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Potato peels as promising low-cost adsorbent for the removal of lead, cadmium, chromium and copper from wastewater

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ABSTRACT

Toxic metals contamination of wastewater is of special concern due to their toxic and non-biodegradable nature. Thus, low-cost adsorbents have recently been given great attention for the treatment of wastewater. The main aim of this work is to characterize and evaluate the effectiveness and sustainability of potato peels as adsorbent for Pb(II), Cr(III), Cd(II) and Cu(II) removal from wastewater. The effects of contact time, pH, adsorbent dosage, particle size, initial concentrations, temperature, kinetics, adsorption isotherm modeling, thermodynamics and reusability studies on Pb(II), Cr(III), Cd(II) and Cu(II) removal were studied. The quantities of Pb(II), Cr(III), Cd(II) and Cu(II) removed increased with decreasing initial concentration of the metal ions. The removal efficiency was increased by increasing the dosage of adsorbent and decreasing the particle size. The percentage removals of the toxic metals were also increased slightly by increasing the solution temperature. Pb(II), Cu(II) and Cr(III) were found to be highly adsorbed at pH 4 and Cd(II) was highly adsorbed at pH 6. The Langmuir isotherm model fits the adsorption of Cu(II), Cr(III) and Pb(II), and the Freundlich isotherm model fits for Cd(II). The pseudo-second-order kinetics model fits the adsorption of Cd(II), Pb(II), Cr(III) and Cu(II) onto potato peels. The results of thermodynamic data showed that the adsorption of Pb(II), Cr(III), Co(II) and Cd(II) was a non-spontaneous and endothermic process. Generally, the study indicates that potato peels adsorbent may be economic reusable and effective alternative low-cost adsorbent for Cd(II), Pb(II), Cu(II) and Cr(III) removal from wastewater.

Keywords: Toxic metals; Wastewater treatment; Potato peels; Batch adsorption; Waste management

1. Introduction

In developing nations, the search for safe drinking water can be a daily crisis. Millions of people die each year due to lack of access to safe water. By the year 2025, it is estimated that about 4–5 billion people will live without clean water [1]. Toxic metals such as Cr(III), Pb(II), Cd(II) and Cu(II) are the most persistent pollutants in the aquatic environment. As a result of rapid population growth and expansion of industrial activities, environmental pollution associated with toxic metals is the main concern of environmentalists. If their levels exceed the permissible limits, they become toxic to living species [1]. The degree to which a living organism is affected by a toxic metal depends on its chemical speciation and the individual's degree of exposure [2]. They originate from sources such as industrial effluents, mining, agricultural processes, landfill leachate, plumbing supplies, welding and electroplating processes, and electrical wiring materials [3].

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Drinking water resources that are contaminated with excessive toxic metals can be detrimental and may cause damage to ulcer, kidney, brain and liver, cancer, and chronic health disorders such as cholera, diarrhea, typhoid and gastrointestinal diseases [4,5]. It is, therefore, important to treat excess toxic metals in industrial effluents before discharging it into surface/groundwater.

Various treatment technologies used for removal of toxic metals from wastewater include biological processes [6], chemical precipitation, ion exchange, chemical oxidation, reduction, reverse osmosis, ultra-filtration, electrodialysis [7], photochemical oxidation [8], coagulation and membrane filtration, and adsorption [9,10]. Each of these techniques has its advantages and disadvantages. Adsorption could be a good alternative technology for the removal of toxic metals from aqueous effluents even at low concentrations because it provides flexibility in design, being inexpensive and environmental friendly, reversible and the adsorbent can be regenerated [7].

The main types of adsorbents that are used for the efficient removal of toxic metal from wastewater include activated carbon, silica-based adsorbents, polymer resins such as active alumina, silica gel, zeolite and metal oxides [11–13]. However, these adsorbents are rarely used for wastewater adsorption. Agricultural byproducts are abundant and locally available natural materials, which are rich sources of low-cost adsorbents [14,15]. Moreover, the application of agricultural wastes as adsorbents offers highly effective technological means to mitigate global warming, solve the disposal problems and save the high preparation cost of adsorbents [16,17].

Many researchers reported the effective use of raw and treated agricultural byproducts as metal adsorbents such as peanut hull [18,19], sugarcane bagasse [20], Hickory wood [21], moss biomass (*Barbula lambarenensis*) [13,22,23], orange peel, sawdust and bagasse [24], coffee residues [25] and coconut husk [26]. Biosorption of cadmium from synthetic wastewater using dry biofilms [27]; lead ions from aqueous solution by waste biomass [28]; and removal of cadmium and lead from aqueous solutions using nitrilotriacetic acid anhydride modified ligno-cellulosic material [29] was effective. The efficiency of adsorption depends on the polarity and functional groups attached to the adsorbent, surface morphology, surface area and pore size distribution of the adsorbent [15,19,30]. However, additional insights into the removal of toxic metals such as lead (Pb), cupper (Cu), cadmium (Cd) and chromium (Cr) using agricultural byproducts from the wastewater is still needed.

Bio-adsorbents, which were produced from agricultural byproducts, may act as a significant material for toxic metal adsorption. Potato peel, an agricultural byproduct is discarded all over the world as useless material. It is causing waste management problems though it has some compost and adsorbent potentiality. It is an abandoned, readily available, low-cost and cheap, environmental friendly biomass in Ethiopia. Considering the above criteria, potato peel was selected to prepare the bio-sorbent and to determine the potentiality and adsorption capacity for removal of toxic metals from wastewater. Hence, this study was conducted to prepare and characterize potato peels for the treatment of Pb(II), Cr(III), Cd(II) and Cu(II) from wastewater, to investigate the effect of initial metal concentrations, pH, dosage, size, solution temperature and contact time on equilibrium under batch adsorptive experiments, and to develop a conceptual model on treatment efficiency of potato peels as an adsorbent.

2. Materials and methods

2.1. Preparation and characterizations of potato peels adsorbent

Composite samples of potato peels were collected from Harar City, Bate town and the Haramaya University student cafeteria. The collected samples were brought to the Laboratory and washed with running water to remove dirt particles and finally rinsed with distilled water. The washed samples were oven-dried at 80°C–110°C for 24 h and the dried samples were crushed and ground into powder. Then, the powdered products were screened to four different particle sizes (<250 μm, 0.25 mm, 0.300 mm and 0.75 mm) and preserved in desiccator for characterization and adsorption studies. The morphology and surface features of potato peels were characterized by scanning electron microscopy (SEM) using a Hitachi TM1000 with EDX detector. The functional groups that may affect the adsorption process were detected by Fourier transforms infrared spectrometer (Shimadzu FTIR-1730S, Japan) studies, and the FTIR measurements were conducted in wavenumber from 4,000 to 400 cm^{-1}. The crystalline structure of potato peels was determined by X-ray diffraction (XRD 7000S, Japan) analysis.

2.2. Preparation of synthetic wastewater

Stock-toxic metal solutions (1,000 mg/L) of Cr(III), Cu(II), Cd(II) and Pb(II) were separately prepared by dissolving potassium dichromate ($K_2Cr_2O_7$), copper sulfate ($CuSO_4 \cdot 5H_2O$), cadmium chloride ($CdCl_2 \cdot H_2O$) and lead nitrate ($Pb(NO_3)_2$) in double-distilled water, respectively. Synthetic wastewater and different initial working concentrations of metal ions were prepared by diluting the stock solutions. The pH of the solutions was adjusted using 0.1 N NaOH and 0.1 N HCl solutions to achieve the desired values.

2.3. Adsorption studies

The processed potato peels powder was employed for the adsorption studies of the metal ions from an aqueous solution. The adsorption processes were carried out in 100 mL bottles placed in a thermostatic water-bath shaker until the equilibrium was reached (except for the effect of dose, the mass of sample used in the experiment was 1 g). The effects of contact time, pH, adsorbent dosage, particle size, initial concentrations and contact time were varied to study the adsorption of Pb(II), Cu(II), Cd(II) and Cr(III) from the given solutions. About 50 mL of aqueous solutions of each toxic metal at initial concentrations from 100 to 300 mg/L were transferred into 100 mL bottles. Then, the potato peel powder was added at different doses (0.1–1 g) with continuous shaking at 150 rpm. The effects of pH (2–10), the solution temperature (20°C–65°C) and time (20–180 min) for Pb(II), Cd(II), Cr(III) and Cu(II) ions adsorption onto potato peel were investigated. The metal ions concentrations in the solution were determined by using atomic absorption spectroscopy (AAS).

All experiments were carried out in triplicate and the mean values were calculated and illustrated. The amount of metals retained in the potato peels (q_e, mg/g) was calculated as follows:

$$q_e = \frac{\left(C_i - C_e\right)\times V}{m} \tag{1}$$

where q_e is the amount adsorbed equilibrium (mg metal/g adsorbent), C_i and C_e are the initial and final (equilibrium) concentrations of each metal in solution (mg/L), V is the solution volume (L) and m is the potato peels mass (g). The percentage removal of each metal in potato peels was also calculated by the following formula:

$$\text{Adsorption}\left(\%\right) = \frac{\left(C_i - C_e\right)\times 100}{C_i} \tag{2}$$

2.4. Regeneration studies

Desorption of Pb(II), Cu(II), Cd(II) and Cr(III) was performed with a 0.1 N HCl solution. The used adsorbents were repeatedly washed with distilled water. The desorbed adsorbents were dried and used for the adsorption experiment to investigate the extent of regeneration and reusability of the spent potato peels. The final metal concentrations in the solutions were determined by AAS. The percentage of desorption values was calculated as follows:

$$\text{Desorption Efficiency}\left(\%\right) = \frac{\text{Desorbed}\times 100}{\text{Adsorbed}} \tag{3}$$

2.5. Adsorption isotherm, kinetics and thermodynamic studies

The fundamentals of the investigated processes were based on the studies of the adsorption isotherms, adsorption thermodynamics and adsorption kinetic mechanisms.

2.5.1. Kinetics of adsorption studies

Adsorption kinetics was studied for different contact time from 5 to 180 min by keeping all other parameters at optimized values. It was studied using the pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion models. The pseudo-first-order model describes the rate of adsorption to be proportional to the number of unoccupied sites by the solutes and is expressed by [31] the equation as follows:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{4}$$

where q_e and q_t are the amounts of metal ion adsorbed (mg/g) at equilibrium and at time t (min), respectively and k_1 is the rate constant (L/min). The constants can be determined from the plot of $\ln(q_e - q_t)$ vs. t. Pseudo-second-order model is assumed that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites [31] expressed as:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where k_2 is equilibrium rate constant (g/mg min), q_e is the amount of adsorption equilibrium and k_2 is the rate constant of the equation (L/min).

The intra-particle diffusion model is estimated to predict the diffusion mechanism of the adsorption process. During the adsorption process, the metal ions transport from the bulk solution phase to the surface of internal active sites. The transfer is usually controlled by intra-particle mass diffusion or boundary-layer diffusion or both. The slowest step would be the overall rate-determining step [32]. Weber–Morris noticed that solute uptake varies with $t^{0.5}$ rather than with the contact time t.

$$q_t = \alpha + k_{\text{int}} \times t^{0.5} \tag{6}$$

where k_{int} is intra-particle diffusion rate constant (mg/g min), α is an intercept of the boundary layer thickness. The intra-particle diffusion is the rate-limiting step if the plot passes through the origin. If the curve represents multi-linearity, it shows the complexity of the adsorption process. Elovich model describes the kinetics of the chemisorption process using the equation:

$$q_t = \frac{1}{B_e \ln(\alpha B_e)} - \frac{1}{B_e \ln t} \tag{7}$$

where α is the initial rate (mg/g min) and B_e is the surface coverage for chemisorptions (g/mg).

2.5.2. Equilibrium adsorption isotherm studies

The Freundlich, Langmuir, Temkin and Redlich–Peterson adsorption isotherm models were used to study the effect of temperature on the adsorbent equilibrium capacity of potato peels for Pb(II), Cu(II), Cd(II) and Cr(III) removal from wastewater. Langmuir isotherm model assumes monolayer adsorption of solutes onto a surface with homogeneous energy of adsorption. The linear form of the Langmuir isotherm is expressed by:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m \times C_e} \tag{8}$$

where C_e is the equilibrium metal concentration (mg/L), q_e is the equilibrium metal uptake (mg/g), q_m is the maximum adsorption capacity (mg/g), and b is the Langmuir constant (L/mg). The main feature of this model can be evidenced by equilibrium parameter (R_L) and is represented by: $R_L = 1/(1 + bC_0)$; where b is the Langmuir constant and C_0 is the initial metal concentration, R_L values indicate the type of isotherm to be irreversible ($R_L = 0$), favorable

($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The values of Langmuir isotherm constants were determined from the linear plot C_e/q_e vs. C_e, which has a slope of $1/q_m$ and the intercept of $1/q_m b$. Freundlich isotherm model is valid for multilayer adsorption on a heterogeneous surface adsorbent with a no uniform distribution of energy [33]. It is expressed by:

$$\log q_e = \frac{1}{n_f \log C_e} + \log K_f \tag{9}$$

where n_f and K_f are Freundlich constants related to adsorption intensity and adsorption capacity, respectively. The constants are determined from the plot of $\log q_e$ vs. $\log C_e$. Redlich–Peterson isotherm model is used to distinguish the physical and chemical nature of adsorption of toxic metals with its mean free energy. Its linear equation is expressed by:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{10}$$

where q_m and β are constants, ε is Polanyi potential given by: $\varepsilon = RT \ln(1 + 1/C_e)$. Values of q_m and β can be determined from the plot of $\ln q_e$ vs. ε^2. β gives the mean adsorption energy of activation or free energy E (kJ/mol) per molecule of the adsorbate when it is transferred to the surface of the solid from the solution and is calculated by: $E = 1/(-2\beta)^{½}$. If the value of $E < 8$ kJ/mol, the adsorption is physisorption and if $E = 8$–16 kJ/mol, the adsorption is chemisorption in nature. Temkin isotherm model is also applied to describe adsorption on heterogeneous surfaces. The main assumption of the model is the heat of adsorption decreases linearly with increasing surface coverage due to the adsorbent and adsorbate interactions [34,35]. The linear form of this model is expressed by:

$$q_e = \left(\frac{RT}{b_T}\right) \ln C_e + \left(\frac{RT}{b_T}\right) \ln A_T \tag{11}$$

where b_T is the Temkin constant related to the heat of adsorption (J/mol), A_T is the equilibrium binding constant (L/g), R is the universal gas constant (8.314 J/mol K) and T is the absolute temperature (K).

2.5.3. Thermodynamic studies

To evaluate the spontaneity and heat change of the processes, thermodynamic parameters were calculated from the Van't Hoff equation, which is expressed by:

$$\ln K_d = \frac{-\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{12}$$

where ΔG is standard free energy, T is the absolute solution temperature, R is the universal gas constant (8.314 J/mol K), ΔH is enthalpy, ΔS is entropy, K_d is adsorption constant (L/mg). From the values of ΔH and ΔS, ΔG was calculated as follows.

$$\Delta G = \Delta H - T\Delta S \tag{13}$$

The plots of $\ln K_D$ vs. $1/T$ were used to determine the $\Delta H°$ and $\Delta S°$ values. The experimental data obtained at temperatures from 20°C to 65°C were used in calculating the thermodynamic parameters.

3. Results and discussion

3.1. Characteristics of the potato peels

The infrared spectrum of potato peels in the range of 4,000 to 400 cm^{-1} before and after the adsorption of metal ions is shown in Fig. 1. The adsorbent displays many peaks reflecting the complex nature of the potato peels. The peak at 3,390 cm^{-1} was due to the OH stretching vibration that indicates the presence of alcohols, phenols and chemisorbed water [36]. The absorption peaks at 3,030–2,800 cm^{-1} were attributable to the –CH, –CH$_2$ and other saturated aliphatic groups. The bands corresponding to the OH and COOH were detected at 2,200; 1,600; 1,440; 1,200 and 1,070 cm^{-1}. The peaks at 1,710 and 1,680 cm^{-1} were due to the C=O stretch of aldehyde and C=C stretch of phenol groups. The peak at 598 cm^{-1} was due to the vibrational bending in the aromatic compounds [37,32]. The absorption spectrum of potato peels with metal ions showed changes due to either complexation, hydrogen bonding or other electrostatic interactions. The intensities of the peaks before metal ions loading adsorption were relatively weaker than those obtained after adsorption [19,27,32].

The surface morphology of potato peels before and after metal adsorption is shown in Fig. 2. Many rough surfaces with varying sizes of potato peels within the particles can be used for trapping toxic metals. The large pores are more easily accessible to metal ions [38]. The SEM analysis after metal ions loading shows different morphology for potato peels. This is due to the impregnation of the metal ions saturation on the surface of potato peels (Fig. 2). The XRD pattern of potato peels before and after metal ions adsorption is also shown in Fig. 3. The XRD pattern shows a typical spectrum of amorphous biomass materials. The intensive peaks at small 2θ angles are characteristics of organized cellulose and porous materials that possess abundant cavities. The most notable diffraction peaks of the potato peels before and after sorption were found below 2θ of 22 and 2θ of 18, respectively. The peak intensities of the potato peels after adsorption were found to be stronger.

3.2. Effect of contact time

The effect of time on the percentage removal of Cu(II), Cd(II), Pb(II) and Cr(III) onto potato peels is shown in Fig. 4. Different durations of contact between metal ions and potato peel powder ranging from 20 to 180 min were assessed. The percentage removal efficiency of potato peels increased for Cu(II) from 65.8% to 71.2%, Pb(II) from 52.5% to 85.2%, Cd(II) from 47.22% to 72.7% and Cr(III) from 35.5% to 68.6% with increasing the contact time. Initially, increase in percentage removal efficiencies of Cu(II), Cd(II), Pb(II) and Cr(III) was relatively rapid. These may be due to the availability of free binding sites. After equilibrium (time, 60 min), there was no significant increase in the percentage removal of these metals (Fig. 4). This may be due to the saturation of binding sites with metal ions. The result showed that, for all initial concentrations, the equilibrium was obtained in the same time (60 min). A similar type of trend has also been reported in other researchers [19,27].

3.3. Effect of solution pH

In this study, the effect of pH on the adsorption process of Cu(II), Cd(II), Pb(II) and Cr(III) onto the potato peels was studied by varying the solution pH in the range of 2–10, and the results are shown in Fig. 5. The adsorption of Cu(II), Cd(II), Pb(II) and Cr(III) can be related to the type and ionic state of the functional groups available for adsorption. pH can affect the surface charges of the adsorbent, the concentration of the metals and the degree of ionization. Pb(II) (79.4%), Cu(II) (72.7%) and Cr(II) (80.0%) ions were found to be highly adsorbed at pH 4 and Cd(II) (73.3%) ions were highly adsorbed at pH 6. Initially, the removal efficiency of these toxic metals tend to increase with increasing pH value (Fig. 5). The process of acquiring

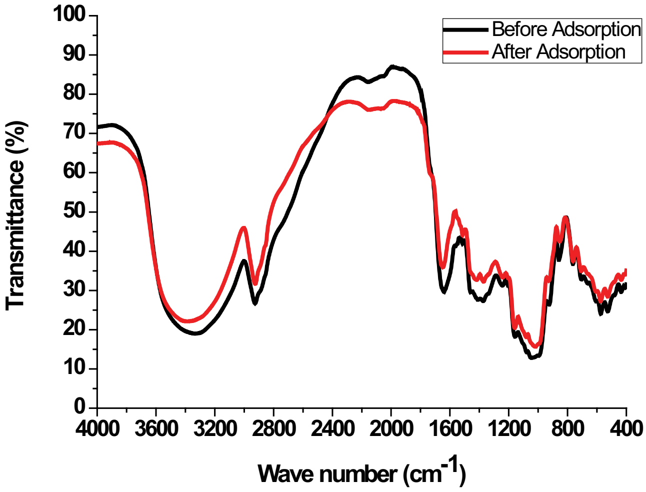


Fig. 1. FTIR spectra of potato peels before and after metal ions adsorption.

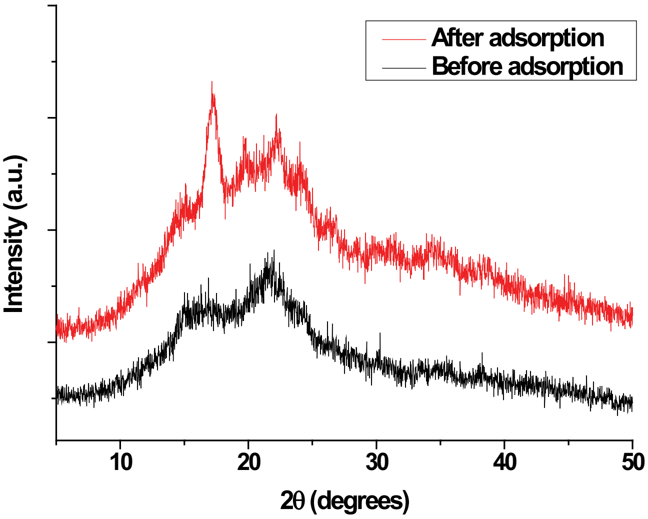
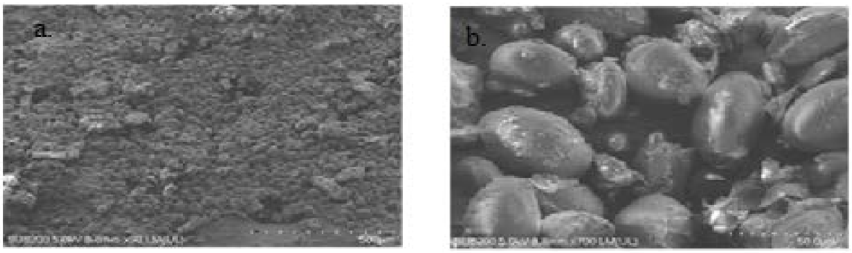


Fig. 3. XRD pattern of potato peels.

Before Adsorption



After Adsorption

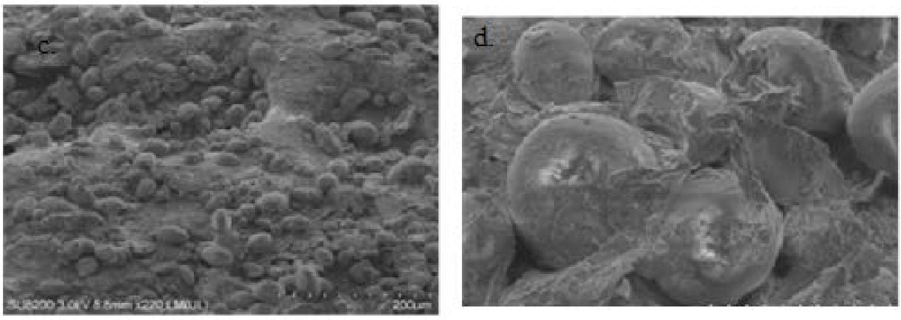


Fig. 2. SEM analysis of potato peels before and after metal ions adsorption.

partially positive and negative surfaces on potato peels depends on the pH of the solution. pH value of 2 is considered to be more acidic, which hampers metallic ions uptake due to the repulsion of similar charge of hydrogen ions and metal ions. At higher pH, the removal efficiency of Cu(II), Cd(II), Pb(II) and Cr(III) ions tended to decrease because of the precipitation of these metal ions out of solution [19].

3.4. Effects of adsorbent dosage

Fig. 6 shows the trends in the metal ions adsorption by potato peels at different doses (0.1–1 g). The experimental results showed that the percentage removal of Cu(II), Pb(II), Cd(II) and Cr(III) increased from 62.1% to 82.1%, 61.3% to 87.5%, 57.1% to 69.4% and 57.5% to 77.5%, respectively, when the adsorbent dose was increased from 0.1 to 1 g. These indicate that these toxic metals adsorption increases with an increase in the amount of biomass. This may be due to the fact that more biomass indicates that more active sites will be available. Hence, there will be more linkages for the formation of complexes with metal ions until saturation [19,27].

3.5. Effect of particle size

Four ranges of particle size, <250 μm, 0.25 mm, 0.30 mm and 0.75 mm, were studied to see the effect of potato peels on Cu(II), Cr(III), Cd(II) and Pb(II) removal from wastewater as shown in Table 1 (100 mg/L, room temperature (25°C), 150 rpm, 1 g adsorbent dose and 1 h shaking for each metal, and optimum pH values of each metal). The smallest potato peels particle size has the highest adsorption efficiency of Cu(II) (67.2%), Cr(III) (69.0%), Cd(II) (68.8%) and Pb(II) (79.0%) removal from the solutions (Table 1). In all cases, the decrease in potato peels particle size increases

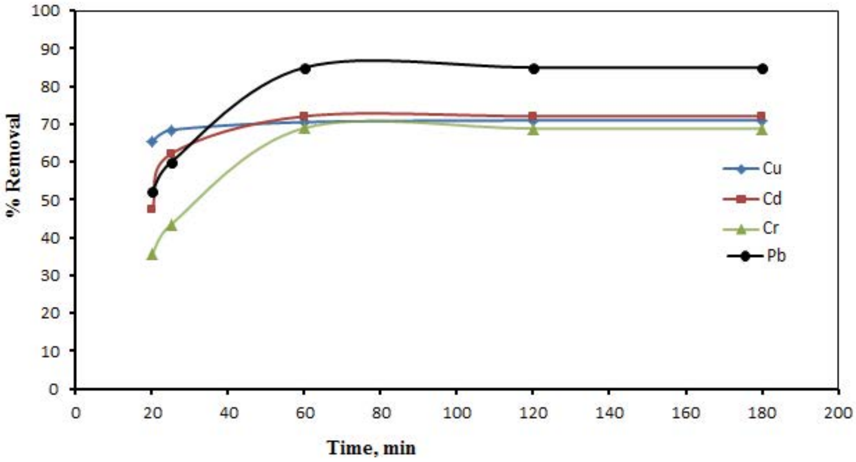


Fig. 4. Effect of time on the percentage removal of metal ions on potato peels for different metal ions solution concentrations. Experiment conditions: initial concentration, 100 mg/L; temperature, room temperature (25°C); adsorbent dose, 1 g; particle size, 250 μm; shaking rate, 150 rpm, and pH, for Cd(II) pH = 6, for Cu(II), Pb(II) and Cr(III) pH = 4.

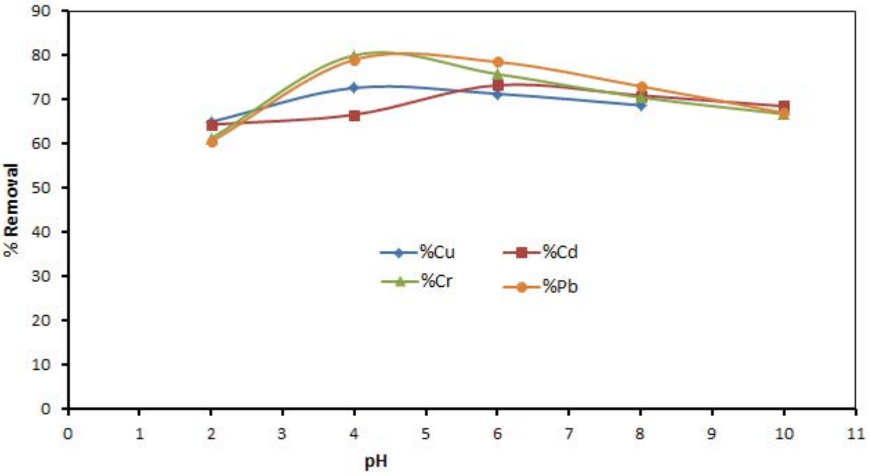


Fig. 5. Effect of pH on the percentage removal of metal ions using potato peels. Experiment conditions: initial concentration, 100 mg/L; temperature, room temperature (25°C); adsorbent dose, 1 g; particle size, 250 μm; shaking rate, 150 rpm; and pH 2–10.

the metal ions uptake. This might be due to the higher accessibility to pores and also the greater surface areas.

3.6. Effect of initial toxic metal ions concentrations

The effect of initial metal concentrations on the adsorption process of Cu(II), Cd(II), Pb(II) and Cr(III) onto potato peels is shown in Fig. 7. As can be seen from the results (Fig. 8), increasing the Cu(II), Cd(II), Pb(II) and Cr(III) initial concentrations (100 to 500 mg/L) decreases the removal percentage efficiency (Cu(II), 75.2%–40.6%, Pb(II), 79.4%–30.4%, Cd(II), 70.6%–47.3% and Cr(III), 91.1%–64.4%). This may be due to the higher initial metal concentration provides a strong driving force to overcome all resistances to the mass transfer from the solutions. But at higher concentrations, this ratio is low due to the minimum accessibility of the binding sites [29,39].

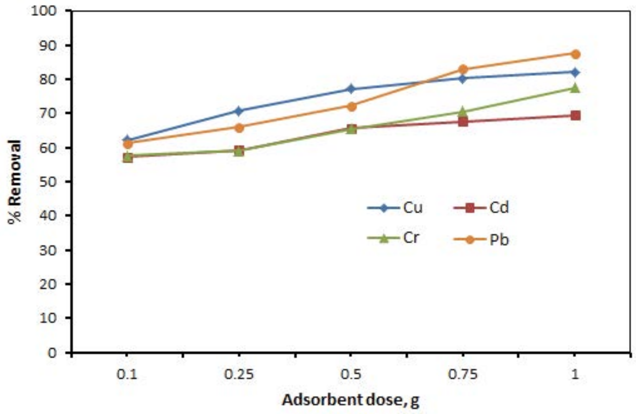


Fig. 6. Effect of adsorbent dose on the percentage removal of metal ions using potato peels. Experiment conditions: initial concentration, 100 mg/L; temperature, room temperature (25°C); adsorbent dose, 0.1–1 g; particle size, 250 µm; shaking rate, 150 rpm, and pH, for Cd(II) pH = 6, for Cu(II), Pb(II) and Cr(III) pH = 4.

3.7. Effect of solution temperature

The experimental results on the study of effect of temperature (20°C–65°C) on the percentage removal of Cu(II), Pb(II), Cd(II) and Cr(III) by the potato peels is shown in Fig. 8. The adsorption efficiency of potato peels was increased slightly (Cu(II) 79.1%–83.4%, Pb(II) 70.7%–76.5%, Cd(II) 62.50%–68.5% and Cr(III) 72.0%–78.0%) as the temperature increased from 20°C to 60°C (Fig. 8). As the temperature of the solution increases, metals diffusion (mass transfer) will also increase. Hence, the adsorption process of these toxic metals onto potato peels was considered as an endothermic process [19,29].

3.8. Kinetics of adsorption studies

The values of adsorption kinetics constants and R^2 calculated from the equation at different contact times are presented in Table 2. The values of R^2 were relatively lower for the pseudo-first-order kinetic model when compared with the pseudo-second-order. This may not be enough to explain the adsorption process of Cd(II), Pb(II), Cu(II) and Cr(III) onto the surface of potato peels. It might be working in the region where the adsorption process occurs very fast. As shown in Table 2, the R^2 values of pseudo-second-order kinetic model for Cd(II) (0.974), Cu(II) (0.994), Cr(III) (0.978) and Pb(II) (0.963) yields a better fit than the

Table 1
Effect of particle sizes on percentage toxic metals removal

	% Removal			
Particle size	Cu	Cd	Cr	Pb
250 µm	67.21	68.83	69.00	79.00
0.25 mm	61.65	58.00	66.00	77.06
0.30 mm	59.30	57.33	65.00	67.61
0.75 mm	57.44	34.67	62.00	47.61

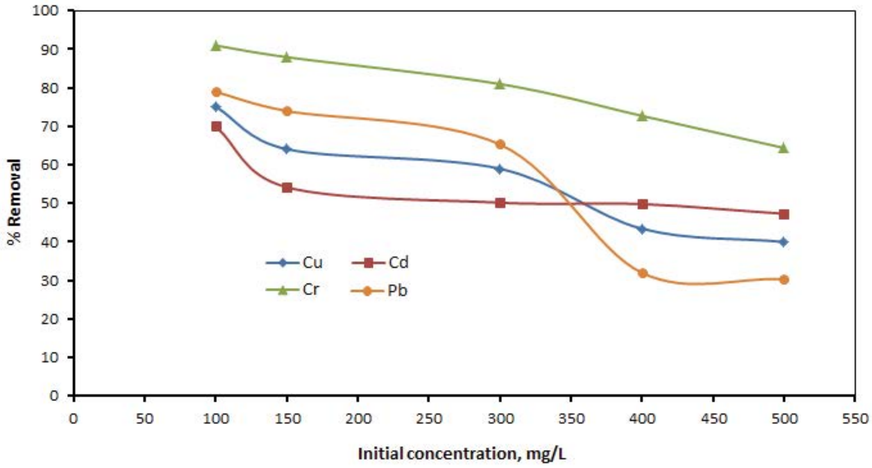


Fig. 7. Effect of initial concentration on the percentage removal of metal ions using potato peels. Experiment conditions: initial concentration, 100–500 mg/L; temperature, room temperature (25°C); adsorbent dose, 1 g; particle size, 250 µm; shaking rate, 150 rpm, and pH, for Cd(II) pH = 6, for Cu(II), Pb(II) and Cr(III) pH = 4.

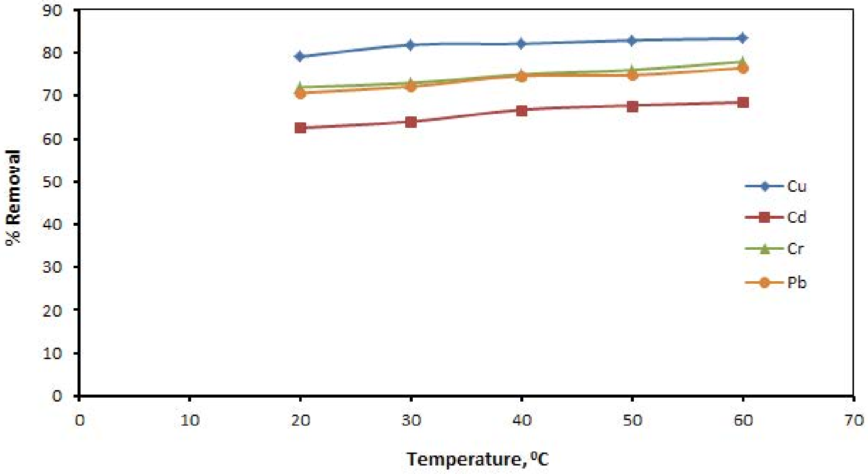


Fig. 8. Effect of temperature on the percentage removal of metal ions using potato peels. Experiment conditions: initial concentration, 100 mg/L; temperature, 20°C–60°C; adsorbent dose, 1 g; particle size, 250 μm; shaking rate, 150 rpm, and pH, for Cd(II) pH = 6, for Cu(II), Pb(II) and Cr(III) pH = 4.

pseudo-first-order kinetic model Cd(II) (0.917), Cu(II) (0.986), Cr(III) (0.947) and Pb(II) (0.938). This suggests that the pseudo-second-order kinetic model was more representative of the kinetic data. Hence, the rate-limiting step may be chemical adsorption for Cd(II), Pb(II), Cu(II) and Cr(III) adsorption onto potato peels. Metal ions exist in aqueous solution as cations can be removed via electrostatic attraction or surface complexation [40,41].

The plot of q vs. $t^{0.5}$ of the intra-particle diffusion model for Cd(II), Pb(II), Cu(II) and Cr(III) onto potato peels is not very linear all the time. This implies that the adsorption processes of these metals show the multistage adsorption on the potato peels. The adsorption of all the metal ions onto potato peels may not be the diffusion control because there will be a boundary layer resistance. However, the non-zero intercepts of the plots and high R^2 values Cd(II) (0.972), Cu(II) (0.991), Cr(III) (0.968) and Pb(II) (0.932)) (Table 2) showed that the intra-particle diffusion model governs the adsorption of Cd(II), Pb(II), Cu(II) and Cr(III) onto potato peels.

The linear Elovich isotherm model parameters for Cd(II), Pb(II), Cu(II) and Cr(III) removal are shown in Table 2. The values of R^2 for this model of Cd(II), Pb(II), Cu(II) and Cr(III) obtained were high (0.830–0.949). These indicate that the diffusion rate-limiting is more prominent in Cd(II), Pb(II), Cu(II) and Cr(III) adsorption by potato peels. The studied adsorption process is controlled by the chemisorption process, that is, the rate can be increased by increasing the adsorption temperature. The kinetic results showed that during Cd(II), Pb(II), Cu(II) and Cr(III) transfer both external and internal diffusions affect the adsorption mechanisms [42].

3.9. Equilibrium adsorption isotherm studies

The parameter values of Langmuir, Freundlich, Temkin and Redlich–Peterson adsorption isotherms and linear correlation coefficients (R^2) are shown in Table 3. As shown in Table 3, the values of R^2 were found to be 0.773–0.999 in the Langmuir isotherm model and 0.458 to 0.977 in the Freundlich isotherm model. All the values of R_L were between 0 and 1 for Cu(II), Pb(II), Cd(II) and Cr(III), which supports the idea that adsorption was favorable (Table 4). The values of R^2 in the Langmuir isotherm model for Cu(II) 0.978, Cr(III) 0.999 and Pb(II) 0.969 yielded better fit than the Freundlich isotherm model (Cu(II) 0.939, Cr(III) 0.977 and Pb(II) 0.458). This suggests that the adsorption of Cu(II), Cr(III) and Pb(II) onto potato peels as a monolayer coverage and uniform adsorption energy. However, R^2 values of the Freundlich isotherm model for Cd(II) 0.939 yield a better fit than the Langmuir isotherm model (Cd(II) 0.773). This suggests that the adsorption of Cd(II) onto potato peels was on heterogeneous surfaces of the adsorbent with different energies.

From Table 3, the values of E calculated for Cd(II) (5.77) and Cu(II) (6.74) were less than 8 kJ/mol, which suggests the physical nature of adsorption. However, the values of

Table 2
Adsorption kinetics constant and R^2 values of Cd(II), Pb(II), Cu(II) and Cr(III) removal at different contact times onto potato peels

Metals	Pseudo-first-order		Pseudo-second-order		Intra-particle diffusion			Elovich		
	K_1 (1/min)	R^2	K_2 (g/mg min)	R^2	C	K_{int} (mg/g min$^{0.5}$)	R^2	β (g/mg)	α (mg/g min)	R^2
Cd(II)	0.08	0.917	0.0034	0.974	9.77	3.69	0.972	0.13	14.21	0.934
Cu(II)	0.03	0.986	0.0059	0.994	23.45	2.20	0.991	0.22	440.76	0.949
Cr(III)	0.08	0.947	0.0029	0.978	9.47	4.29	0.968	0.11	13.28	0.932
Pb(II)	0.03	0.938	0.0029	0.963	14.58	3.12	0.932	0.16	37.33	0.830

Table 3
Constants of Langmuir, Freundlich, Temkin and Redlich–Peterson isotherm models for the adsorption of metal ions onto potato peels

	Langmuir isotherm			Freundlich isotherm			Temkin isotherm		Redlich–Peterson isotherm			
	q_m (mg/g)	b (L/mg)	R^2	K_f(mg/g)	N_f	R^2	b_T (J/mol)	R^2	q_m (mg/g)	β (mol²/kJ²)	E (kJ/mol)	R^2
Cu(II)	15.63	0.02	0.978	4.06	1.68	0.939	721.90	0.924	13.41	0.01	6.74	0.892
Cd(II)	200.00	0.0048	0.773	4.09	1.69	0.939	64.09	0.889	107.93	0.02	5.77	0.765
Pb(II)	14.93	0.14	0.969	5.33	5.26	0.458	1,152.90	0.349	16.65	0.01	9.13	0.693
Cr(II)	38.46	0.03	0.999	3.71	2.3	0.977	307.28	0.994	31.16	0.01	10.00	0.954

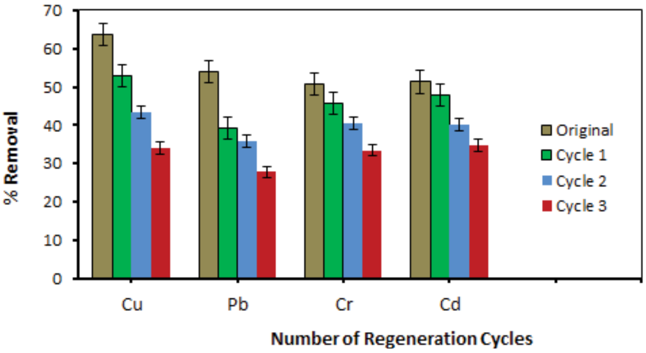


Fig. 9. Recycling study of Cd(II), Pb(II), Cu(II) and Cr(III) onto potato peels.

Table 4
R_L values at different initial Cu(II), Pb(II), Cd(II) and Cr(III) concentrations

Initial metal concentration	R_L values			
	Cu(II)	Cd(II)	Pb(II)	Cr(III)
100.00	0.62	0.28	0.94	0.75
150.00	0.71	0.36	0.96	0.82
300.00	0.83	0.53	0.98	0.90
400.00	0.87	0.60	0.98	0.92
500.00	0.89	0.66	0.99	0.94

E for Cr(III) (10.00) and Pb(II) (9.13) greater than 8 kJ/mol suggest the chemical nature of adsorption.

Table 3 shows the Temkin isotherm model calculated parameters related to the heat of adsorption (b_T) of Cu(II), Pb(II), Cd(II) and Cr(III) removal onto potato peels. The values of b_T (J/mol) for Pb(II) (1,152.90), Cd(II) (64.09), Cu(II) (721.90) and Cr(II) (307.28) were greater than 8 J/mol indicate that the interaction between metals and potato peels was strong. These imply that the adsorption process of these metals onto potato peel can be expressed as chemisorption in nature.

3.10. Thermodynamic study

The values of ΔH°, ΔS° and ΔG° for Cd(II), Pb(II), Cu(II) and Cr(III) adsorption onto potato peels are listed in Table 5. The positive values of ΔH° for these metals indicated that the adsorption reaction was an endothermic process (Table 5). The ΔS° has also positive values for all the metals analyzed in the study. The positive values of ΔG° also suggested that the adsorption reaction of Cd(II), Pb(II), Cu(II) and Cr(III) onto potato peels was non-spontaneous in nature. Hence, for the adsorption reaction to occur, energy is required. For example, shaking as energy is necessary. As the temperature increases, the values of ΔG° decrease.

3.11. Reusability studies of potato peels

Potato peels are generally available and abundant in Ethiopia. It is simply thrown into the environment and thus has a negative impact on it. In this study, to investigate the extent of regeneration and reusability of potato peels, solutions of constant feed concentrations were run by using the optimized values of all parameters. As Fig. 9 shows that the percentage removal of Cu(II) (63.6%–33.9%), Pb(II) (54.0%–27.8%), Cd(II) (51.3%–34.7%) and Cr(III) (50.8%–33.5%) decreased as the number of cycles increased. The use of potato peels as a low-cost adsorbent in industries that release toxic metals such as Cd(II), Pb(II), Cu(II) and Cr(III) in wastewater provides a financial benefit.

Table 5
Thermodynamic parameters calculated for the adsorption of Cd(II), Pb(II), Cu(II) and Cr(III) onto potato peels

Metals	ΔH° (kJ/mol)	ΔS° (J/mol K)	ΔG° (kJ/mol)				
			25°C	35°C	45°C	55°C	65°C
Cd(II)	5,884.17	18.27	440.62	257.95	75.28	–107.39	–290.06
Pb(II)	6,201.79	9.01	3,515.94	3,425.81	3,335.68	3,245.55	3,155.42
Cu(II)	5,388.63	7.03	3,292.48	3,222.13	3,151.79	3,081.45	3,011.11
Cr(III)	6,678.21	10.97	3,410.09	3,300.42	3,190.76	3,081.09	2,971.42

4. Conclusions

This study shows the potential of using potato peel as a low-cost adsorbent for Cd(II), Pb(II), Cu(II) and Cr(III) removal from wastewater. The removal efficiency was increased by increasing the dosage of the adsorbent and decreasing the particle size. The percentage removal of Cd(II), Pb(II), Cu(II) and Cr(III) was increased slightly by increasing the temperature of the solution. The adsorption equilibrium data obtained for the removal of Cu(II), Cr(III) and Pb(II) ions onto the adsorbents studied showed best fit to the Langmuir isotherm and Cd(II) best fit to the Freundlich isotherm. The reaction is thermodynamically favorable and follows pseudo-second-order kinetics. The study indicates that potato peels adsorbent may be economic reusable and effective alternative low-cost adsorbent for Cd(II), Pb(II), Cu(II) and Cr(III) removal from wastewater.

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