point of view in the biosorption process. The biosorption percentage of Pb(II), Cd(II), and Ni(II) by ACPD at various biosorbent dosages and solution temperatures is shown in Fig. 5. According to this figure, as the biosorbent dosage increases, the removal of metal ions increases. This is mainly due to an increase in the number of active sites on the surface of the ACPD [34]. Fig. 5 confirms that, for ACPD dosages higher than 5 g/L, the adsorbed metal ions remain almost constant with no notable change. This can be explained by an aggregation of biosorbent particles and a reduction of active sites on the surface of ACPD [35]. Accordingly, the optimum biosorbent dose for the biosorption tests was considered as 5 g/L.

Temperature is another important parameter in the biosorption process of heavy metal ions. This parameter identifies the suitability of the biosorption process at different thermal conditions and shows the dependency of the biosorption capacity on the exothermic or endothermic system [35]. Fig. 5 shows the effect of temperature on the biosorption of Pb(II), Cd(II), and Ni(II) using ACPD. This figure implies that an increase in the solution temperature is accompanied by a decrease in the biosorption rate, thus proving that the process is exothermic. According to other literature [36,37], this may be due to an increased tendency of metal ions to separate from the ACPD surface and be released into the solution. Thus, among studied temperatures (25, 35, and 45°C) the solution temperature 25°C was used for further tests.

3.5. Kinetic study

In order to study the kinetics of metal ions biosorption using ACPD and better identification of the biosorption process, pseudo- first order, pseudo- second order, and intra-particle diffusion models were applied. Equations of these kinetic models are shown below [38]:

$$\text{Pseudo-second order:} \quad \ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{5}$$

where q_e (mg/g) is adsorbed metal ions in equilibrium state, q_t (mg/g)is adsorbed metal ions at each time, and k_1 (1/min) is biosorption constant.

$$\text{Pseudo-second order:} \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

where k_2 (g/mg·g)is the second order kinetics rate constant. The values of q_e and k_2 are obtained as slope and intercept of t/q_t plot versus t.

The biosorption process is a sequential process which is defined as the involvement of solute mass transfer to the biosorbent. Intra-particle diffusion plays an important role in the biosorption progression and can be described using the following equation [19]:

$$\text{Intra-particle diffusion:} \quad q_t = k_{\text{int}} t^{0.5} + I \tag{7}$$

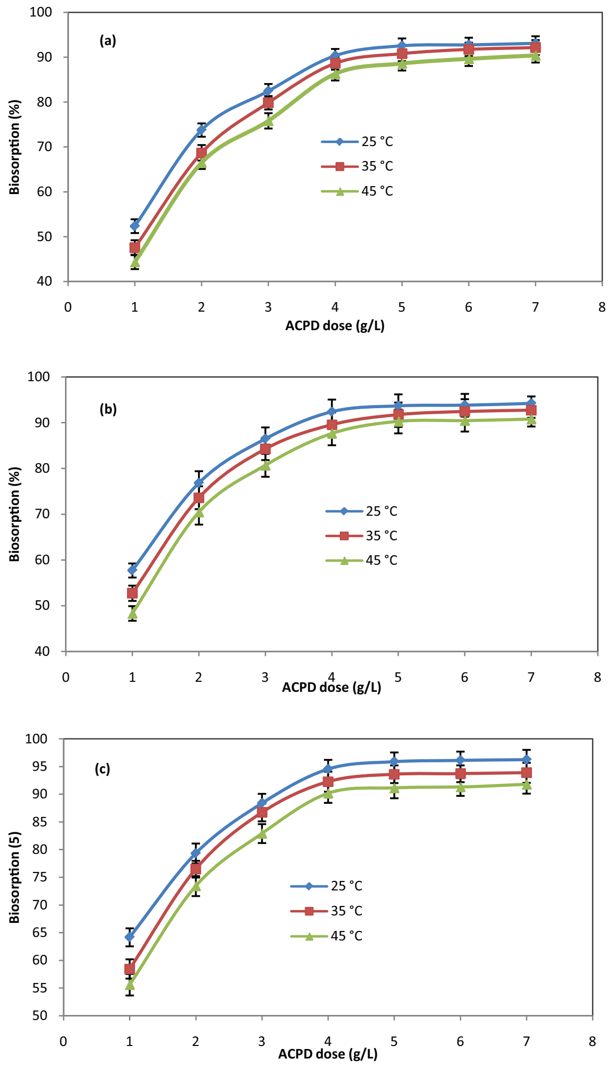

Fig. 5. Effect of biosorbent dosage and temperature on biosorption of (a) Ni(II), (b) Cd(II), and (c) Pb(II) (pH = 6, contact time: 100 min, metal ions concentration: 10 mg/L).

where k_{int} is the intra-particle diffusion constant (mg/g·min$^{0.5}$) and I is a constant (the thickness of boundary layer).

The results of the kinetics study are shown in Table 1. The results revealed that the correlation coefficient (R^2) of the pseudo- second order model is more appropriate and can describe the kinetic behavior of Pb(II), Cd(II), and Ni(II) biosorption in comparison with the pseudo- first order and intra-particle diffusion models. R^2 values for Pb(II), Cd(II), and Ni(II) biosorption by ACPD were obtained at 0.9999, 0.9997, and 0.9998, respectively. It is also noted that the biosorption capacity using pseudo- second order model ($q_{e,cal}$) is very close to experimental biosorption capacity ($q_{e,exp}$), thus confirming that the pseudo- second order model is highly consistent with experimental data rather than the two other kinetic models. This observation is in agreement with the kinetic study of heavy metals adsorption [39–41], which states that the pseudo- second order model can better describe the adsorption process.

3.6. Isotherm study

The distribution of metal ions between liquid and solid (biosorbent) phases can be described with isotherm models, including the Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) models. The Freundlich model assumes that metal ion biosorption is completed on a heterogeneous layer of a sorbent surface. This model is empirical and suitable for intermediate to high concentrations and cannot describe the behavior of solutions with low concentrations [42]. This model is described as below:

$$\ln q_e = \ln k_f + \frac{1}{n}\ln C_e \tag{8}$$

where C_e (mg/L) is the equilibrium concentration of metal ions in the solution and k_f and n are the model constants showing the relationship between biosorption capacity and biosorption intensity, respectively. The value of n is defined as the degree of deviation from the linear state. If n parameter is = 1, >1, and <1 the biosorption process will be linear, physical, and chemical, respectively [16].

Table 1
Kinetic models parameters for biosorption of Pb(II), Cd(II), and Ni(II) by ACPD

Models	Parameters	Pb(II)	Ni(II)	Cd(II)
–	$q_{e,exp}$ mg/g	2.383	2.285	2.332
Pseudo first order	k_1 (min^{-1})	0.0418	0.0393	0.0382
Pb: $y = -0.0418x - 0.0427$	$q_{e,cal}$ (mg/g)	0.958	1.203	1.026
Cd: $y = -0.0382x + 0.0261$	R^2	0.9865	0.9857	0.9912
Ni: $y = -0.0393x + 0.1849$				
Pseudo second order	k_2 (g/mg min)	0.112	0.086	0.071
Pb: $y = 0.4097x + 1.4943$	$q_{e,cal}$ (mg/g)	2.44	2.406	2.374
Cd: $y = 0.4156x + 1.9997$	R^2	0.9999	0.9998	0.9997
Ni: $y = 0.4212x + 2.4703$				
Intra-particle diffusion	k_{int} (mg/g min$^{1/2}$)	0.0737	0.0857	0.0949
Pb: $y = 0.0737x + 1.5791$	I (mg/g)	1.5791	1.3928	1.2428
Cd: $y = 0.0857x + 1.3928$	R^2	0.7974	0.8179	0.8242
Ni: $y = 0.0949x + 1.2428$				

The Langmuir isotherm model assumes that metal ion biosorption occurs on the homogeneous surface of an adsorbent layer with no interaction between the metal ions on the surface of the adsorbent [24]. The linear form of the Langmuir model is presented as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{9}$$

In this equation, q_m (mg/g) and k_L (L/g) are biosorption capacity and biosorption energy, respectively. These constant parameters can be obtained as the slope and intercept of the linear equation of C_e/q_e vs. C_e, respectively. One of the other effective parameters affirming the characteristics of the Langmuir model is biosorption intensity (R_L). This value implies the quality of biosorption isotherm model. If $R_L > 1$, $R_L = 0$, $R_L = 1$, and $0 < R_L < 1$ then the process is undesirable, irreversible, linear, and desirable, respectively [19]. The value of R_L is calculated using Eq. (10):

$$R_L = \frac{1}{1 + k_L C_0} \tag{10}$$

In addition to the Langmuir and Freundlich models, the D-R model was frequently used in previous studies. This model does not assume that biosorption is homogeneous or has potential and the ability of biosorption is constant. Besides, this model is applicable to determine the type of biosorption process (physical or chemical). The linear form of this equation is as follows:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \tag{11}$$

where β (mol²/J²) and q_m (mg/g) are D-R model constants and ε is Polanyi potential calculated by $\varepsilon = RT \ln(1 + 1/C_e)$. R is the universal gas constant (8.314 J/mol·K) and T is the absolute temperature. The constants of D-R model are determined through plotting $\ln q_e$ *vs* ε^2 and β and q_m are the slope and intercept of the plotted line, respectively.

The value of β represents the average free energy of biosorption (E) and is calculated by Eq. (12):

$$E = \frac{1}{\sqrt{2\beta}} \tag{12}$$

The amount of average free energy of biosorption determines the type of adsorption. If E is between 8 and 16 kJ/mol, the biosorption process is an ion-change type and, if E is less than 8 kJ/mol, it shows that biosorption mechanism is physical [19]:

The obtained parameters of Langmuir, Freundlich, and D-R isotherm models are shown in Table 2. The results confirmed that the calculated regression coefficient (R^2) in the Freundlich model is better when compared with other models and close to unity; this affirms that the Freundlich model can better describe the isotherm behavior of the process and also shows the heterogeneity of ACPD surface for metal ions biosorption. The calculated correlation coefficients in the Freundlich model are 0.9974, 0.9934, and 0.9967 for Pb(II), Cd(II), and Ni(II) ions, respectively. Besides this, the values of n in the Freundlich model are 1.167, 1.18 and 1.242 for Pb(II), Cd(II), and Ni(II), respectively. These values prove that Pb(II), Cd(II), and Ni(II) biosorption processes with ACPD are physical and occur on multi layers within the heterogeneous surfaces [1].

The values of R_L at various initial concentrations of metal ions are shown in Table 2. R_L value at 10–100 mg/L concentration of Pb(II), Cd(II), and Ni(II) ions are determined in the range of 0.137–0.613, 0.139–0.618 and 0.213–0.730, respectively. This parameter shows that the biosorption process of the metal ions with ACPD is appropriate and favorable. Besides this, the maximum value of the measured biosorption using the Langmuir isotherm model for Pb(II), Cd(II), and Ni(II) ions were 68.02, 50.505, and 61.349 mg/g, respectively. In Table 3, the biosorption capacity of ACPD in comparison with other different adsorbents is shown. This table indicates that ACPD contains higher capacity compared with most of the biosorbents. Therefore, the ACPD biosorbent can be used as a low-cost product in the removal of heavy metal ions from aqueous solutions and industrial wastewaters. From Table 2, the average released energy of biosorption (i.e. E parameter of D-R isotherm) for Pb(II), Cd(II), and Ni(II) is 1.244, 1.020, and 0.887 kJ/mol, respectively. These values

Table 2
Parameters of the isotherm models for biosorption of Pb(II), Cd(II), and Ni(II) onto ACPD

Models	Parameter	Pb (II)	Ni(II)	Cd (II)
Langmuir	q_m (mg/g)	68.02	61.349	50.505
Pb: $y = 0.0146x + 0.2233$	K_L (L/mg)	0.0629	0.0369	0.0618
Cd: $y = 0.0198x + 0.3199$	R^2	0.9928	0.9372	0.9818
Ni: $y = 0.0163x + 0.4417$	R_L	0.137–0.613	0.213–0.730	0.139–0.621
Freundlich	n	1.167	1.242	1.18
Pb: $y = 0.8566x + 1.4375$	K_f (mg/g (L/mg)$^{1/n}$)	4.21	3.11	2.316
Cd: $y = 0.8047x + 1.1351$	R^2	0.9974	0.9967	0.9934
Ni: $y = 0.8472x + 0.8399$				
Dubinin–Radushkevich (D-R)	E (KJ/mol)	1.244	0.877	1.020
Pb: $y = -0.0323x + 2.762$	q_m (mg/g)	15.831	13.915	14.645
Cd: $y = -0.048x + 2.6841$	$\beta \times 10^{-5}$ (mol²/J²)	0.0323	0.0657	0.048
Ni: $y = -0.0657x + 2.633$	R^2	0.8273	0.7708	0.8046

Table 3
Comparison of biosorption capacity of ACPD with various biosorbent

Biosorbent	Pb(II)	Cd(II)	Ni(II)	Reference
Macrofungus (*Lactariusscrobiculatus)*	56.2	53.1	–	[43]
Macrofungus (*Amanita rubescens)*	38.4	27.3	–	[44]
Chitosan–MAA nanoparticles	13.72	2.42	1.13	[45]
Hydroxyapatite/chitosan	12.04	–	8.54	[46]
Chitosan/magnetite	63.33	–	52.55	[47]
Modified apple pomace	178.57	112.35	51	[48]
Coconut dregs residue	9.74	–	5.86	[49]
Bacillus laterosporus	–	86.2	46.72	[50]
Carbon aerogel	34.72	15.53	–	[51]
Pomegranate peel	–	–	52.2	[52]
Olive cake	19.53	10.56	–	[53]
ACPD	68.02	50.505	61.349	Present study

Table 4
Thermodynamic parameters for biosorption of Pb (II), Cd (II), and Ni (II) onto ACPD

Metal	K_D			$\Delta H°$ (KJ/mol)	$\Delta S°$ (J/mol.K)	$\Delta G°$ (KJ/mol)		
	298.15 K	308.15 K	318.15 K			298.15 K	308.15 K	318.15 K
Pb(II): $y = 3.8619x - 11.43$	4.641	2.934	2.057	–32.107	–95.029	–3.804	–2.757	–1.907
Cd(II): $y = 2.2128x - 6.3514$	2.959	2.2242	1.857	–18.397	–52.805	–2.689	–2.048	–1.637
Ni(II): $y = 2.2261x - 6.5505$	2.488	1.978	1.555	–18.507	–54.46	–2.259	–1.747	–1.167

confirm that the metals' biosorption process using ACPD is physical as E value is < 8 kJ/mol [41].

3.7. Thermodynamic study

Thermodynamic parameters, such as enthalpy ($\Delta H°$), entropy ($\Delta S°$) and Gibb's free energy ($\Delta G°$) for Pb(II), Ni(II), and Cd(II) biosorption onto ACPD, were determined at different temperatures (298.15–318.15 K). The thermodynamic parameters are calculated using the following equations [36]:

$$\Delta G° = -RT \ln K_c \tag{13}$$

where R is universal gas constant (8.314 J/mol·K), T is absolute temperature in Kelvin and K_C is equilibrium constant. The value of equilibrium biosorption constant is determined with Eq. (14) [37]:

$$K_c = \frac{C_A}{C_S} \tag{14}$$

where C_A (mg/L) is the amount of adsorbed metal ion on the surface of the biosorbent at equilibrium condition, and C_S (mg/L) is the residual metal ion in the solution at equilibrium condition.

To determine the thermodynamic parameters of enthalpy ($\Delta H°$) and entropy ($\Delta S°$), the following equation is used:

$$\ln K_C = \frac{-\Delta G°}{RT} = \frac{-\Delta H°}{RT} + \frac{\Delta S°}{R} \tag{15}$$

The values of $\Delta H°$ and $\Delta S°$ are calculated as slope and intercept of ln K_C *vs* 1/T graph (Table 4). Thermodynamic parameters of Pb(II), Cd(II), and Ni(II) biosorption process with ACPD are shown in Table 4. Gibb's free energy in all solution temperatures and for three types of metal ions was a negative value, affirming that the process was desirable and spontaneous. By increasing the temperature, the Gibb's free energy values were decreased, which show that the degree of spontaneous biosorption was also decreased. The value of $\Delta S°$ for Pb(II), Cd(II), and Ni(II) biosorption was –95.029, –52.805, and –54.46 J/mol·K, respectively. The negative value of $\Delta S°$ implies that random collisions between the solid surface (ACPD) and adsorbate is reduced during the biosorption process. Enthalpy values of the biosorption process for metal ions of Pb(II), Cd(II), and Ni(II) was –32.107, –18.397, and –18.507 kJ/mol, respectively, which confirms that the biosorption process is exothermic and physical in this study, as $\Delta H°$< 40 kJ/mol [54].

3.8. Desorption and reusability

A desorption study of ACPD was performed by HNO_3 solution at different concentrations (0.25–1.5 M), the results are shown in Fig. 6. This figure reveals that increasing the concentration of HNO_3 results in an increase in desorption percentage of Pb(II), Cd(II), and Ni(II) from the surface of ACPD; this trend is observed up to 1 M concentration. At higher concentrations, the percentage of desorption did not change significantly. Therefore, 1 M HNO_3 was selected as optimum concentration of desorption process, which was 95.34, 96.33, and 95.05% for Pb(II), Cd(II), and Ni(II), respectively.

Fig. 7 shows the reusability ability of ACPD for Pb(II), Cd(II), and Ni(II) biosorption in aqueous solution after six stages of adsorption-desorption. A decrease in biosorption capacity of ACPD for all three metals was less than 3%, indicating that a decrease in biosorption capacity was negligible during the biosorption-desorption process. This also confirms that ACPD can be restored for Pb(II), Cd(II), and Ni(II) biosorption without a considerable decrease in biosorption capacity. The reusability ability of the ACPD for metals removal was much higher than that of *phoenix dactylifera* seeds for dye adsorption [55] and waste-date stones for Cr(VI) adsorption [56], which was mainly due to the method of the biosorbent preparation.

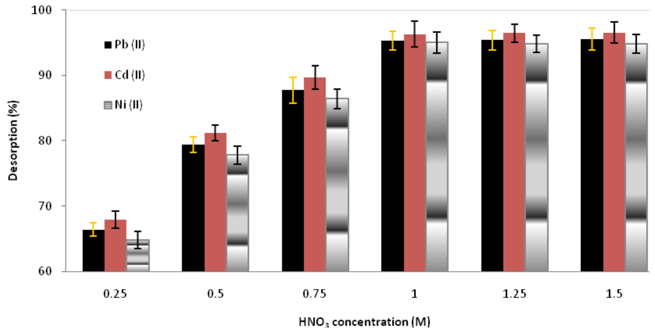

Fig. 6. Effect of HNO_3 concentration on Pb(II), Cd(II), and Ni(II) desorption.

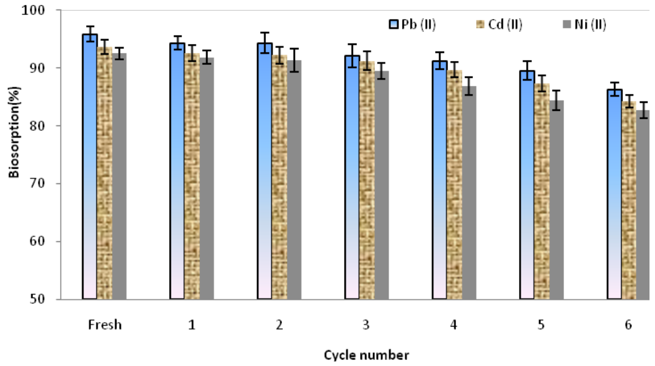

Fig. 7. Reusability of ACPD with repeated adsorption–desorption cycle (pH = 6, ACPD dosage: 5 g/l, initial concentration: 10 mg/L, temperature: 25°C).

Table 5

Treatment of the shipyard wastewater by ACPD (ACPD dosage: 5 g/L, pH = 6, contact time: 100 min, temperature: 25°C)

Component	Original value	After treatment
pH	6.38	6.4
COD, mg/L	188	59
Ni (II), mg/L	15.7	1.6
Pb (II), mg/L	9.4	0
Cd (II), mg/L	21.5	1.8
Alkalinity, mg/L $CaCO_3$	840	831

3.9. Comparison of unmodified biosorbent and ACPD

The unmodified biosorbent and ACPD were compared for their metals biosorption efficiency at optimal conditions (pH: 6, biosorbent dose: 5 g/L, metal concentration: 10 mg/L, temperature: 25°C). The biosorption efficiency of Pb(II), Cd(II), and Ni(II) by unmodified biosorbent and ACPD was obtained at 67.4, 65.7, and 62.3% and 94.5, 92.4, and 90.3%, respectively. The difference between these two types of biosorbent could be explained by their surface area, which obtained 30.98 and 386.2 m^2/g for unmodified biosorbent and ACPD, respectively. The surface area of ACPD was more than 10-fold greater than that of the unmodified biosorbent. This observation confirmed the oil submerging method is an alternative for increasing the surface area of the adsorbent and, consequently, their removal efficiency.

3.10. Real wastewater treatment

Upon completion of the optimization tests, a bulk of real wastewater was sampled from the shipyard plant in Bushehr city, Iran. The wastewater was treated by the prepared biosorbent under optimal conditions and the results are presented in Table 5. From Table 5, it is clear that the concentration of Pb(II), Cd(II), and Ni(II) was decreased by about 100, 91.6, and 89.8%, respectively, after being treated by ACPD. Further, it could be noted that the COD parameter was also decreased under its standard value for discharge to the water bodies (i.e. 60 mg/L). Thus, all the evidence implied that the ACPD biosorbent is an efficient and empirical method for eliminating the wastewaters containing heavy metals.

4. Conclusions

In the present study, the activated carbon derived from *Phoenix dactylifera* (ACPD) using a new method of oil submerging was produced for treating of Pb(II), Cd(II), and Ni(II) ions from aqueous solutions. The following conclusions could be derived:

- The optimum conditions for Pb(II), Cd(II), and Ni(II) ions removal using ACPD was obtained as pH of 6, a temperature of 25°C, initial concentration of metal ions of 10 mg/L, contact time of 100 min, and ACPD dose of 5 g/L.

- The results showed that the pseudo- second order model can better describe the kinetic behavior of the process compared with the other two models (pseudo- first order and intra-particle diffusion).
- The Freundlich isotherm model could better define the equilibrium data than other studied models.
- Thermodynamic parameters of enthalpy, entropy, and Gibb's free energy showed that the process of metal ions biosorption was possible, spontaneous, and exothermic.
- After the 6th usage of the ACPD for Pb(II), Cd(II), and Ni(II) ions biosorption, it preserved the efficiency with a maximum 3% lower than the efficiency of the fresh one.
- The shipyard plantwastewater was successfully treated by ACPD.

Hence, it could be concluded that the prepared biosorbent is an affordable andefficient alternative for treating heavy metals-laden wastewaters.

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