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Kinetics and equilibrium study of adsorptive removal of cadmium ions from aqueous solutions by utilizing lime peel as a biosorbent

Mohammad Kazem Saberian[a], Ali Kargari[b,*], Mansooreh Soleimani[b], Mohammad Amin Alaei Shahmirzadi[b], Elham Mofarrah[b]

[a]*Applied Chemistry Group, Islamic Azad University, Omidieh Branch, Omidieh, Iran, Tel.: +98 21 64543197; email: saberian_mk@yahoo.com*
[b]*Department of Chemical Engineering, Amirkabir University of Technology (Tehran Polytechnic), Tehran, Iran, Tel.: +98 21 64543197/+98 21 66405847; email: kargari@aut.ac.ir/ali_kargari@yahoo.com (A. Kargari), Tel.: +98 21 64543152; email: Soleimanim@aut.ac.ir (M. Soleimani), Tel.: +98 912 2312634; email: amin.alaei@yahoo.com (M.A. Alaei Shahmirzadi), Tel.: +98 21 64543170; email: mofarrah@aut.ac.ir (E. Mofarrah)*

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ABSTRACT

This work investigates the potential of utilizing lime peel wastes as a low-cost adsorbent for the adsorption of cadmium ions from aquatic media. The batch system was employed for determining the adsorption performance and optimum operating conditions and parameter values such as feed concentration, adsorbent concentration, the adsorbent particle size, contact time, and initial pH for the feed. The Langmuir, Freundlich, Dubinin–Radushkevich, and Sips isotherm models were examined to evaluate the adsorption results. Regression analysis indicates that the adsorption data is well-fitted to the Freundlich isotherm. Moreover, kinetic analysis of obtained data was carried out using three models including pseudo-first-order, pseudo-second-order, and, Weber–Morris intraparticle diffusion. The pseudo-second-order model fitted the experimental data better than the others. According to thermodynamic analysis, the adsorption of cadmium on lime peel was found to be spontaneous and endothermic. The removal percentage of cadmium reached 90% which proves that lime peel wastes have great potential to be employed as biosorbent for cadmium separation from aqueous media. The regeneration of the loaded adsorbent showed that 77.8% ± 1.6% of the cadmium adsorbed on the adsorbent could be recovered by contacting the adsorbent with a 0.1 M HCl solution after four adsorption–desorption cycle.

Keywords: Cadmium; Adsorption; Lime peel wastes; Kinetics; Adsorption isotherm

1. Introduction

Heavy metals are defined as the metallic elements in the periodic table, in groups 3–16 that are in periods 4 and higher which their atomic weight is in the range of 63.5 and 200.6 g/mol [1,2]. Various toxic heavy metal ions are discharged through some industrial plants such as metal plating, paper, and fertilizer industries, and constitute one of the major causes of water pollution. Heavy metals are not degraded and may enter the human body through different pathways such as the food chain or drinking water, resulting in health and environmental problems [3]. The most observed toxic heavy metals in industrial wastewaters include zinc (Zn), copper (Cu), arsenic (As), nickel (Ni), mercury (Hg), cadmium (Cd), lead (Pb), and chromium (Cr). Cd is considered a very hazardous material for both environment and the human body because it interferes with iron metabolism [4].

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[*] Corresponding author.

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Wastewaters containing heavy metal could be treated through several processes such as flotation, photocatalysis, chemical precipitation, membrane filtration, electrodialysis, co-precipitation/adsorption, ion exchange, coagulation, and flocculation.

Most of the conventional methods have several drawbacks such as high cost because these processes consume a high quantity of energy and chemicals as well as cause secondary pollution of hazardous sludge formation, and low removal efficiency when heavy metal concentration is low. Nevertheless, the adsorption process showed numerous advantages over the conventional process in wastewater treatment including low cost, simplicity of design, and operation [5].

The biosorbents based on agricultural wastes could be employed in wastewater treatment applications around the world. This type of adsorbent have taken into the consideration due to its abundance and low cost, and suitable chemical and physical properties [6,7]. The most common agro-based adsorbents reported in the literature are potato peels, coconut shells, orange peel, sawdust, black gram husk, sugarcane bagasse, rice husk, eggshell, seed shells, coffee husks, oil palm shells, sugar-beet pectin gels, etc. [8].

Among different types of agricultural wastes, the peels of fruits, especially Citrus, could be served as an efficient biosorbent for the adsorption of contaminants especially heavy metal ions because of having different functional groups that can improve the sorption efficiency. Utilization of fruit peels as adsorbent has two benefits compared to conventional ones: (1) the volume of the adsorption column could be decreased, and (2) obtained biosorbent can adsorb pollutants from wastewater at a reasonable cost [5]. Annadurai et al. [9] used banana and orange peels to investigate their efficiency in heavy metal removal from aqueous solution. The amount of heavy metal adsorption increased in the order of Pb^{2+} > Ni^{2+} > Zn^{2+} > Cu^{2+} > Co^{2+} for both adsorbents with increasing pH and remained constant at pH > 7 that is in consistency with zeta potentials. Li et al. [10] prepared a biosorbent from orange peel cellulose to remove Cd^{2+} from wastewater. The peel was modified by different methods including washing, alkali saponification, cross-linking by temperature, and citric acid as the reagent. The ion sorption capacity improved with an increase in the cross-linking temperature and the maximum capacity took place at 80°C. Citric acid and cellulosic hydroxyl groups of orange peels form an ester group and enhance the chemical complexation between biosorbent and cadmium cation. Saikaew and Kaewsarn [11] prepared argo-based adsorbent from fruit peel wastes of corn, durian, pummelo, and banana. The adsorption removal of adsorbents is in the order of banana peel > durian > pummelo > corn peels. Fourier-transform infrared spectroscopy (FTIR) showed that fruit peels have carboxyl, hydroxyl, and amide groups on their surface, which provides a binding site for cadmium ion removal. Husoon et al. [12] investigated the ability of argo-based adsorbents (orange and lemon peels) to remove copper and lead from wastewater effluent. Lemon peels had a higher capability than orange ones. Recently, Saha and Saha [13] studied the biosorption capacity of mango leaves (*Mangifera indica*) for the adsorption of hexavalent chromium from wastewater. FTIR spectroscopy indicated the existence of –OH, C=O, and C–O groups on the adsorbent surfaces that provides significant interactions and chemical binding with chromium ions.

The FTIR spectrum of lime peel indicates the existence of alcohols and phenols functional groups, which can react with cations (Cd in the present study) and form a complex [14]. Since the lime peels are free of charge and abundant in Fars Province, Iran (about 180,000 tons of lime are produced annually), they can be used for heavy metal removal only by drying the peels and without further purification. The management of lime peel wastes is a crucial environmental problem for lime processing industries. Applying the lime peel as a biosorbent for heavy metal removal is an attractive alternative to conventional treatment methods and has twofold benefits for the environment.

Lime peel is produced in large amounts as a by-product in lemon juice-producing factories during a short period (nearly from September to the end of November). Although there are some applications for the lime peels like extracting lime flavor and pectin, they need complex facilities that usually could not be found in these factories. On the other hand, the lime peels could not be used as feed for the animals because of very its bitter taste and deep flavor. Then, the lime peels are usually landfilled which is harmful because it acidifies the soil. Therefore, finding a method for using the lime peels in large volumes seems to be important. For the application of lime peel as a biosorbent, they need just to be washed, dried, and grind without further processing. To the best of our knowledge, the present study is one of the first attempts where lime peel has been employed as an efficient and novel biosorbent for cadmium removal because of biodegradability, non-toxicity, and presence of cellulose connected by β 1–4 bonds on the surface of the lime peel which acts as agent for the formation of the complex via metal ions. Low-cost adsorbents like lime peels are of interest for application as biosorbents because they need to be pretreated and are also available in large amounts. Research in this field is currently done by several research teams over the world.

The present work aims to evaluate the adsorption capacity of Darab (A region in Fars Province, Iran) domestic lime peel wastes as a bioadsorbent for the removal of Cd^{2+} ions from aquatic media. The effects of important and affective parameters such as feed concentration, feed pH, operating temperature, adsorbent loading, and particle size on the removal efficiency of cadmium ions are considered. The equilibrium and kinetic experiments are performed and various models for the equilibrium and kinetic behavior of the adsorbent are investigated.

2. Experimental set-up

2.1. Materials

The stock feed solution (1,000 mg/L cadmium) was prepared by dissolving 2.744 g of the reagent grade cadmium nitrate tetrahydrate ($Cd(NO_3)_2{\cdot}4H_2O$ from Merck & Co., Germany) in double-distilled water. The feed solutions were prepared by dilution of the stock solution to the desired concentration with double distilled water. Reagent grade sodium hydroxide (NaOH) and hydrochloric acid (HCl), both from Merck & Co., Germany, were used for adjustment of the feed solutions' pH value at the desired values.

2.2. Apparatus

A digital vacuum oven (Model VO 400, Memmert, Germany) was used to dry the washed lime peels. Also, a laboratory mill (A11 Basic Analytical Mill, Ika, Germany) and a laboratory screen shaker system (Haver/W.S.Tyler® Test Sieve Shakers, Model Haever EmL 200 digital plus Haver & Boecker, Germany) equipped with the stainless steel screens were employed to ground and classify dried lime peels, respectively. The pH of the solutions was measured by a precision pH meter (inoLab® pH 7110, WTI, Germany). The temperature of the solution was adjusted by a digital thermostatic water bath (Model WNE-14, Memmert, Germany) during the contact of the feed and the adsorbent. The cadmium concentration in the desired aqueous solutions was determined using an Atomic Absorption Spectrophotometer (AAS) (Model AAnalyst 300, PerkinElmer, Waltham, Massachusetts, USA). Moreover, the nitrogen adsorption–desorption technique was applied to measure the pore features of the adsorbent including surface area, pore size, and pore volume by Brunauer–Emmett–Teller (BET) isotherms. These data were obtained using a QUADRASORB Analyzer (Quantachrome Instruments, USA) at 70°C. The FTIR spectra were used to determine the types of functional groups in the chemical structure of lime peel as well as possible interactions between adsorbent and adsorbate. A Thermo Scientific™ Nicolet™ iS10, Smart iTX model (Thermo Fisher Scientific Inc., USA) was employed in the range of 400–4,000 cm^{-1}. The morphology of lime peel before and after the adsorption experiment was observed using field emission scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDX) apparatus (FEI SEM QUANTA 200 EDX EDS SILICON DRIFT 2017, USA) at an excitation voltage of 25 kV. Samples were sputter-coated with a thin layer of gold under a vacuum in the COXEM PVD Sputter Coater (South Korea).

2.3. Collection and preparation of adsorbent

The waste lime peels were collected from the local fruit orchards in Darab, Fars Province, Iran. They were first cut into small pieces, then washed several times until the pH reached neutral, and finally dried in the vacuum oven at 80°C for a day. The dried lime peels were grounded in a laboratory mill and classified by a laboratory vibrating screen. Different mesh sizes according to ASTM-E11 (–18 + 35, –35 + 40, –40 + 70, –70 + 140) were collected and kept in a desiccator to prevent the sample from gathering moisture.

2.4. Adsorption experiments

The biosorption of Cd ions onto the prepared adsorbent was performed in batch mode. In each experiment, an Erlenmeyer containing 500 mL of cadmium solution with a predetermined concentration and adjusted pH, was placed in the water bath and stirred by a magnetic system until the desired temperature. Then, the desired amount of the adsorbent powder with known mesh size was added to the solution under stirring. The uniform samplings were performed at different times until equilibrium was established. The adsorbent was separated from the aqueous solution using a fine filter (Whatman™ No. 42), and the concentration of Cd ions was measured using analysis of the left-over solution by AAS. The effect of various parameters such as initial cadmium concentration (5–40 mg/L), adsorbent concentration (3–15 g/L), adsorbent mesh size (four mesh sizes), adsorption temperature (293–323 K), and contact time (3–36 h) was studied in different experiments. To minimize the error and evaluate the repeatability of the measurement, each experiment was repeated three times, and the arithmetic average results are reported. The removal efficiency of the cadmium ions [R (%)] and the amount of Cd uptake at equilibrium (q_e) (mg/g) were calculated as follows:

$$\text{Removal}(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

$$q_e = \frac{C_0 - C_e}{m} V \tag{2}$$

where C_0 and C_e are the initial and equilibrium adsorbate concentration in solution (mg/L), respectively; m is the dried mass of the used adsorbent (g), and V is the volume of adsorbate solution (L).

2.5. Desorption experiments

To examine the regeneration of the adsorbent, the adsorbent samples were washed using an HCl solution. first, 10 g/L of saturated lime peel was added into the Erlenmeyer containing 500 mL of 0.1 M solution of HCl before shaking at 20°C for 120 min finally, the centrifugation method was applied to separate the liquid and solid phases (5 min at 3,000 rpm). The concentration of cadmium ions was measured before and after desorption experiments using the Atomic Absorption Spectrophotometer (AAS).

2.6. Determination of zero-point charge

The pH_{zpc} of lime peel was determined using the solid addition method which is proposed in the literature [15,16]. First, 50 mL of 0.01 M NaCl solution was added into a 100 mL Erlenmeyer. The pH of the sample was adjusted in the range of 2–10 by the addition of 0.1 M HCl or NaOH solution. the initial value of pH was measured using a digital pH meter. Next, 0.1 g of lime peel adsorbent was added into Erlenmeyer, then underwent rigorous shaking for 48 h. finally, the final pH of the solution sample was measured and plotted against the initial pH. The pH at which the curve crossed the line initial pH = final pH was considered as pH_{zpc}.

3. Results and discussion

3.1. Characterization of biosorbent

The FTIR spectrum of lime peel powder and its spectral characteristics before and after the cadmium adsorption experiment are shown in Fig. 1, to confirm the presence of functional groups in the lime peel chemical structure before and after cadmium adsorption.

These functional groups can greatly affect the chemical reactivity and adsorption capacity of the biosorbent. The lime peel powder showed a peak at 3,430.90 cm^{-1},

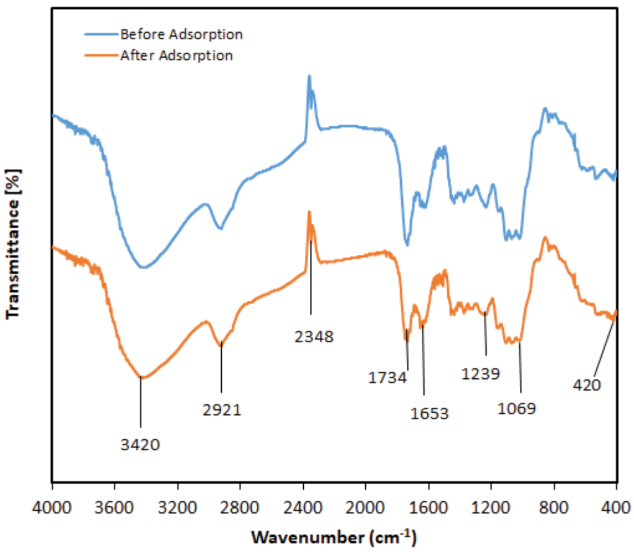

Fig. 1. Fourier-transform infrared spectrum for the lime peel powder before and after cadmium adsorption.

indicating alcohol and phenol functional groups with the presence of the O–H stretch bond. The presence of peaks at 2,929.42 cm^{-1} represents the C–H stretch of the alkane group. The peak at 1,760–1,690 cm^{-1} and the peak at 1,320–1,210 cm^{-1} show the C=O stretch and C–O stretch of the carboxylic acids. These carboxylic functional groups could be originated from the pectin present in the lime peel. The peaks at 1015.52, and 1103.64 cm^{-1} are ascribed to C–N stretching vibrations in the aliphatic amine [11,17].

The FTIR spectrum displays that lime peel powder consists of hydroxyl groups, which have a high affinity towards heavy metals (especially cadmium in the present study). After contacting the adsorbent with the cadmium solution at pH 6.0, the adsorbent was filtered, washed, dried, and analyzed again by FTIR. The transmittance spectrum shows that peaks at 1,760–1,690 cm^{-1} and the peak at 1,320–1,210 cm^{-1} are the carboxylic acids characterization peaks that have been subjected to change indicating the formation of the ligand of –COOH through the affinity between the cadmium ions and the–COO– through the chemical bonding rather than only through the van der Waals forces [11,18].

Surface area and pore size are the main parameters for characterizing the adsorbent. The multipoint BET and single point BET surface areas were found to be 28.50 and 5.28 m^2/g, respectively. Moreover, the pore volume and pore diameter of the lime peel biosorbent was obtained to be 0.0173 cc/g and 38.3 Å, respectively. These results are similar to values reported in the literature for some biosorbents [19,20].

SEM image and EDX spectrum of lime peel adsorbent before and after adsorption of Cd^{2+} ions are shown in Fig. 2. It is clear that the surface of lime peel adsorbent has a disorganized and porous surface containing pores, edges, cavities, and corners of different sizes and shapes. After the adsorption of Cd^{2+} ions from an aqueous solution, there is a significant change in the SEM micrograph of the adsorbent. The pores and cavities of the adsorbent are clogged and covered by ions. Furthermore, the EDX result also indicated that carbon and oxygen are the main constituents of the adsorbent. Furthermore, the presence of a Cd peak in EDX analysis as well as surface features of the adsorbent confirmed the Cd^{2+} ions adsorption onto the lime peel. The Cd elemental mapping displayed the uniform adsorption of Cd ions on biochar due to the surface homogeneity.

3.2. Effect of contact time

The adsorption of cadmium on biosorbent was carried out at several contact times (t_c) to determine its optimum value and the results are shown in Fig. 3. Contact time is known as an important parameter because of its superb effect on energy optimization. The results demonstrate that Cd^{2+} ion removal using lime peel is a relatively slow process, and the removal efficiency reached a maximum value of 90% after 36 h. At the beginning of the adsorption process, the initial adsorption rate was high (more than 80% removal within less than 3 h). This is because a large fraction of adsorption sites are accessible at the surface of the adsorbent (the surface area of the raw lime peel is about 5.70 m^2/g based on BET data) providing a high chance for the cadmium ions to adsorb on the external surface of the adsorbent. As soon as the surface adsorption sites are approximately saturated, the adsorption process continues within both either pores or the internal structure of the adsorbent through the intraparticle diffusion mechanism [21]. The BET results revealed that no considerable pore and internal area are accessible for this adsorbent.

For the systems that need long times to reach the equilibrium, there are several solutions: (1) The use of a multistage adsorption system (preferentially counter-current) in which the feed solution is passed through the first stage and after a certain time of contact it is sent to the second stage to become in contact with the adsorbent with a different condition, (2) The use of counter-current cascade systems in which the feed is contacted with the adsorbent in a continuous counter-current system where the system never reaches to equilibrium.

3.3. Effect of feed pH

The efficiency of ion adsorption is significantly influenced by the pH of the feed solution and the results are illustrated in Fig. 4a. In addition, the pH_{zpc} of lime peel was determined using the solid addition method (Fig. 4b), described in the 2.6 section. The pH_{zpc} of the lime peel was obtained at about 3.06 which is in good consistency with literature that reported the pH_{zpc} of lime peel and citrus about 3–4 [22,23]. Therefore, the charge of lime peel is negative and positive above and below of pH_{zpc}, respectively, which has a great impact on the adsorption of ionic species from an aqueous solution.

The dominant form of cadmium ions in aqueous solutions is the form of Cd^{2+} and the divalent cadmium cations are bonded to the active surfaces of the adsorbent through the functional groups such as $(–O–O–)^{2-}$ that release H^+ into the solution.

$$\mathrm{Ar(OH)_2 + M^{+2} + H_2O \rightarrow ArO_2M + 2H^+ + H_2O} \tag{3}$$

where Ar is a functional group, such as the carboxylic groups of polysaccharides, the alcohols or phenols functional

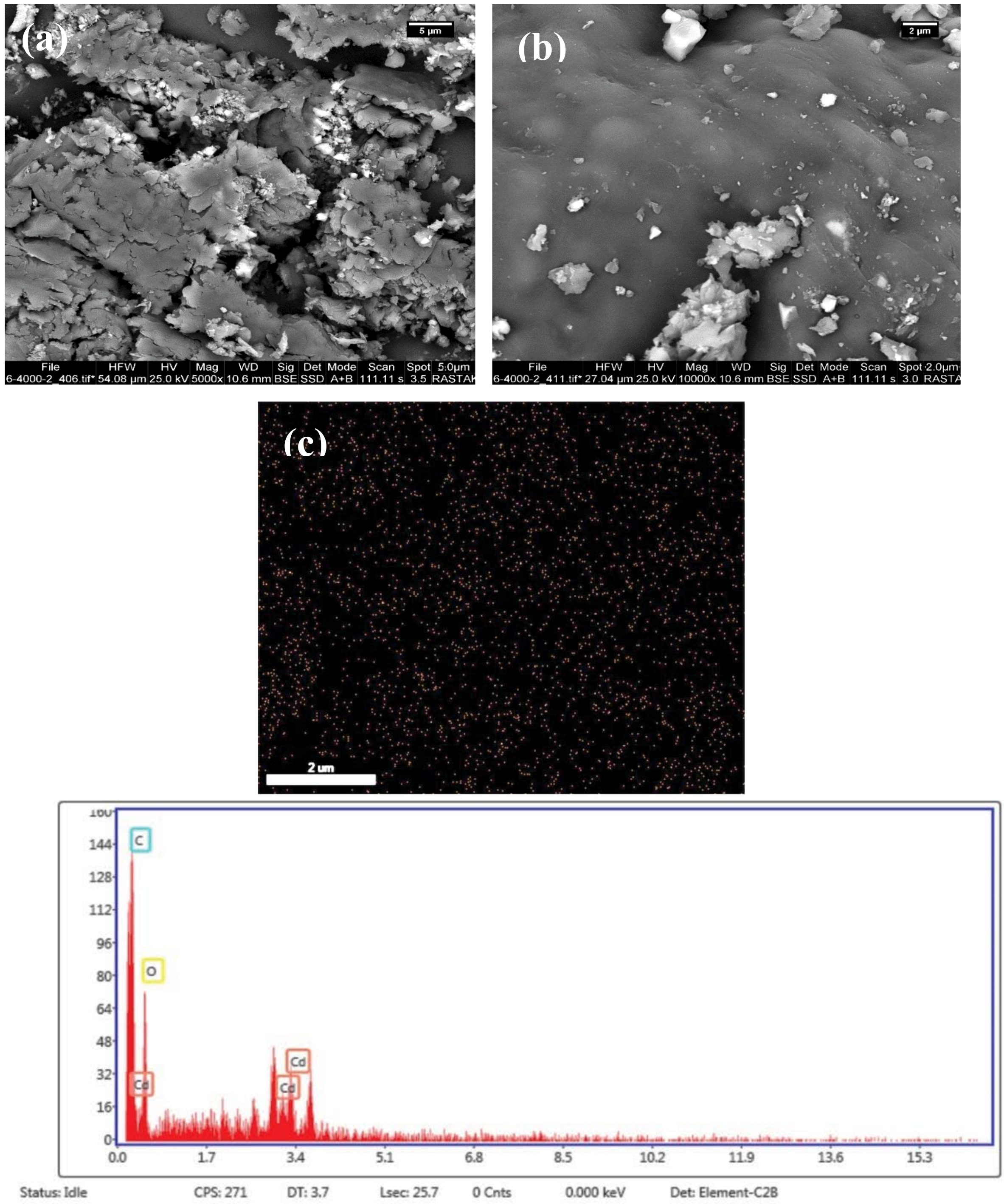

Fig. 2. Scanning electron microscopy-energy-dispersive X-ray spectroscopy analysis of the lime peel. Scanning electron microscopy image of the lime peel (a) before and (b) after adsorption of Cd(II) ions, (c) energy-dispersive X-ray spectroscopy-mapping for cadmium element on the lime peel powder after cadmium adsorption.

groups of lime peel, or hemicellulosic materials, and M represents the metal ions [24]. Eq. (3) shows that only cations can react and form a complex with the functional groups of the adsorbent surface.

It has been reported that cadmium ions start to precipitate at pH = 8.2 [25]. Therefore, the maximum pH value for the adsorption experiments was selected as 8. At low pH values, that is, pH = 1, there is a competition between H^+ and Cd^{2+} for the adsorption and formation of the complex on the adsorbent according to Eq. (3). In acidic solutions, the concentration of H^+ is much higher than Cd^{2+} and as a result, the dominant adsorbed ion is H^+. As the pH is increased toward

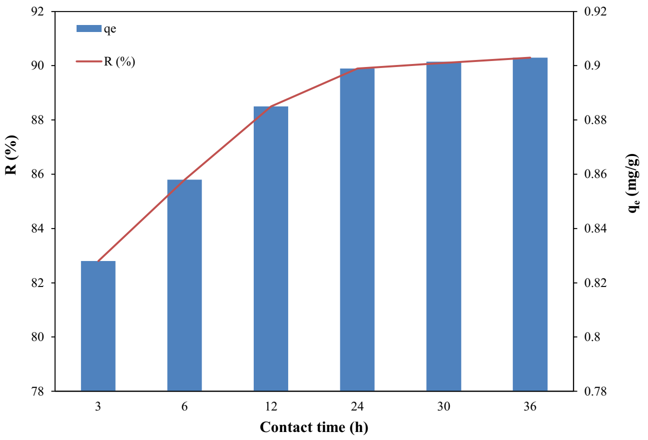

Fig. 3. Effect of contact time on the Cd(II) removal efficiency by lime peel (pH = 6; C_{ad} = 10 g/L; C_0 = 10 mg/L; d_p = (–18 + 35); T = 20°C).

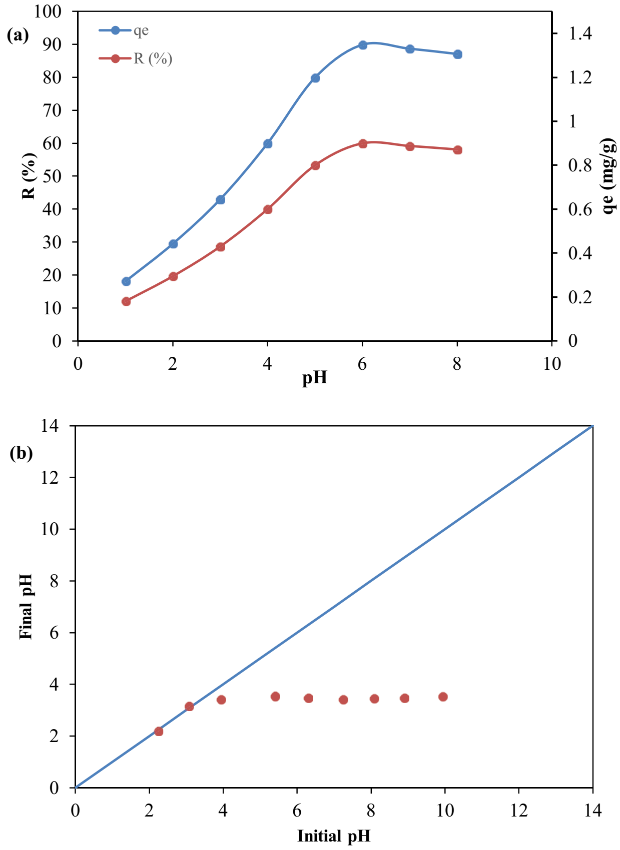

Fig. 4. (a) Effect of pH on the Cd(II) removal efficiency by lime peel at equilibrium condition (C_{ad} = 10 g/L; C_0 = 10 mg/L; d_p = (–18 + 35) and T = 20°C). (b) Determination of the pH_{pzc} of the lime peel using the solid addition method.

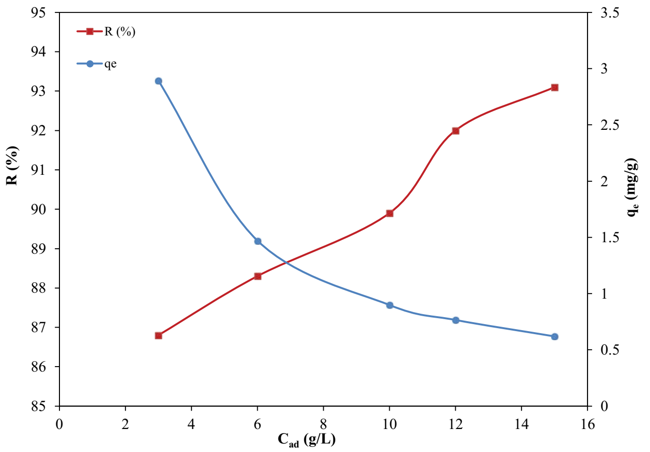

Fig. 5. Effect of the adsorbent concentration on the Cd(II) equilibrium removal efficiency by lime peel at equilibrium (pH = 6; C_0 = 10 mg/L; d_p = (–18 + 35); T = 20°C).

neutral, the ability of divalent Cd^{2+} ions enhance compared to the monovalent $H^{+,}$ and therefore, the amount of the adsorbed Cd^{2+} increases [26,27].

The removal efficiency reached a maximum of 89.9% at pH = 6. At higher pH values, there is a competition between the free OH– ions in the solution and $(–O–O–)^{2–}$ or radicals at the adsorbent surface for reaction with Cd^{2+} cations. As the OH^- is more accessible to Cd^{2+}, the amount of adsorbed cadmium ions on the adsorbent is reduced. Moreover, the feed pH was adjusted by NaOH solution which added a large number of Na^+ ions into the solution, competing with Cd^{2+} for adsorption onto the adsorbent. Consequently, by increasing the pH value over 6, the adsorption efficiency decreased.

3.4. Effect of adsorbent concentration

It is well known that the amount of adsorbent has a direct effect on the adsorption efficiency. Fig. 5 shows the equilibrium adsorption efficiency of Cd^{2+} at which the adsorption efficiency is increased gradually from 87% to 93% with increasing the concentration of the adsorbent from 3 to 15 g/L, respectively. However, the q_e value decreased from 2.89 to 0.62 mg/g. Nearly a linear dependency was found between the adsorption efficiency and adsorbent concentration.

At low adsorbent concentrations, there are not enough adsorption sites available for all of the metal ions dissolved in aquatic media and therefore a competition between dissolved species to occupy limited vacant adsorption sites could be assumed. By increasing the adsorbent concentration, the accessible surface area, and vacant active sites for the adsorption are increased. An increase in adsorbent dosage provides more adsorption sites, leading to higher removal efficiency (as confirmed by the experimental results). From operational aspects, the lower amount of adsorbent is more favorable because the handling of solids is more expensive than liquids and gases. On the other hand, from an economical aspect, as the amount of adsorbent increases, the cost of adsorbent also increases as well and therefore the lowest amount of adsorbent should be used for the operation. Fig. 5 suggested the adsorbent concentration of 10 g/L is suitable because at this adsorbent concentration, the removal efficiency is nearly 90%, and increasing the adsorbent concentration to 15 g/L would increase the removal efficiency by only 3%. One may consider the lower adsorbent concentration, that is, 3 g/L with an efficiency of nearly 87%, which may be satisfactory enough for some applications. As the amount of the adsorbent is increased, the amount of the species that could be adsorbed increases directly but is not proportional to the amount of the adsorbent. This could be explained by the dual sorption mechanism in which, when the adsorption driving force is low, the adsorption takes place through mono-layer adsorption while when the driving force for adsorption is high, the adsorbate could be adsorbed as multi-layer adsorption. At a constant feed concentration, when a small amount of adsorbent is used, the amount of the adsorbed species is quietly low and the concentration of the species at the solution remains high enough to force the adsorption through a multi-layer adsorption mechanism. Then, the adsorbent would become highly saturated with the adsorbate. As the concentration of the adsorbent is increased, the concentration of the adsorbate species falls very soon and the driving force for the adsorption decreased, considerably. Therefore, there will be many unoccupied active sites for the adsorption and this will force the adsorption at equilibrium to be as more or less mono-layer adsorption. Then, the adsorption capacity would not decrease with an increase in the adsorbate concentration [14,28]. However, the concentration of the adsorbent depends on the desired standards for the effluent and the type of adsorption operation (continuous or batch).

3.5. Effect of adsorbent particle size

Literature survey indicates that the reduction of adsorbent particle size remarkably enhances the adsorption efficiency according to equilibrium results and adsorption kinetics experiments [28]. The effect of adsorbent US mesh size (varied from 18 to 140) on Cd^{2+} ions removal is exhibited in Fig. 6. The Cd^{2+} ions removal increased from 87.5% to 93% by increasing the mesh size from 18–35 to 70–140, respectively. Mesh size is inversely proportional to the particle size of the adsorbent. The obtained results revealed that the amount of adsorbed ions increased with reducing particle size (increasing surface area), and did not have a linear relationship with it. The improved removal efficiency can be due to a significant increase in the surface area of lime peel adsorbent by reducing the particle size, resulting in more adsorption sites becoming available for absorbing Cd^{2+} ions. The result is logical because the BET results revealed that the specific surface area of the lime peel is very small (Section 3.1 – Characterization of biosorbent). It displays that the accessible sites on the surface of the adsorbent are responsible for adsorption and there is no considerable internal area for the adsorption. Therefore, smaller particles exhibit a higher specific surface area for adsorption. On the other hand, handling small particles and fine powders are much more difficult than coarse powders and granular solids.

3.6. Effect of feed concentration

The effect of initial Cd^{2+} ion concentration in the feed solution on the adsorption efficiency of lime peel is shown in Fig. 7. It is well known that any adsorbent has a limited adsorption capacity for a specific species. An increase in the initial metal concentration from 5 to 40 mg/L led to a reduction in cadmium ion removal from 93.0% to 77.7% and improvement in ions uptake increased from 0.465 to 3.108 mg/g, respectively. The results could be attributed to the decrease in the ratio of available surface-active sites per total cadmium ions as the feed concentration is increased. At higher Cd^{2+} concentrations, an excess amount of ions are present in the aqueous solution to occupy the adsorption site of lime peel; hence, the adsorption site is saturated faster [29]. Another reason may be related to the fact that by increasing the initial concentration of dissolved species, a continuous decline in the proportion of covalent interactions and an enhancement in the proportion of electrostatic interactions occurred at adsorption sites with a lower affinity toward metal ions. Moreover, the higher ion uptake in the concentrated solution may be due to stronger adsorption driving force for mass transfer between adsorbate in the aqueous media and the adsorbent surface [30].

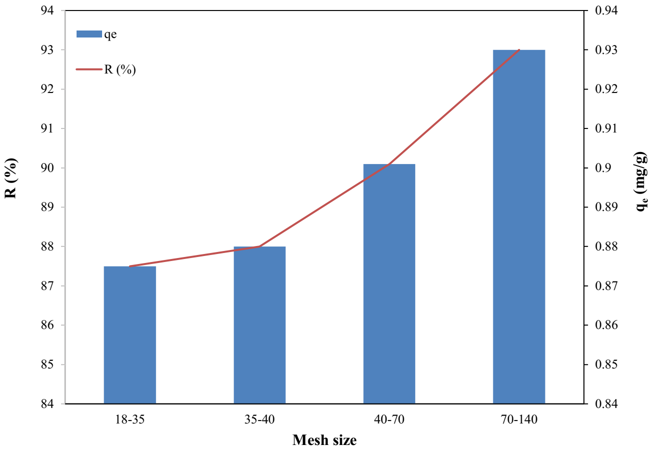

Fig. 6. Effect of adsorbent particle size (US mesh size) on the Cd(II) removal efficiency by lime peel at equilibrium condition (pH = 6; C_{ad} = 10 g/L; C_0 = 10 mg/L; T = 20°C).

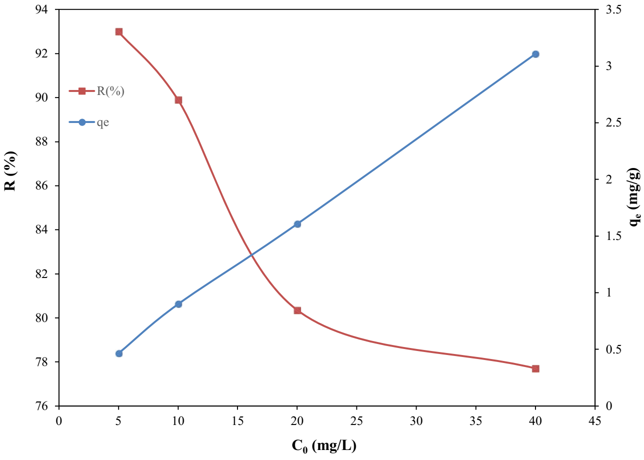

Fig. 7. Effect of the initial concentration on the Cd(II) removal efficiency by lime peel at equilibrium condition (pH = 6; C_{ad} = 10 g/L; d_p = (–18 + 35); T = 20°C).

3.7. Effect of adsorption temperature

Temperature is an influential operating parameter in the adsorption of ionic species from aqueous solutions. The temperature of the adsorption process was varied in the range of 293–323 K to assess its effects on cadmium adsorption. Table 1 shows the removal of Cd^{2+} ions increased from 86.2% to 90.8% with increasing temperatures from 293 to 323 K, respectively. The results confirm that a temperature increment causes a removal enhancement on the active sites of lime peel. As the temperature is increased, the external mass transfer for the adsorption increases through a decrease in liquid viscosity and a decrease in the boundary layer thickness around the adsorbent particle. The decrease in boundary layer thickness can be attributed to dehydration of the adsorption site of the lime peel adsorbent [28].

Thermodynamic quantities of this system including the changes in Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were calculated from the experimental data using Khan and Singh method [31]:

$$K_d = \frac{q_e}{C_e} \tag{4}$$

$$K_c = 1{,}000 K_d \tag{5}$$

$$\Delta G = -RT \ln\left(K_c\right) \tag{6}$$

$$\ln\left(K_c\right) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \tag{7}$$

where K_c is the distribution coefficient for the adsorbate, q_e is the amount of Cd^{2+} uptake at equilibrium (mg/g), C_e is the equilibrium concentration of Cd^{2+} ions in the solution (mg/L), R is the universal gas constant (8.314 J/mol·K), and T is the temperature (K). The values of ΔH and ΔS can be determined from the slope and intercept of the plot of ln(K_c) vs. (1/T) (Van't Hoff plot), respectively, using a linear fitting (Fig. 8). Table 2 includes the value of the thermodynamic parameters for the studied system. The negative values of Gibbs free energy showed that the sorption of Cd^{2+} on the lime peel is favorable and thermodynamically spontaneous. Considering the variation of ΔG values with temperature, the degree of spontaneity for adsorption of Cd^{2+} on lime peel increases with increasing temperature, displaying that this process is more feasible at higher temperatures. The positive sign of ΔH shows that the adsorption of Cd^{2+} ions on lime peel is endothermic and reveals that the transfer of metal ions from aqueous media to the solid phase (adsorbent) is assisted by heat absorption. The positive sign of the entropy displays that the adsorption of cadmium ions onto the lime peel is irreversible and reinforces the formation of an ion-adsorbent complex and energy is redistributed between the adsorbent and the adsorbent. The adsorbed heavy metal ions are more ordered than those presented adjacent to the adsorbent so the ratio of the number of ions interacting with the adsorbent to the number of the free heavy metal ion is lower than that in the adsorbed state. Therefore, by increasing the adsorption of Cd^{2+} on the adsorbent, the distribution of rotational and translational energies between smaller numbers of molecules will happen which results in a positive value for ΔS and the randomness at the adsorbent–adsorbate interface increases during the ion sorption [32].

3.8. Kinetic modeling

Calculation of kinetic parameters is a powerful tool to determine the sorption mechanism, the rate, and the kinetic of the used biosorbent for solute removal. Three well-known kinetic models including pseudo-first-order based on solid capacity, pseudo-second-order based on solid–phase sorption, and Weber–Morris intraparticle diffusion model have been applied.

3.8.1. Pseudo-first-order model

Lagergren's first-order rate equation (pseudo-first-order model) is extensively employed for the kinetic study

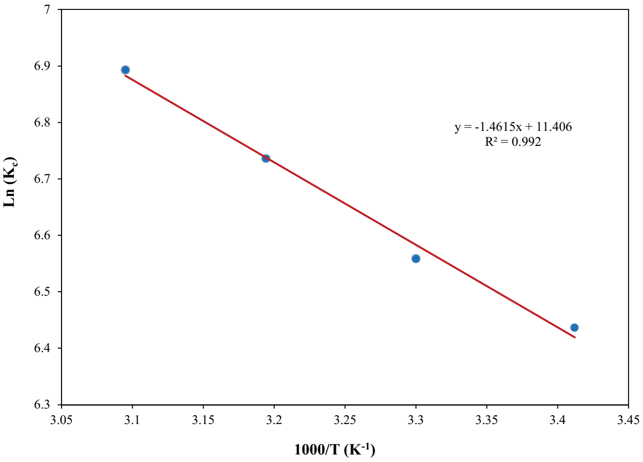

Fig. 8. Variation of sorption equilibrium of Cd(II) ions onto lime peel with temperature (pH = 6; C_{ad} = 10 g/L; C_0 = 10 mg/L; d_p = (–18 + 35).

Table 1
Effect of temperature on efficiencies of Cd^{2+} removal by lime peel (pH = 6; t_c = 24 h; C_0 = 10 mg/L; d_p = (–18 + 35); C_{ad} = 10 g/L)

T (°C)	Removal (%)
20	86.2
30	87.6
40	89.4
50	90.8

Table 2
Thermodynamic parameters for the adsorption of Cd^{2+} on lime peel at various temperatures

T (K)	K_c	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol·K)
293	624	–15.67	12.15	94.82
303	706	–16.52		
313	843	–17.53		
323	987	–18.51		

of ions sorption. This model was found to be suitable for only the beginning of the adsorption process (for example 20–30 min) and not for the long period of contact times and was strongly affected by the initial concentration of the adsorbate and adsorption system [33]. The linear form of the pseudo-first-order equation is given as [5]:

$$\ln\left(q_e - q_t\right) = \ln\left(q_e\right) - k_f t \tag{8}$$

where q_e and q_t are the amounts of cadmium adsorbed (mg/g) at equilibrium and at time t and k_f (min^{-1}) is the equilibrium rate constant of pseudo-first-order adsorption.

Fig. 9 shows the linearized form plot for the pseudo-first-order kinetic of cadmium ion adsorption on the prepared adsorbent. The values of k_f and q_e(cal.) were obtained from the slope and intercept of the linear plot of $\ln(q_e - q_t)$ vs. t, as tabulated in Table 3. The results indicate that the theoretical values for q_e, that is, q_e(cal.) calculated from the pseudo-first-order kinetic model are not in good agreement with the values obtained from the experiments, that is, q_e(exp.).

3.8.2. Pseudo-second-order model

The pseudo-second-order kinetic model is employed when chemical adsorption is the rate-limiting step and the constant parameters depend on operating parameters, especially the initial concentration of the adsorbate due to the longer time for reaching equilibrium [33]. The kinetics was also studied by the linear form of the pseudo-second-order kinetic model expressed as [4]:

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t \tag{9}$$

where k_s is the rate constant of pseudo-second-order kinetics in (g/mg·min). The constants of the pseudo-second-order model were calculated from the linearized plot of t/q_t vs. t that are shown in Fig. 10 and Table 4. Data reveal that the calculated adsorption capacities (q_e(cal.)) from the pseudo-second-order kinetic model are in good agreement with the experimental values (q_e(exp)). The regression coefficient, R^2, for the pseudo-second-order kinetic model was obtained as 1.0 indicating that the kinetic model could be favorably used for the present adsorption system.

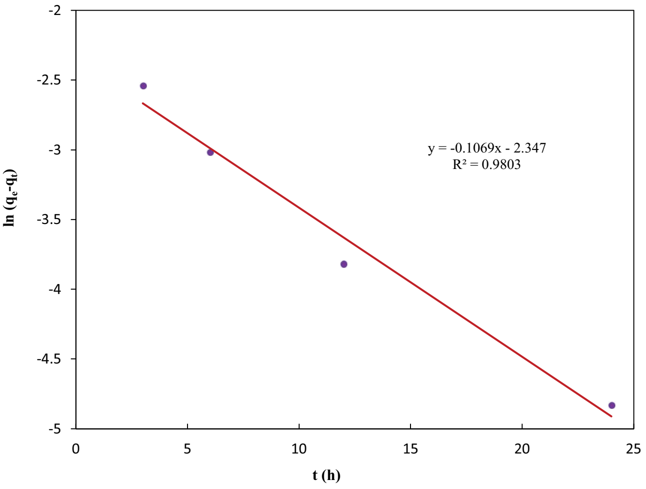

Fig. 9. Pseudo-first-order kinetic model plot of cadmium adsorption on lime peel adsorbent (pH = 6; C_{ad} = 10 g/L; C_0 = 10 mg/L; d_p = (–18 + 35); T = 20°C).

Table 3
Comparison of pseudo-first-order and pseudo-second-order model parameters, and calculated amount adsorbed, q_e(cal.) and experimental amount adsorbed, q_e(exp.) values

Pseudo-first-order model				
C_0 (mg/L)	q_e(exp.) (mg/g)	k_f (h^{-1})	q_e(cal.) (mg/g)	R^2
10	0.907	0.106	0.095	0.980
Pseudo-second-order model				
C_0 (mg/L)	q_e(exp.) (mg/g)	k_s (g/mg·h)	q_e(cal.) (mg/g)	R^2
10	0.907	2.87	0.916	1

3.8.3. Weber–Morris intraparticle diffusion model

The types of solutes diffusion inside the adsorbent pores, on its surface, and/or a combination of them may control the sorption of dissolved ions via adsorbent. Diffusion of solutes from the sorbent surface into the sorbent pores may occur through intraparticle diffusion, and its possible occurrence could be validated by the Weber–Morris intraparticle diffusion kinetic model, as follows [34]:

$$q_t = k_{\text{id}} t^{1/2} + C \tag{10}$$

where k_{id} (mg/g·min$^{1/2}$) is the intraparticle diffusion rate constant and C is the intercept related to the thickness of the boundary layer. The value of k_{id} was obtained from the slope of the linear plot of cadmium adsorbed (q_t) at the time (t) vs. $t^{1/2}$, as shown in Fig. 11. If this plot passes through the origin, it can be considered that intraparticle diffusion is the sole rate-controlling mechanism. Fig. 11 shows two separate linear plots revealing that Cd(II) adsorption on lime peel is performed in two or more steps.

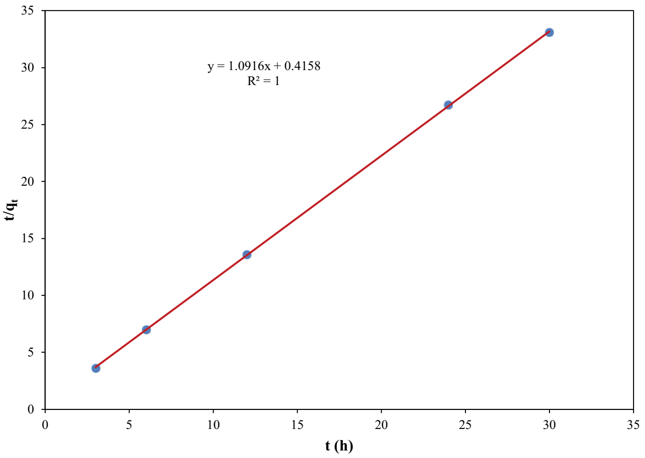

Fig. 10. Pseudo-second-order kinetic model plot of cadmium adsorption on lime peel adsorbent (pH = 6; C_{ad} = 10 g/L; C_0 = 10 mg/L; d_p = (–18 + 35); T = 20°C).

Table 4
Regression parameters for the Freundlich, Langmuir, and Dubinin–Radushkevich adsorption isotherms at 293 K

Freundlich model		
K_f	0.842	$L^n/g\cdot mg^{n-1}$
n	1.77	–
R^2	0.987	–
Langmuir model		
Q^0_{max}	4.120	mg/g
K_L	0.259	L/mg
R^2	0.859	–
Dubinin–Radushkevich model		
q_m	1.98	mg/g
K_D	0.143	mol²/kJ²
R^2	0.797	–
Sips model		
K_s	0.449	L/mg
a_s	–0.443	L/mg
β_s	0.242	–
R^2	0.996	–

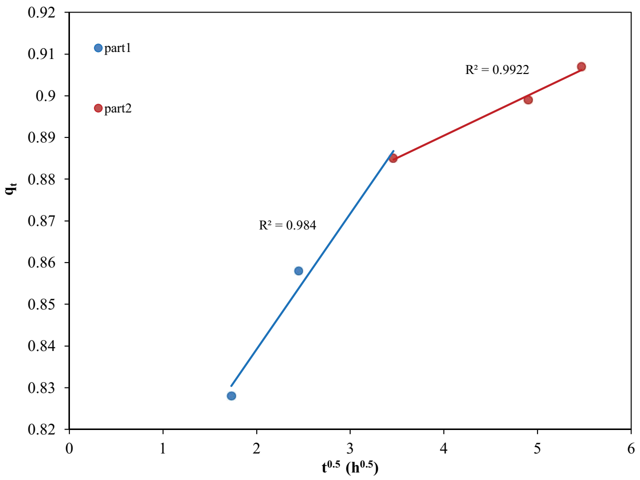

Fig. 11. Weber–Morris intraparticle diffusion model plots of cadmium adsorption on lime peel adsorbent (pH = 6; C_{ad} = 10 g/L; C_0 = 10 mg/L; d_p = (–18 + 35); T = 20°C).

The first linear part (part I) could be related to the rapid saturation of accessible sorption site on the surface of lime peel through the intraparticle transport mechanism, which is relatively fast. The second linear part (part II) could be related to intradiffusion of solutes which is very slow. However, none of the lines pass through the origin which indicates that the adsorption takes place by both of the mechanisms so that at the initial times the surface diffusion mechanism is governed, and pore diffusion is minor but at higher times of adsorption, the pore diffusion mechanism is the governed mechanism and surface diffusion is minor [5].

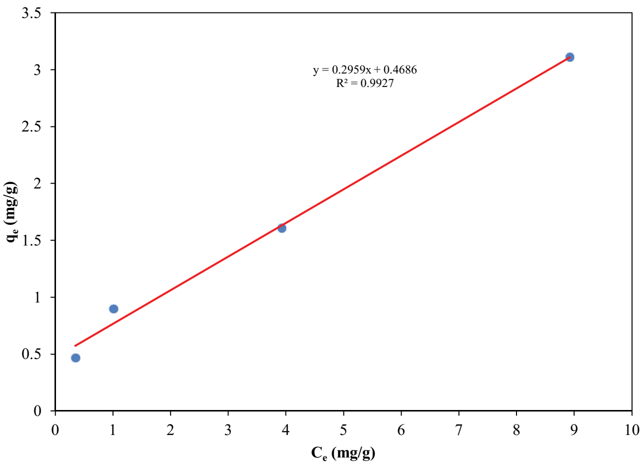

Fig. 12. Adsorption isotherm for lime peel using different initial metal concentrations (pH = 6; C_{ad} = 10 g/L; C_0 = 5–40 mg/L; d_p = (–18 + 35); T = 20°C).

3.9. Adsorption capacity and isotherms

The equilibrium adsorption capacity and the related parameters are the key factors in process design because they determine the partitioning between the solid and liquid phases. As the adsorption process goes on, the concentration of solutes on the surface and/or inside the pores increases until the sorption reaches an equilibrium; at which, there is a clearly defined distribution of metal ions between the solid and liquid phases.

The equilibrium adsorption studies were carried out at a cadmium ion concentration of 5–40 mg/L, the adsorbent concentration of 10 g/L, pH = 6, and temperature of 20°C and the adsorption capacity at different equilibrium concentrations was plotted as shown in Fig. 12.

The figure shows that at constant adsorbent concentration, the sorption capacity is directly and linearly proportional to the concentration of the solute. In this regard, the adsorption equilibrium data were examined by the Freundlich, Langmuir, and Dubinin–Radushkevich isotherm models in order to better understand the governed mechanism in the adsorption process and physicochemical properties of the surface.

3.9.1. Freundlich model

The Freundlich model is applicable for non-ideal systems and multilayer adsorption on adsorbents with surface heterogeneity and with sites that have different energies of sorption. It is not suitable to apply this model for very high and low concentrations of solutes. The linear form of the Freundlich model is described by the following equation:

$$\ln(q_e) = \frac{1}{n}\ln(C_e) + \ln(K_f) \tag{11}$$

where K_f ($L^n/g\cdot mg^{n-1}$) and n are Freundlich constants, associated with adsorption capacity and adsorption intensity, respectively [21]. The plot of $\ln(q_e)$ vs. $\ln(C_e)$ was constructed as Fig. 13 to obtain the values of K_f and n

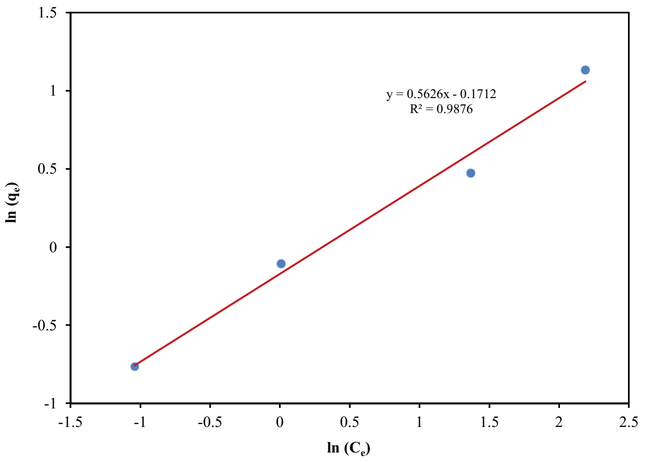

Fig. 13. Linearized Freundlich isotherms for adsorption of Cd(II) by lime peel (pH = 6; C_{ad} = 10 g/L; C_0 = 5–40 mg/L; d_p = (–18 + 35); T = 20°C).

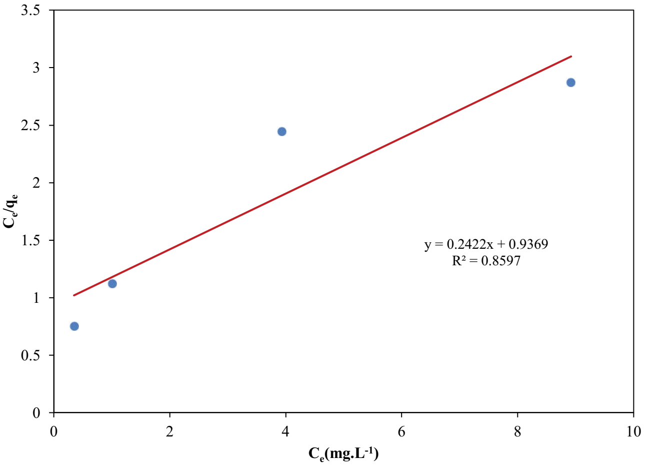

Fig. 14. Linearized Langmuir isotherms for adsorption of Cd(II) by lime peel (pH = 6; C_{ad} = 10 g/L; C_0 = 5–40 mg/L; d_p = (–18 + 35); T = 20°C).

from the intercept and slope of the linearized plot. It was found that there is a correlation coefficient value of 0.987 between the experimental and model values indicating that the Freundlich isotherm model is suitable for describing the adsorption capacity of the adsorbent for the adsorption of cadmium ions as indicated in Table 4. The value of n determines the surface heterogeneity and intensity of interaction between adsorbent and adsorbate. It is desirable that the value of n should be higher than unity [35]. Therefore, the lime peel-Cd(II) system can be considered a desirable system according to the Freundlich isotherm due to n = 1.77. According to the literature survey, this model is favorable for most biosorption systems [35].

3.9.2. Langmuir model

The Langmuir model is the most widely used isotherm that has been derived from the assumptions mentioned in the literature [36]. The linear form of the Langmuir equation, which considers monolayer adsorption onto a surface with no lateral interaction between the adsorbed species, is given below [Eq. (10)]:

$$\frac{C_e}{q_e} = \frac{1}{Q^{\circ}_{\max}} C_e + \frac{1}{Q^{\circ}_{\max} K_L} \quad (12)$$

where C_e (mg/L) is the equilibrium metal ion concentration in the solution, q_e (mg/g) is the amount of Cd uptake at equilibrium, $Q^0_{\max}$ (mg/g) is the Langmuir constant related to the maximum monolayer adsorption capacity, and K_L is a constant related to the affinity between an adsorbent and adsorbate [6].

Table 5
Adsorbent regeneration in different adsorption–desorption cycles

Cycle	Regeneration (%)
1	84.2 ± 2.3
2	80.7 ± 3.7
3	78.7 ± 1.8
4	77.8 ± 1.6

The plot of C_e/q_e as a function of C_e for the adsorption of cadmium is shown in Fig. 14. Values of the monolayer capacity ($Q^0_{\max}$) and the equilibrium constant (K_L) has been obtained from the intercept and slope of this plot and parameters of the sorption data are given in Table 4. According to the low value of the correlation coefficient, R^2 = 0.859, the adsorption of cadmium ions on lime peel does not obey the Langmuir isotherm model.

3.9.3. Dubinin–Radushkevich model

The equilibrium data were also analyzed by the Dubinin–Radushkevich isotherm to predict the energy of adsorption per unit mass of the adsorbate and the maximum adsorption capacity of the adsorbent. The linearized form of this model is expressed as follows:

$$\ln\left(q_e\right) = \ln\left(q_m\right) - K_D \varepsilon^2 \quad (13)$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (14)$$

$$E = \frac{1}{\sqrt{2K_D}} \quad (15)$$

where ε is the Polanyi potential, q_e is the equilibrium adsorption capacity (mg/g), q_m is the adsorption capacity of the sorbent (mg/g) and C_e is the equilibrium concentration of the metal ion in the solution (mg/L). K_D (mol²/kJ²) is a constant related to the mean adsorption energy [E (kJ/mol)], R is the universal gas constant (kJ/K·mol), and T is the temperature (K) [3].

Fig. 15 shows the plot of the Dubinin–Radushkevich model. The regression parameters and correlation coefficient (R^2 = 0.799), which are presented in Table 4 show that the Dubinin–Radushkevich model is not in agreement with the experimental results. According to the obtained results,

Table 6
Maximum adsorption capacity of some biosorbents for cadmium ions removal from aqueous solution

Biosorbent	$Q^0_{\max}$ (mg/g)	Condition	Co-ions	References
Coconut copra meal	4.92	T = 299 K; C_0 = 10.5–201 mg/dm^3; shaking time = 2 h; shaking rate = 150 rpm; adsorbent dosage = 20 mg/L	–	[38]
Caulerpa lentillifera	4.69	T = 294 K; pH = 5; C_0 = 0.1–1.1 mol/m^3; shaking time = 1 h; shaking rate = 150 rpm; adsorbent dosage = 0.5 g	–	[39]
Vegetal biomass (olive pits)	9.39	T = 294 K; C_0 = 5–450 mg/L; shaking time = 0.5 h; shaking rate = 250 rpm; adsorbent dosage = 5 g/L	–	[40]
Chlorella vulgaris	0.02	T = 298 K; pH = 5–5.5; C_0 = 2–20 × 10^{-3} M; shaking time = 70 min; shaking rate = 200 rpm; adsorbent dosage = 0.4 g	–	[41]
Sugar beet pulp	0.37	T = 298 K; pH = 4; C_0 = 10–150 mg/L; shaking time = 2 h; adsorbent dosage = 1 g/L	–	[42]
Activated sludge	28.10	T = 298 K; pH = 4; C_0 = 25–150 mg/L; shaking time = 24 h; shaking rate = 150 rpm; adsorbent dosage = 1 g/L	Ni^{2+}	[43]
Lime peel	4.12	T = 293 K; pH = 6; C_0 = 50–40 mg/L; shaking time = 24 h; adsorbent dosage = 10 g/L	–	Present study

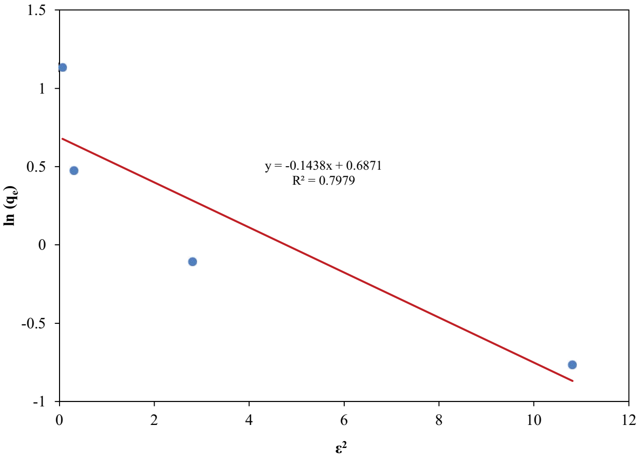

Fig. 15. Linearized Dubinin–Radushkevich isotherms for adsorption of Cd(II) by lime peel (pH = 6; C_{ad} = 10 g/L; C_0 = 5–40 mg/L; d_p = (–18 + 35); T = 20°C).

the E value was 3.57 kJ/mol for Cd(II) adsorption on lime peel powder, showing the occurrence of physical adsorption. This result is not reliable because of the low correlation coefficient (R^2 = 0.799). However, the physical adsorption of metal ions on biosorbents is reported in the literature [24].

3.9.4. Sips model

The Sips isotherm is a combination of the Langmuir and Freundlich models and is written as:

$$q_e = \frac{q_s K_s C_e^{\beta_s}}{1 + K_s C_e^{\beta_s}} \tag{16}$$

where K_s (L/mg) is the affinity constant and β_s describes the surface heterogeneity [37]. The suitability of the Sips model to be fitted to the experimental results is presented in Table 4.

3.10. Desorption study

Regeneration of used adsorbents is crucial for reducing the process cost. Regeneration of the used adsorbents in this study was investigated by washing the spent lime peel with a 0.1 M aqueous HCl. The used adsorbent was contacted with the 0.1 M HCl solution under stirring at 25°C for 24 h and then the suspension was filtered with No. 42 Whatman filter paper and the filtrate was analyzed for Cd^{2+} concentration. The results indicated that the desorption efficiency of the lime peel adsorbent was about 84.2% ± 2.3% for the first cycle of adsorption. The adsorption–desorption cycle was repeated four times and the results are presented in Table 5.

As a comparison with the literature, maximum sorption capacities based on the Langmuir model for the adsorption of cadmium ions on different types of biosorbents are tabulated in Table 6.

4. Conclusions

Untreated lime peel powder was introduced as a low-cost and environmental-friendly bioadsorbent for cadmium ions removal from aqueous solutions, successfully. The analysis of the experimental data showed that although this adsorbent has a low BET surface, its adsorption capacity is comparable to many untreated bioadsorbents. The FTIR analysis before and after cadmium adsorption showed that the affinity between cadmium cations and the carboxylic functional groups of the adsorbent is the main mechanism for cadmium adsorption. The maximum adsorption capacity of the adsorbent was obtained at T = 293 K, pH = 6, C_0 = 50–40 mg/L, contact time = 24 h, adsorbent dosage = 10 g/L as 4.12 mg/g adsorbent, which is comparable to most bioadsorbents. The analysis of the effect of temperature on the adsorption showed that cadmium adsorption on the lime peel powder is spontaneous, endothermic, and limited by diffusion of the adsorbate in the adsorbent. The above results suggest that the lime peel powder has the potential to be used as a low-cost bioadsorbent for the removal of cadmium ions from contaminated waters and soil-remediation wash waters. Both the percolation and contact-filtration methods would be effective for contacting the adsorbent and feed solution but the contact filtration followed by a high-pressure filter press would be preferable because it makes possible the use of finer adsorbent particles.

Symbols

C — Intraparticle diffusion model constant
C_0 — Initial concentration of Cd(II) ions in solution, mg/L
C_e — Equilibrium concentration of Cd(II) ions in solution, mg/L
E — Mean adsorption energy, kJ/mol
K_c — Equilibrium constant
K_d — Adsorbate distribution coefficient, L/g
K_D — Dubinin–Radushkevich constant related to the mean adsorption energy, mol^2/kJ^2
k_f — The pseudo-first-order rate constant, min^{-1}
K_f — Freundlich constant indicative of the adsorption capacity of the adsorbent, mg/g
k_{id} — Intraparticle diffusion model rate constant, mg/g·min$^{1/2}$
K_L — Langmuir constant related to the affinity between an adsorbent and adsorbate, L/mg
k_s — Pseudo-second-order rate constant, g/min
m — Dried mass of the used adsorbent, g
n — Freundlich exponent related to adsorption intensity
q_e — Equilibrium adsorption capacity, mg/g
q_m — Dubinin–Radushkevich constant indicative of the adsorption capacity of the adsorbent, mg/g
Q^0_{max} — Langmuir constant related to the maximum monolayer adsorption capacity, mg/g
q_t — Metal sorption capacity of the adsorbent at time t, mg/g
R — Universal gas constant, 8.314 J/K·mol
T — Temperature, K
V — The volume of adsorbate solution, L
ε — Polanyi potential, J/mol
ΔG — Gibbs free energy change, kJ/mol
ΔH — Enthalpy change, kJ/mol
ΔS — Entropy change, kJ/mol·K

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