



Adsorption/desorption of Cd(II), Cu(II) and Pb(II) using chemically modified orange peel: Equilibrium and kinetic studies

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ABSTRACT

Waste materials from industries such as food processing may act as cost effective and efficient bio-sorbents to remove toxic contaminants from wastewater. This study aimed to establish an optimized condition and closed loop application of processed orange peel for metals removal. A comparative study of the adsorption capacity of the chemically modified orange peel was performed against environmentally problematic metal ions, namely, Cd²⁺, Cu²⁺ and Pb²⁺, from aqueous solutions. Chemically modified orange peel (MOP) showed a significantly higher metal uptake capacity compared to original orange peel (OP). Fourier Transform Infrared (FTIR) Spectra of peel showed that the carboxylic group peak shifted from 1637 to 1644 cm⁻¹ after Pb (II) ions binding, indicated the involvement of carboxyl groups in Pb(II) ions binding. The metals uptake by MOP was rapid and the equilibrium time was 30 min at constant temperature and pH. Sorption kinetics followed a second-order model. The mechanism of metal sorption by MOP gave good fits for Freundlich and Langmuir models. Desorption of metals and regeneration of the biosorbent was attained simultaneously by acid elution. Even after four cycles of adsorption-elution, the adsorption capacity was regained completely and adsorption efficiency of metal was maintained at around 90%.

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1. Introduction

Environmental problems have become more frequent and complex in recent decades, as a result of human population growth and increasing industrialization [1]. Industrial activities such as mining and metal processing can lead to heavy metal contamination in surface water, groundwater, or the sea [2,3]. Heavy metals are the main hazardous non-degradable substances, persistence and can be accumulate in the environment elements such as food chain, thus may pose a significant danger to human health [4,5].

There are various methods for removing heavy metals including chemical precipitation, membrane filtration, ion exchange, liquid extraction or electro-dialysis [6]. However, these methods are not widely used due to their high cost and low feasibility for small-scale industries [7].

The widespread industrial use of low-cost adsorbents for wastewater treatment is strongly recommended at present, due to their local availability, technical feasibility, engineering applicability and cost effectiveness [8,9]. Most agriculture wastes or by-products are considered to be low value products. Different types

of biomass have been investigated for biosorption of heavy metals [10–23] and so on.

Orange peel is one of the valuable biomass wastes. In the world, the orange product represents 75% of the total citrus fruits [24]. Egypt is one of the major producers. Orange peel can cause a significant disposal problem. Therefore, efforts have been made in this paper to investigate the uptake of Cd, Cu and Pb ions from synthetic industrial wastewater using processed orange peel.

2. Materials and methods

2.1. Biomass preparation

orange peel was selected because it is generated in large quantities as solid waste from local fruit juice.

2.1.1. Original orange peel (OP)

Original or Native orange peel has been washed with tap water, then rinsed with double-de-ionized water and dried in the sun light for ≈ 6 days until reached a constant weight. Dried peel was ground and sieved through 0.2 mm pore size. For preservation, it was kept in plastic-stopper bottles.

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2.1.2. Chemically modified orange peel (MOP) or protonated peel

Protonation was carried out by soaking the native peel in 0.1M HNO₃ (10 g of peel/L) for 6 h, rinsing with double-de-ionized water, and dried in the sun light for \cong 6 days until reached a constant weight, in order to remove naturally present ions (e.g., Ca²⁺) from the orange peel and thus obtain a better defined chemically modified orange peel where all weakly acidic sites are occupied by protons, as proposed by Schiewer and Volesky [25]. The dried orange peel was crushed, ground and passed through 0.2 mm sieve. There was no significant weight loss during protonation process.

For preservation, it was kept in plastic-stopper bottles and to minimize contact with humidity, all these bottles were preserved in desiccators.

2.2. Metal solutions

Salts (CdCl₂·5/2H₂O, CuSO₄·5H₂O and Pb(NO₃)₂) used in the preparation of the synthetic metal bearing solutions were supplied by Merck-Germany as analytical grade. The synthetic wastewater solutions were then prepared by diluting the stock standard of concentration 1000 mg/L of each metal by using de-ionized water.

2.3. Analytical methods

2.3.1. Determination of metals concentration

The concentrations of metals in all samples were determined according to APHA [26] using Atomic Absorption Spectrometer (Varian-SpectrAA (220)) with graphite furnace accessory and equipped with deuterium arc background corrector (Varian Australia, Pty Ltd, Manufacturing site). Precision of the metal measurement was determined by analyzing (in triplicate) the metal concentration of all samples.

2.3.2. Quality control

For each series of measurements absorption calibration curve was constructed composed of a blank and three or more standards from Merck (Germany). Accuracy and precision of the metals measurement were confirmed using external standard reference material 1643e, from National Institute Standards and Technology (NIST), for trace elements in water and as a quality control sample.

2.3.3. FTIR spectroscopy measurements

Samples of original, protonated and protonated orange peel after metal binding were confirmed by a FTIR spectrometer. The samples were ground well to make KBr pellets under hydraulic pressure of 400 kg/cm² and spectra were recorded in the range of 400–4000 cm⁻¹. In each scan, the amounts of the sample and KBr were kept constant in order to know the changes in the intensities of characteristic peaks with respect to the structural changes.

2.4. Batch biosorption studies

Each of the batch biosorption studies was carried out by contacting the biomass with the metal ions at pH 5.0 \pm 0.1 in a glass tube. Studies were conducted at room temperature (25 \pm 0.1 °C) to determine the effects of contact time, sorbent dosage and initial ions concentration on the biosorption of Cd (II), Cu (II) and Pb(II) ions. Each experiment was conducted in a mechanical shaker at 200 rpm. All samples were filtered through Whatman filter paper (No. 42) and the metal ions concentration was determined in the filtrate. To distinguish between possible metal precipitation and actual metal sorption, controls were used without biosorbent materials.

All the experiments were carried out in triplicate and the mean of the quantitative results were used for further calculations, the

percent relative standard deviation for results was calculated and if the value of standard deviation for any sample was greater than 5% the data were not used.

2.4.1. Sorption kinetics

The kinetic studies were carried out by conducting batch sorption experiments with initial metals concentration of 20 mg/L at different time periods varying between 5 min and 120 min. Various models were used to analyze the kinetics of the sorption process [27].

2.4.2. Effect of sorbent dosage

The sorbent dosage was varied from 0.1 to 1.00 g using a fixed volume of 25 mL of 20 mg/L of metal solution at the equilibrium time for each metal.

2.4.3. Sorption isotherms

Were measured by varying the initial metal ion concentrations and keeping the biosorbent mass constant. Different sorption models were used for comparison with experimental data [28].

2.4.4. Desorption and regeneration

To investigate the possibility of repeated use of the adsorbent, desorption and regeneration experiments were also conducted. For the desorption experiment, modified orange peel containing Pb (II) was transferred to a flask containing 25 mL of 0.2M HCl desorbing agent. The mixture was shaken at 200 rpm using a rotary shaker for 30 min. After elution, the modified orange peel was rinsed three times with de-ionized water to remove any traces of acid and suspended again in lead solution for the next adsorption cycle. The adsorption–desorption cycle was repeated four times using the same modified orange peel and in every cycle the initial lead concentration was 100 mg/L. The adsorption efficiency of lead metal ions onto modified orange peel for each cycle and the distribution ratio (K_d) were calculated.

3. Results and discussion

Orange peel principally consists of cellulose, hemi-cellulose, pectin substances, chlorophyll pigments and other low molecular weight compounds like limonene, orange and so on [29]. Pectin is poly α 1-4-galacturonic acids, with varying degree of methylation of carboxylic acid residues [30]. The important feature of orange peel is that it contains hydroxyl, and carboxyl groups which are important sites for metal sorption [31]. Therefore, the objective of this investigation is to study the synergistic effect of initial metals concentration, adsorbent dosage and agitation time on removal of Cd (II), Cu (II) and Pb(II) ions using orange peel or its chemically modified adsorbent; to study the adsorption kinetics models of Cd (II), Cu (II) and Pb(II) ions examining the change in adsorption rate with time and to use the adsorption isotherms models (Langmuir, Freundlich and Dubinin-Kaganer-Radushkevich (DKR)) in order to correlate the experimental results.

3.1. Comparison of original and modified sorbent

A comparison of metal uptake capacities of original and modified orange peel was performed. Metal uptake capacities were determined by contacting 0.5 g of the original and modified orange peels with a synthetic solution of Cd ions in a mechanical shaker at 200 rpm for 1 h. A relatively high initial concentration of 600 mg/L (10.676 meq/L) of Cd (II) ions were chosen in order to achieve saturation of all sites so that the sorption capacity could be determined. A pH value of 5.0 \pm 0.1 was maintained throughout the experiment by adding 0.1 N NaOH or HCl. At this pH value, there

would be little competition between metal ions and protons compared to lower pH values, which lead to high metal uptake [32]. The metal uptake per gram of biosorbent material was determined by employing the mass balance. If C_0 and C_e are the initial and final metal concentration (mg/L or meq/L) respectively, V is the suspension volume (L) and m is the mass of biosorbent material (g), the equilibrium metal uptake q_e (mg/g or meq/g) can be calculated as:

$$q_e = \frac{v(C_0 - C_e)}{m} \quad (1)$$

A comparison of adsorption capacity of the two sorbents, showed that modified orange peel has higher Cd uptake of 11.2 mg/g (0.199 meq/g) than original orange peel of 6.94 mg/g (0.12 meq/g). Our results obtained in this study were more or less in agreement with the same Cd ions uptake capacity for the different types of citrus peel [9,33,34].

As the active binding sites for metals are supposed to be functional groups of hydroxyl and carboxyl in cellulose, chemical modification has shown great promise in improving the cation exchange capacity due to the increase of functional groups. Therefore, protonation of orange peel by using 0.1N HNO_3 to remove excess cations such as calcium or sodium that could interfere with metal sorption and to create a more defined sorbent material which enhances binding of heavy metals by decreasing the competition between different ions like K^+ , and Ca^{2+} with heavy metal ions like Cd^{2+} [25].

Therefore, further experiments were carried out for protonated or chemically modified orange peel.

3.2. Kinetic modeling

Sorption kinetics

As equilibrium time is one of the important parameters for selecting a wastewater treatment system, the time consumed for wastewater disposal should be considered. As shown in Fig. 1 the sorption of Cd (II), Cu (II) and Pb(II) ions onto the modified orange peel was rapid for the first 10 min and equilibrium was reached

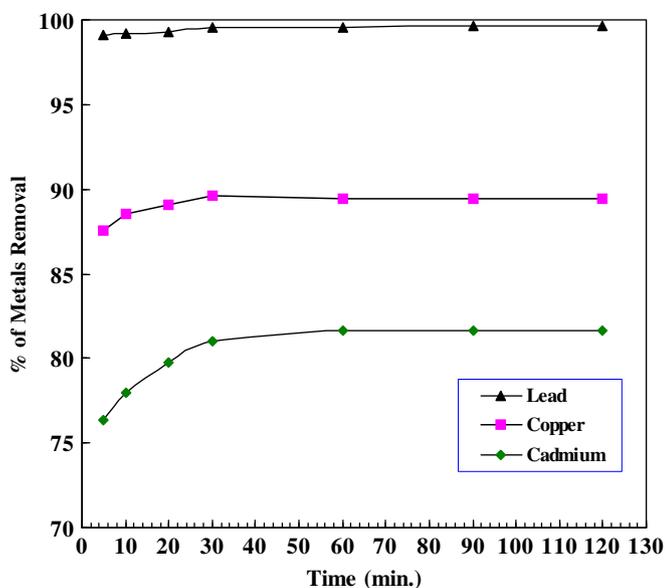


Fig. 1. Effect of contact time on the removal of Cd^{2+} , Cu^{2+} and Pb^{2+} by adsorption onto modified orange peel at an initial concentration 20 mg/L, pH 5.0 ± 0.1 and 4 g/L adsorbent weight.

within 30 min. Therefore, the period of 30 min was considered as the optimum time, where the removal percentages followed the order:

$$\text{Pb (99.5\%)} > \text{Cu (89.57\%)} > \text{Cd (81.03\%)}$$

Schiewer and Patil [35] reported that biosorption of divalent cations by pectin-rich fruit wastes are usually rapid with the equilibrium being reached in less than 1 h.

Kinetic characteristic in a sorbent depends not only on the presence of the active metal site but also depends on the accessibility of the metal site without steric hindrance which is greatly determined by the matrices of the sorbent. This means that, the mechanism of sorption depends on the physical and chemical characteristics of the sorbent as well as on the mass transfer process. Therefore, the rate kinetics of Cd, Cu and Pb ions sorption onto modified orange peel were analyzed using pseudo first-order, pseudo-second order and Elovich kinetic model, which are the most commonly used models [27]. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients (R^2 , values close to 1). The relatively higher value is the more applicable model to the kinetics of Cd, Cu and Pb ions sorption.

3.2.1. Pseudo first-order kinetic model

The kinetic data were modified with the Lagergren first-order model [36] which is the earliest known one describing the adsorption rate based on the adsorption capacity. The integral form of the pseudo first-order model generally expressed as follows:

$$\log(q_e - q_t) = \log q_e - k_{1,ads} * t / 2.303 \quad (2)$$

Where q_e (meq/g) and q_t are the amounts of adsorbed metal ions on the biosorbent at the equilibrium and at time t , respectively and $k_{1,ads}$ is the Lagergren rate constant of the first-order biosorption (min^{-1}).

The model is based on the assumption that the rate is proportional to the number of free sites. If the pseudo first-order kinetics is applicable, a plot of $\log(q_e - q_t)$ versus t should provide a linear relationship from which $k_{1,ads}$ and predicted q_e can be determined from the slope and intercept of the plot, respectively (Fig. 2). The variation in rate should be proportional to the first power of concentration for strict surface adsorption. However, the relationship between initial solute concentration and rate of adsorption will not be linear when pore diffusion limits the adsorption process.

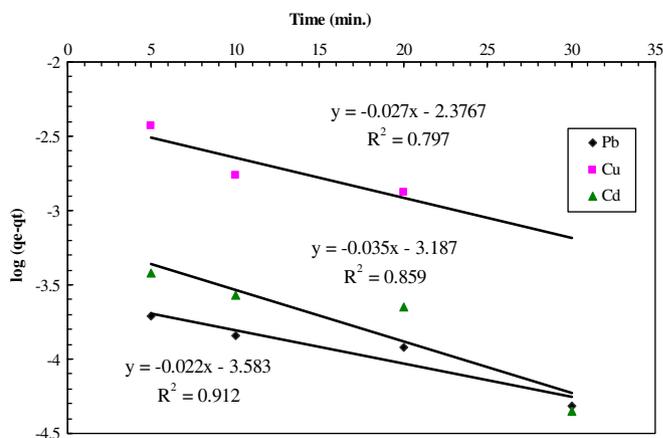


Fig. 2. Pseudo-first order for the biosorption of Cd(II), Cu (II) and Pb (II) onto modified orange peel at 25 °C and pH 5.0.

It was observed from Fig. 2 and Table 1 that first-order model failed to provide a realistic estimate of q_e of adsorbed Cd, Cu and Pb ions onto modified orange peel. Where, the experimental values of q_e (0.006, 0.172 and 0.050 meq/g) were higher than the fitted values (0.065×10^{-2} , 0.421×10^{-2} and 0.026×10^{-2} meq/g) for Cd, Cu and Pb ions respectively. This underestimation of the amount of binding sites is probably due to the fact that q_e was determined from the y-intercept ($t = 0$). The intercept is most strongly affected by the short term metal uptake which is usually much lower than the equilibrium uptake. It can be concluded that this is a general disadvantage of using the linearized first-order model. On the other hand, the experimental q_e values do not agree with the calculated ones which obtained from the linear plots even when the correlation coefficients R^2 are relatively high. This showed that the adsorption of Cd, Cu and Pb ions onto modified orange peel is not appropriate to describe the entire process and not a first-order reaction.

3.2.2. Pseudo-second order model

The kinetics of adsorption process may also be analyzed by pseudo second-order rate equation [37]. The pseudo-second-order model is based on the assumption that biosorption follows a second-order mechanism, whereby the rate of sorption is proportional to the square of the number of unoccupied sites. The linearized form of the equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{K_{2,ads} * q_e^2} + \frac{t}{q_e} \quad (3)$$

Where $k_{2,ads}$ is the rate constant of second-order biosorption (g/meq min).

The linearized second-order plot of t/q against t (Fig. 3) according to Eq. (3) resulted in straight lines for Cd, Cu and Pb ions and led to the determination of the second-order rate constants $k_{2,ads}$ and q_e from the slope and the y-intercept (Table 1). The q_e values were very close to the experimentally determined ones, a first sign of the appropriateness of this model. The R^2 values for the second-order kinetic model were 1 for the adsorption of Cd Cu and Pb ions onto modified orange peel (Table 1). Our results in agreement with Schiewer and Patil [35], who showed that biosorption of divalent metals by protonated pectin peels was fitted a second-order model better than a first-order model.

Based on theoretical considerations, the reaction of a divalent metal ion (M) binding to two free binding sites (B) can be explained by the following expressions:



This means that the sorption rate would be proportional to the metal concentration and the square of the number of free sites which corresponds to the term $(qe - q)^2$ in the second-order model. The better fit of the second-order model, therefore, indicates that a 1:2 binding stoichiometry applies, where one divalent metal binds to two monovalent binding sites.

Cruz et al. [38], who compared a pseudo-first-order Lagergren model and a second-order model, similarly found that the second-order model was superior for the binding of divalent cations by the

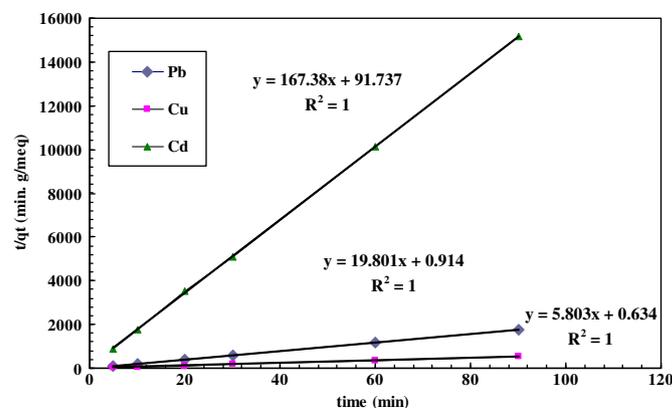


Fig. 3. Pseudo-second order for the biosorption of Cd(II) Cu (II) and Pb (II) onto modified orange peel at 25 °C and pH 5.0.

brown alga *Sargassum*. They concluded that the biosorption reaction was the rate-limiting step.

3.2.3. Elovich kinetic model

Elovich kinetic equation is another rate equation based on the adsorption capacity, which is generally expressed as [39–41]:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q) \quad (4)$$

Where α is the initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) and β is the desorption constant (gmg^{-1}) during any one experiment. It is simplified by assuming $\alpha\beta t \gg t$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$. Eq. (4) becomes form as followed:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (5)$$

If Cd(II), Cu (II) and Pb (II) adsorption by modified orange peel fits the Elovich model, a plot of q_t versus $\ln(t)$ should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \times \ln(\alpha\beta)$ (Fig. 4). Thus, the constants can be obtained from the slope and the intercept of the straight line. Correlation coefficients R^2 obtained by Elovich model were higher than that obtained from pseudo first-order model and comparable to that obtained from pseudo second-order model. Furthermore, the Elovich equation is for general application to chemisorption kinetics. The equation has been applied satisfactory to some chemisorption processes and has been found to cover a wide range of slow adsorption rates. The equation is often valid for systems in which the adsorbing surface is heterogeneous [42].

Finally, several authors investigated that citrus peels for pectin production have the ability of sorption of metal ions from aqueous solutions [21,43,44].

3.3. Effect of adsorbent dose

Various amounts of adsorbent modified orange peel ranging from 0.1 to 1 g were used (Fig. 5). The percentage removal (A%) of

Table 1

Pseudo-first and -second order rate constants and equilibrium metal uptake for Cd (II), Cu (II) and Pb(II) binding onto modified orange peel.

Metals	q_e Expe. (meq/g)	First-order kinetic			Second-order kinetic		
		$K_{1,ads}$	q_e Model (meq/g)	R^2	$K_{2,ads}$	q_e Model (meq/g)	R^2
Cd	0.006	0.080	0.065×10^{-2}	0.86	305.85	0.0060	1
Cu	0.172	0.062	0.421×10^{-2}	0.797	53.115	0.172	1
Pb	0.050	0.052	0.026×10^{-2}	0.912	428	0.052	1

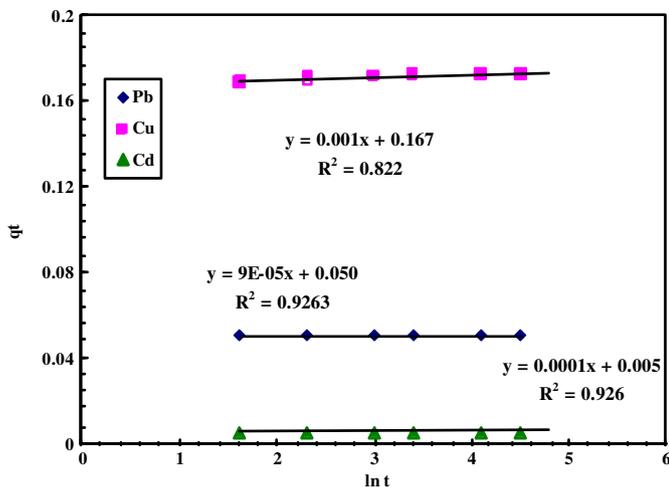


Fig. 4. Elovich model plot for the adsorption of Cd(II), Cu(II) and Pb(II) onto modified orange peel at 25 °C and pH 5.0.

Cd (II), Cu (II) and Pb(II) ions varied linearly with the amount of the adsorbent and amount of adsorbate. The increase in A% with an increase in adsorbent dosage is due to the availability of larger surface area and more adsorption sites. At adsorbent dosage >0.1 g for Pb(II), >0.5 g for Cu (II) and >0.8 g for Cd (II) the incremental of metal removal becomes very low, as the surface metal ions concentration and the solution metal ions concentration come to equilibrium with each other [45]. Thus, increased adsorbent dosage did not enhance the removal percentage of the studied metal ions. However, for Cu (II) the decrease in A% with increase in the adsorbent dose is mainly due to un-saturation of adsorption sites through the adsorption reaction. Where, the aggregation of adsorption sites would lead to a decrease in the total surface area of the adsorbent [46].

3.4. Effect of metal concentrations on the distribution ratio (K_d)

The distribution ratios (K_d) of Cd, Cu and Pb ions onto modified orange peel as a function of their concentrations were studied at constant temperature (25 ± 0.1 °C) by varying the metal concentration from 100 to 600 mg/L while keeping all other parameters constant.

The distribution ratio (K_d) was calculated using the equation:

$$K_d = \frac{\text{amount of metal in adsorbent}}{\text{amount of metal in solution}} \times \frac{V}{m} \quad (6)$$

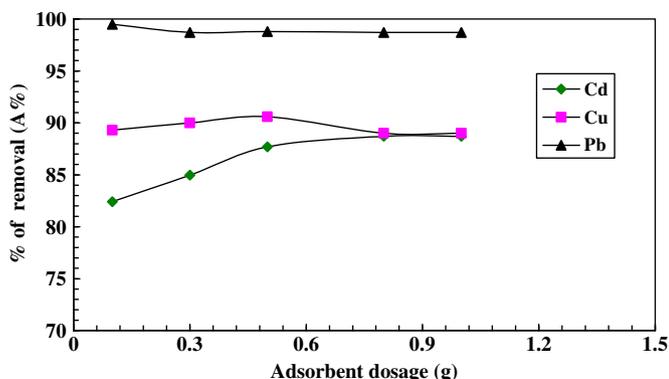


Fig. 5. Effect of adsorbent dose on the removal of Cd(II), Cu(II) and Pb(II) using modified orange peel at 25 °C and pH 5.0.

Where V is the volume of the solution (mL) and m is the weight of the adsorbent (g).

The percent of metals adsorption and K_d (mL/g) can be correlated by the following equation:

$$\text{Adsorption(\%)} = \frac{100K_d}{K_d + V/m} \quad (7)$$

Fig. 6 illustrates K_d as a function of metal ions concentrations. The K_d values increase with decreasing concentration of metal ions. In other words, the K_d values increase as dilution of metal ions in solution proceeds. These results indicate that energetically less favorable sites become involved with increasing metal concentration in the aqueous solution. The maximal exchange levels attained were as follow:

$$Pb^{2+} (96.3\%) > Cu^{2+} (93.3\%) > Cd^{2+} (85\%).$$

3.5. Equilibrium studies and isotherm modeling

3.5.1. Langmuir and Freundlich models

The equilibrium adsorption isotherms are one of the promising data to understand the mechanism of the adsorption. Various isotherm equations are well known and Langmuir, Freundlich, and Dubinin–Radushkevich (DKR) isotherms are the selected isotherms to be studied [47].

The uptake of Cd(II), Cu(II) and Pb(II) onto modified orange peel as functions of their concentrations was studied by varying the metal concentrations from 100 to 600 mg/L while keeping all other parameters constant with respect to optimum dose, time for each metal, temperature and pH. Blank tests without biosorbent were performed to confirm that metal precipitation doesn't interfere with metal biosorption.

Due to their simplicity, the Langmuir and Freundlich equations are the most widely used models to describe the relationship between equilibrium metal uptake (q_e) and final concentrations (C_e) at equilibrium.

The Langmuir isotherm relationship is given as:

$$q_e = \frac{Kq_{\max}C_e}{(1 + KC_e)} \quad (8)$$

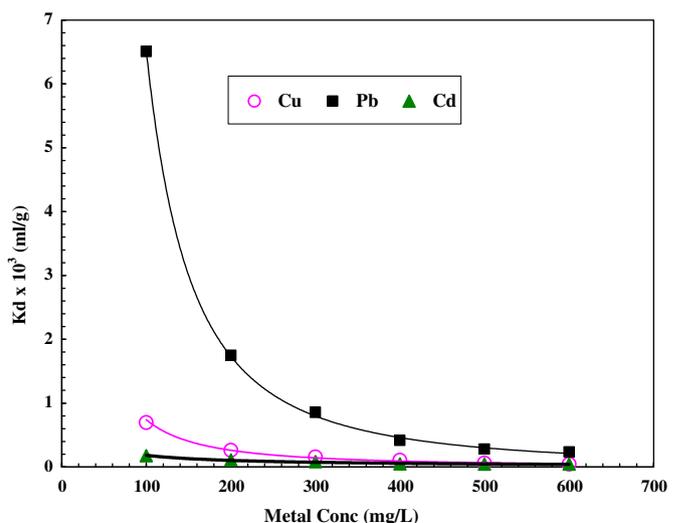


Fig. 6. The effect of metal ions concentration on their distribution ratios (K_d) onto modified orange peel at 25 °C and pH 5.0.

Table 2
Summary of isotherm model parameters for modified orange peel.

Metals	Langmuir model			Freundlich model		
	K	q_{\max} (mg/g)	R^2	K_f	n	R^2
Cd	1.58	13.7	0.97	0.713	1.97	0.97
Cu	3.03	15.27	0.998	2.86	3.33	0.96
Pb	12.5	73.53	0.99	18.84	4.15	0.97

Where, K (L/g) is the equilibrium adsorption constant which is related to the affinity of the binding sites and q_{\max} (mg/g) is the maximum amount of metal ion per unit mass of biosorbent when all binding sites are occupied.

The Langmuir parameters can be determined from a linearized form of Eq. (8) (by plotting C_e/q_e versus C_e), represented by:

$$\frac{C_e}{q_e} = \frac{1}{Kq_{\max}} + \frac{C_e}{q_{\max}} \quad (9)$$

The Freundlich equation is given by:

$$q_e = K_f C_e^{1/n} \quad (10)$$

Where k_f and n are the Freundlich constants and are related to the adsorption capacity of the biosorbent and the adsorption intensity. To simplify the determination of k_f and $1/n$, Eq. (10) can be linearized in logarithmic form which allows the determination of the unknown parameters by plotting $\log q_e$ versus $\log C_e$:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (11)$$

The choice between Langmuir and Freundlich isotherms depends mainly on the nature of equilibrium data [48], where, the adsorption phenomena at the solid–liquid interface were commonly described by the adsorption isotherm mode and adsorption isotherms are essential data source for practical design

of adsorption systems and understanding of relation with adsorbent and adsorbate [49]. Langmuir and Freundlich isotherm parameters are listed in Table 2. Langmuir isotherm assumes monolayer adsorption, the R^2 values for all the metal ions were very close to 1 which revealed the extremely good applicability of the Langmuir model to these adsorptions. The Freundlich model has generally been considered as an empirical equation based on adsorption on a heterogeneous surface and has also been used widely to fit experimental data [50]. Compared with Langmuir isotherm, all the R^2 values of Freundlich model were also greater than 0.95. As indicated from Table 2 and Fig. 7, the coefficients of determination (R^2) of both models were more or less greater than 0.9 indicating that both models were adequately describing the experimental data of metal biosorption experiments. Similar results were obtained by Hussein et al. [51], on their studies of heavy metals biosorption from wastewater using *Pseudomonas* sp.

According to the maximum adsorption capacities (Table 2), the selectivity sequence can be given as $Pb^{2+} > Cu^{2+} > Cd^{2+}$. Lead ions have a preferential uptake compared to the other metals. This may be attributed to the low tendency of lead ions to form strong complex although it can form hydrated ions [52]. Furthermore, based on the Langmuir isotherm, the results in Table 3 showed that the biosorption capacities for Cd(II), Cu(II) and Pb(II) using simple protonated peel were greater than the original peel as reported in the literature.

3.5.2. Dubinin–Kaganer–Radushkevich isotherms (DKR isotherms)

Langmuir and Freundlich isotherms do not give any idea about sorption mechanism. The DKR isotherm is an analogue of Langmuir type but it is more general because it does not assume a homogeneous surface or constant sorption potential [53].

The linearized DKR isotherm equation can be written as:

$$\ln q_e = \ln X_m - \beta \varepsilon^2 \quad (12)$$

where q_e is the number of metal ions adsorbed per unit weight of adsorbent (mol/g), X_m is the maximum sorption capacity, β is the

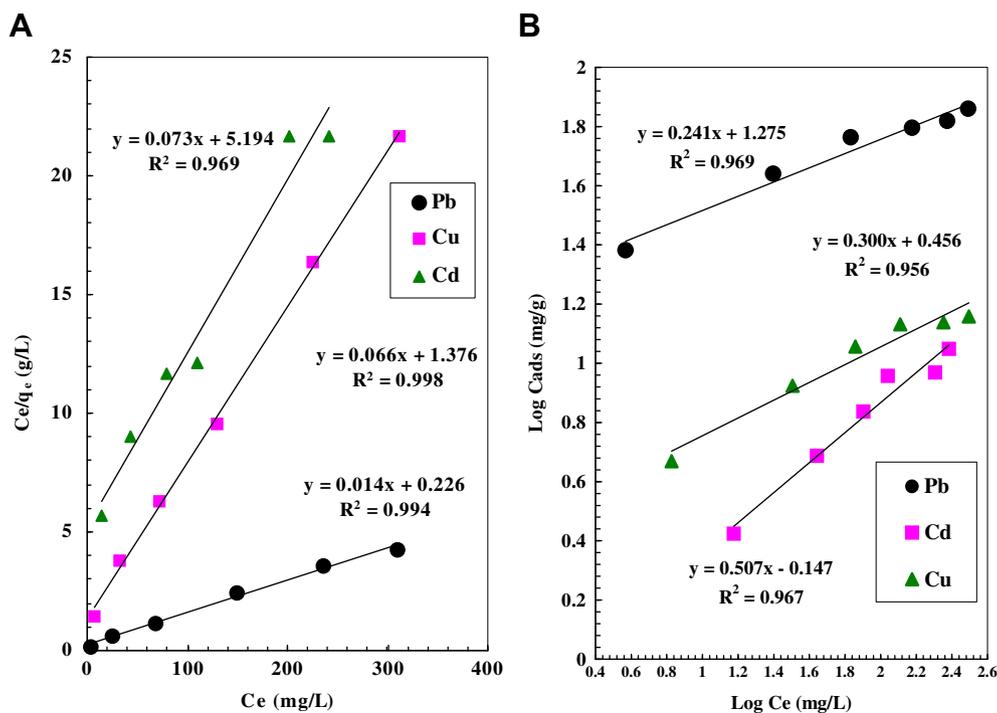


Fig. 7. Langmuir (A), Freundlich (B) adsorption isotherms of metal ions onto modified orange peel.

Table 3
Comparative studies for maximum sorption uptake of native and protonated orange peel.

Metals	q_{\max} (mg/g)	References
Cd(II)	4.16	[23]
	13.7	This study
Cu(II)	3.19	[17]
	15.27	This study
Pb(II)	11.41	[22]
	73.53	This study

activity coefficient related to mean sorption energy and ϵ is the Polanyi potential which is given by:

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (13)$$

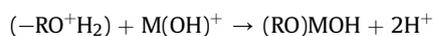
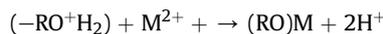
Where R is the gas constant (J/mol K) and T is the temperature (K). The saturation limit X_m may represent the total specific micropore volume of the sorbent. The sorption potential is independent of the temperature but varies according to the nature of sorbent and sorbate [54]. The slope of the plot of $\ln q_e$ versus ϵ^2 gives β (mol²/J²) and the intercept yields the sorption capacity X_m (mol/g). The sorption space in the vicinity of a solid surface is characterized by a series of equi-potential surfaces having the same sorption potential. The sorption energy can also be worked out using Eq. (14):

$$E = \frac{1}{\sqrt{-2\beta}} \quad (14)$$

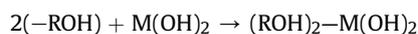
Fig. 8 represents $\ln q_e$ against ϵ^2 for Cd(II), Cu(II) and Pb(II) sorption on modified orange peel. The DKR parameters are calculated from the slope of the line and listed in Table 4. The results show that, the E values are 9.83 for Cd(II), 12.1 for Cu(II) and 14.8 kJ/mol for Pb(II) on modified orange peel. The positive values of E indicate that the sorption process is endothermic and that higher solution temperature will favor the sorption process [55]. The energy values for the studied heavy metals sorption on modified orange peel have adsorption energies < 40 kJ/mol which indicate that the sorption process is physisorption [56]. Furthermore, all metals under investigation have the orders of an ion-exchange mechanism, in which the sorption energy lies within 8–16 kJ/mol [57,58].

At pH 5–6 there are three species present in solution as suggested by Elliott and Huang [59]: M^{2+} in very small quantity and $M(OH)^+$ and $M(OH)_2$ in large quantities. These species are adsorbed at the surface of the modified adsorbent by ion exchange mechanism with the functional groups present in the modified adsorbent or by hydrogen bonding as shown below:

(a) Ion exchange



(b) Hydrogen bonding



Where -R represents the matrix of adsorbent.

3.6. FTIR characterization of functional groups and their contribution to metal binding

Lead has a preferential uptake compared to the other metals. Therefore, FTIR spectra were recorded for original, protonated orange peel before and after lead ions binding as shown in (Fig. 9). Carefully, the examination of the obtained spectra have the typical peaks for -OH groups at 3410–3427 cm⁻¹, alkyl CH at 2925–2926 cm⁻¹, the C=O bond of non-ionic carboxylic acids at 1740–1741 cm⁻¹, asymmetric/antisymmetrical C=O vibration of ionic carboxylate groups at 1637–1644 cm⁻¹ and symmetrical vibration of ionic carboxylic groups at variable wave numbers around 1428 cm⁻¹ (Table 5).

The comparisons of FTIR spectra of original and protonated orange peel after lead ions binding revealed that the absorption peak of the carboxylate (-COO⁻) groups shifted significantly from 1637.27 cm⁻¹–1644.98 cm⁻¹. This shift in wave number corresponds to a change in bonding energy of the functional group, indicating that the bonding pattern of carboxylate groups changes after biosorption. Therefore, this result confirmed the involvement

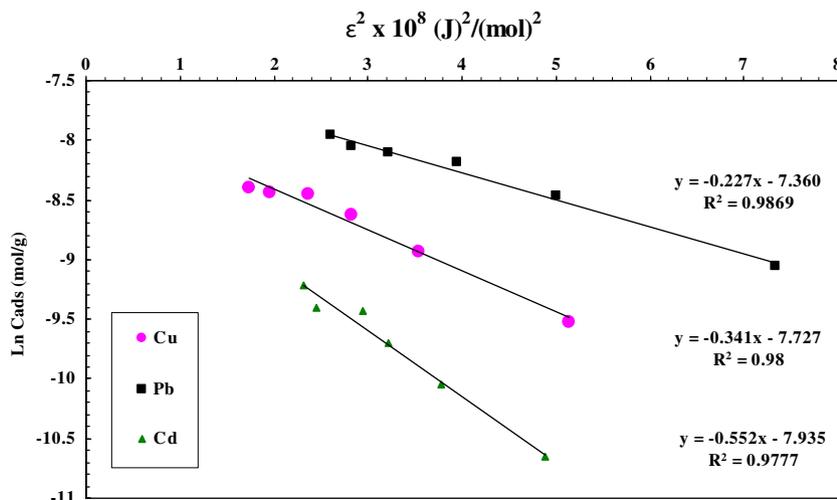


Fig. 8. DKR adsorption isotherms of metal ions onto modified orange peels.

Table 4
Summary of DKR model parameters for modified orange peel.

Metals	X_m (mol/g)	β (mol ² /J ²)	Sorption energy (E, KJ/mol)	Correlation coefficient R^2
Cadmium	3.579×10^{-4}	-0.552×10^{-8}	9.52	0.978
Copper	4.41×10^{-4}	-0.341×10^{-8}	12.10	0.98
Lead	6.36×10^{-4}	-0.227×10^{-8}	14.8	0.987

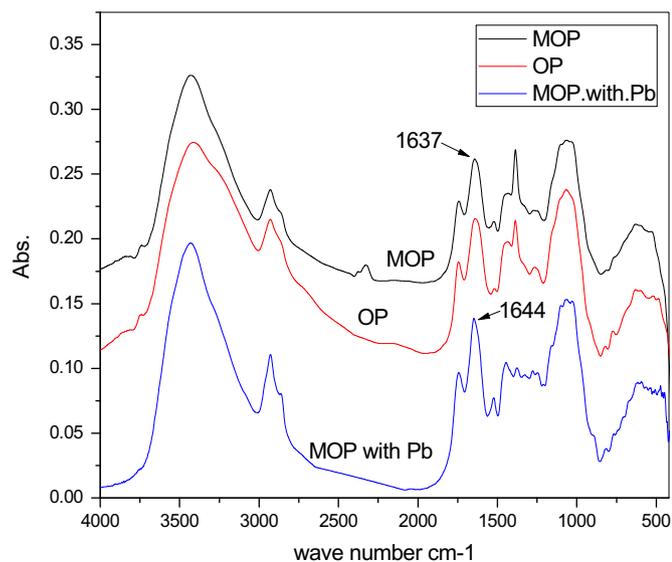


Fig. 9. FTIR spectra of orange peel, chemically modified orange peel and after Pb²⁺ binding for modified orange peel.

of carboxylic acid groups in binding of Pb ions with the protonated orange peel.

Similar peaks were observed for seaweed and their component alginic acid, where the peak around 1640 cm⁻¹ was attributed to metal chelates of carboxyl groups [60–63]. The comparison of the peel spectra with the pectin spectra lead to the conclusion that carboxylic acid groups of pectin were likely responsible for binding Pb²⁺ by orange peel.

3.7. Adsorption/desorption of modified orange peel

Stability is especially important when the same biosorbent material is reused in multiple adsorption and desorption cycles [35]. Therefore, the reusability of modified orange peel biomass was examined based on adsorption/desorption ability.

Table 5
Wave number of Infrared absorption peaks of different orange peel samples.

	OP	MOP	MOP with Pb
OH groups of alcohol and carboxylic acids [61–63]	3410.49	3426.89	3427
C–H bonds of aliphatic acids, symmetric or asymmetric [64]	2926.45	2925.48	2925.48
C=O bond of non-ionic carboxylic acids and esters (–COOH, –COOCH ₃) [64,65]	1741.41	1740	1741.4
Ionic carboxylic groups (–COO–), asymmetric/antisymmetrical [63,64,66,67]	1637.27	1639.2	1644.98
Ionic carboxylic groups (–COO–), symmetric [63,64,67]	1432.85	1428.99	1443.46
OH of alcoholic groups [66]	1063.55	1063.55	1057.76

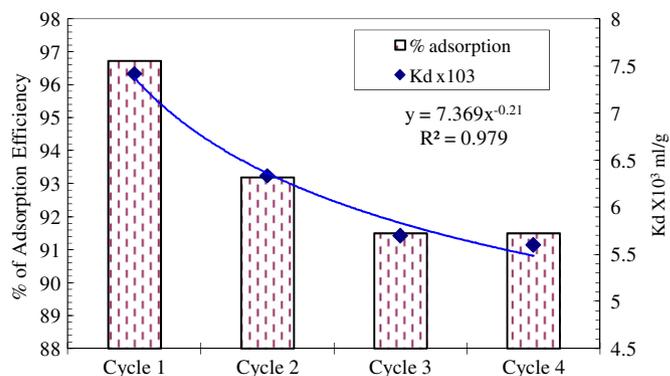


Fig. 10. Four repetitive cycle of sorption and desorption for lead ion on modified orange peel as a function of residual concentration at the optimum removal condition.

The viability of the recovery process is assured by the high efficiency of the metal regeneration processes for the exhausted modified orange peel with 0.2M HCl. Maranon and Sastre [68] reported that the regeneration of the exhausted orange waste with HCl was the most commonly used for initiation of regeneration cycle.

Furthermore, in order to investigate the reproducibility of modified orange peel, the adsorption–desorption cycle was repeated four times using the same biomass of modified orange peel at the same optimum operating condition for Pb²⁺ as it has a preferential uptake compared to the other metals. The Pb²⁺ adsorption percentages (%) and distribution ratio (K_d) were calculated, whose initial concentration was 100 mg/L (Fig. 10). The exhausted modified orange peel was converted to the hydrogen form for maximum lead adsorption capacity using a solution of 0.2M HCl. The obtained results show that, in the first cycle, the removal efficiency by biosorption was more than 96% for Pb²⁺. From the second to four cycles, the modified orange peel biomass had slightly changed adsorption ability ranged from 93.5 to 91.5.

4. Conclusion

From this study, it can be concluded that, ease and simple pretreatment of the inexpensive biosorbent made of orange peel biomass show high-sorption performance of heavy metals and high feasibility of desorption and regeneration of sorption capacity. Moreover, a comparison of different isotherm models revealed that the modified biosorption data perfectly fitted the Langmuir and Freundlich adsorption isotherms models with regression coefficient $R^2 > 0.95$ for all the studied metal ions. The modified biosorption kinetic studies indicated that the experimental data followed the second-order kinetic reaction. These appropriate features will contribute to the reuse of this orange peel biomass as a novel biosorbent material in practical application for removal of heavy metals from industrial wastewater.

References

- [1] P. Kunz, S.G. Peralta-Zamora, N.D. Moraes, Novas tendências no tratamento de efluentes têxteis, *Quím. Nova* 25 (2002) 78–82 í.
- [2] K.S. Low, C.K. Lee, S.C. Liew, Sorption of cadmium and lead from aqueous solution by spent grain, *Process Biochem.* 36 (2000) 59–64.
- [3] E. Valdman, L. Erijman, F.L.P. Pessoa, S.G.F. Leite, Continuous biosorption of Cu and Zn by immobilized waste biomass *Sargassum* sp, *Process Biochem.* 36 (2001) 869–873.
- [4] P. Kaewsarn, Q. Yu, Cadmium(II) removal from aqueous solutions by pre-modified biomass of marine alga *Padina* sp, *Environ. Pollut.* 112 (2001) 209–213.
- [5] G. Yan, T. Viraraghavan, Heavy metal removal in a biosorption column by immobilized *M. rouxii* biomass, *Bioresour. Technol.* 78 (2001) 243–249.

