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Evaluation of potato peel as a novel adsorbent for the removal of Cu(II) from aqueous solutions: equilibrium, kinetic, and thermodynamic studies

El-Khamssa Guechi, Oualid Hamdaoui*

Laboratory of Environmental Engineering, Faculty of Engineering, Department of Process Engineering, Badji Mokhtar-Annaba University, P.O. Box 12, 23000 Annaba, Algeria, Tel./Fax: +213 38876560; emails: guichi_wahida@yahoo.fr (E.-K. Guechi), ohamdaoui@yahoo.fr, oualid.hamdaoui@univ-annaba.dz (O. Hamdaoui)

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ABSTRACT

In this study, potato peel (PP) was evaluated for its ability to remove Cu(II) ions from synthetic aqueous solutions under various operating conditions in a batch process. The effect of experimental parameters such as adsorbent dose (0.25–1.5), initial pH (2–5), stirring speed (0–800 rpm), temperature (25–55˚C), ionic strength (0.25–5 g/400 mL), adsorbent particle size (0.16–1.5 mm), and initial Cu(II) concentrations (25–300 mg/L) on the removal of Cu(II) was investigated. The adsorption kinetics uptake for Cu(II) by PP at various initial metal ions concentrations was analyzed using the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. It was found that the pseudo-second-order kinetic equation was the best applicable model to describe the adsorption kinetic data. The experimental data were analyzed by four adsorption isotherms, namely the Langmuir, Freundlich, Temkin, and Elovich models. Equilibrium data fitted well both to the Langmuir and Freundlich models with a maximum adsorption capacity of 84.74 mg/g at 25˚C. Thermodynamic parameters of Cu(II) adsorption on PP have also been calculated. These results demonstrate that the PP is a suitable adsorbent for the removal of Cu(II) ions from aqueous solutions.

Keywords: Adsorption; Cu(II); Agricultural waste; Potato peel; Kinetics; Isotherm

1. Introduction

Many toxic heavy metals have been discharged into the aquatic environment as industrial wastes, causing serious water pollution. Especially those accumulated within the living organisms as well as in human body are more dangerous [1]. According to the World Health Organization [2], the most toxic metals are aluminum, chromium, magnesium, iron, cobalt, nickel, copper, zinc, cadmium, mercury, and lead. Heavy metal ions, such as Cu(II), Cd(II), Hg(II), Zn(II), and Pb(II), have been recognized as ecotoxicological hazardous substances, and their chronic toxicities and accumulation abilities in living organism have been of great interest in the last years [3]. Therefore, the removal of heavy metals from waters and wastewaters is important to protect public health and wildlife. Copper and its compounds are ubiquitous in the environment, and thus, Cu(II) is found frequently in surface water [4]. The primary sources of Cu(II) in industrial wastewaters are metal-process pickling baths and plating baths. Cu(II) may also be present in wastewater from a variety of chemical manufacturing processes employing Cu(II) salts or Cu(II) catalyst [5].

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*Corresponding author.

Cu(II) is essential to human life and health but, like all heavy metals, is potentially toxic as well. Cu(II) is highly toxic as it is carcinogen and mutagen in nature [6]. The maximum allowable limit for Cu(II) in discharged water was set by the Environmental Protection Agency to be 1.3 mg/L [7]. To attain these values, different remediation techniques for treatment of wastewater can be applied. Heavy metals can successfully be recovered from solution by precipitation as hydroxides or carbonates, by membrane filtration, and by capture on synthetic ion exchangers. These methods are much less efficient for concentrations lower than about 100 mg/L for which they can be prohibitively expensive and can even fail to achieve legal limits. For these low concentrations, it is preferable to use adsorption techniques [8]. The adsorption technique is one of the preferred methods for removal of heavy metals because of its efficiency and low cost. Conventional adsorbents such as granular or powdered activated carbon are not always popular as they are not economically viable and technically efficient [9]. Non-conventional materials have been tested in a large scale for this purpose [10–15]. There are many studies for removing Cu(II) ions from aqueous solutions using adsorption. It has been reported that sago processing waste [16], algae [17], wheat shell [18], seafood processing waste sludge [19], and sawdust [3,4] have been studied to determine the adsorption capacity of Cu(II) ions. The study of adsorption is of great importance from an environmental point of view, as it can be considered as an alternative technique for removing toxic pollutants from wastewaters. Therefore, there is a need for the search of low-cost and easily available materials, which can adsorb Cu(II). Undoubtedly, agricultural waste materials are presently the most challenging topics, which is gaining stern considerations during the past several decades. To the best of our knowledge, potato peel (PP) was not tested as an adsorbent for the removal of Cu(II) from aqueous solutions.

The aim of this work was to investigate the potential of PP as a novel adsorbent for the removal of Cu(II) from synthetic aqueous solutions. Batch adsorption studies were conducted to investigate the effects of various parameters such Cu(II) initial concentration, adsorbent dose, pH, temperature, ionic strength, and particle size on Cu(II) adsorption. The adsorption kinetics were analyzed using pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. Equilibrium data were modeled using four different equations: Langmuir, Freundlich, Temkin, and Elovich. Additionally, thermodynamic parameters for the adsorption of Cu(II) ions were determined.

2. Materials and methods

2.1. Adsorbate

Cu(II) solutions of desired concentration have been prepared by dissolving the appropriate amount of $CuSO_4 \cdot 5H_2O$ (analytical grade), purchased from Merck, in distilled water. Test samples of various concentrations in the range of 25–300 mg/L were prepared from this stock solution. For pH adjustments, analytically pure H_2SO_4 and NaOH were used.

2.2. Preparation and characterization of PP

PP used in the present study was obtained from the university canteen. It was washed, dried, crushed, and sieved to desired mesh size (0.5–2 mm). Finally, the obtained material was then dried in an air-circulating oven at 50°C for 7 d and stored in a desiccator until use. Fourier transform infrared (FTIR-8400S) analysis was applied on the PP to determine the surface functional groups, where the spectra were recorded from 4,000 to 400 cm^{-1}.

2.3. Batch adsorption kinetic and equilibrium studies

The effects of experimental parameters such as adsorbent dose (0.15–1.5 g/400 mL), pH (2–5), stirring speed (0–800 rpm), ionic strength (0–5 g/400 mL), particle size (0.16–1.5 mm), temperature (25–55°C), and initial metal ions concentration (25–300 mg/L) on the adsorption of Cu(II) were studied.

The initial concentration of Cu(II) solution was 200 mg/L for all experiments, except for those carried out to examine the effect of the initial Cu(II) concentration. For Cu(II) removal kinetic experiments, the batch method was used because of its simplicity: 0.25 g of adsorbent was contacted with 400 mL of metal ions solution in a sealed flask agitated vigorously by a magnetic stirrer using a water bath maintained at a constant temperature (25°C). The stirring speed was kept constant at 400 rpm. The experiments were performed at the pH that resulted from dissolving the copper salt in water (around 5) without further adjustment, except for those conducted to examine the effect of solution pH.

To study the effect of initial solution pH on Cu(II) adsorption, 0.25 g of PP was agitated with 400 mL of Cu(II) solution of 200 mg/L initial concentration at 25°C. The experiments were conducted at different pH values ranging from 2 to 5. The solution pH was adjusted using 0.1 N H_2SO_4 or NaOH aqueous solutions. Agitation was provided for a period that is sufficient to reach equilibrium with a constant stirring speed of 400 rpm.

The effect of temperature on the adsorption of Cu(II) was studied by contacting 0.25 g of adsorbent with 400 mL of metal ions solution at 200 mg/L initial concentration at different temperatures (25–55˚C).

The influence of ionic strength on the adsorption of Cu(II) by PP was studied with a constant initial concentration of 200 mg/L, adsorbent mass of 0.25 g, solution volume of 400 mL, and temperature of 25˚C. The ionic strength of the Cu(II) solution was modified using different dosages of NaCl (0.25–5 g/400 mL).

The procedure of equilibrium experiments was basically identical to those of kinetic tests. Adsorption equilibrium experiments were carried out by adding a fixed amount of PP (0.1 g) into a number of sealed glass flasks containing a definite volume (200 mL in each case) of different initial concentrations (50–600 mg/L) of Cu(II) solution. The flasks were placed in a thermostatic water bath in order to maintain a constant temperature (25, 35, 45, or 55˚C), and stirring was provided at 400 rpm to ensure equilibrium was reached.

Each run of the experiments was replicated at least two times, and the mean values were reported. The maximum standard deviation obtained for duplicate or triplicate measurements of the adsorbed amount was ±2%.

3. Results and discussion

3.1. Characterization of PP

FTIR (SHIMADZU FTIR-8400S) analysis was applied on the PP before and after adsorption of Cu (II) ions, to determine the surface functional groups, where the spectra were recorded from 4,000 to 400 cm^{-1}. FTIR spectra for PP before and after Cu(II) adsorption are shown in Fig. 1. It can be seen from the spectra that strong peaks were detected at 3,450 cm^{-1} and 2,930–2,854 cm^{-1}, respectively, representing the –OH stretch of phenol group of cellulose and lignin and –CH and $–CH_2$ stretch of aliphatic compound. However, in the spectrum of PP before Cu (II) adsorption, the peaks detected at 1,735 and 1,636 cm^{-1} were recorded to C=O stretch of aldehyde group and C=C stretch of phenol group, respectively [20,21]. In this spectrum, it was also found other functional groups at 1,507.78, 1,370.20, 892, and 660 cm^{-1} that can be attributed to N–H deformation, C–O–H bend, C–N stretch, and C–O–H twists, respectively [22]. The novel peaks detected after Cu(II) adsorption were located at 2,376, 1,890, 1,242, 1,110, 1,076, and 957 cm^{-1}, respectively, assigned to N–H stretch, C=O stretch of ketone group, Si–C stretch, C–O–C asymmetric stretch, P–H deformation or C–O stretch, and Si–OH asymmetric stretch. The intensities of the peaks of the spectrum before Cu(II) adsorption were weaker than those obtained after adsorption. It is clear that the adsorbent displays a number of peaks, reflecting the complex nature of the PP.

Fig. 2(a) and (b) shows the SEM of PP sample before and after Cu(II) adsorption, respectively. The PP exhibits a rough and porous (caves) surface structure which enhanced the adsorption of Cu(II) ions.

3.2. Effect of operational parameters

3.2.1. Effect of adsorbent dose

The effect of a variation of adsorbent mass on the adsorption kinetics of Cu(II) on PP is reported in Fig. 3, which shows a series of contact time curves for different PP doses in the range of 0.15–1.5 g/400 mL. The amount of metal ions adsorbed per unit mass of adsorbent decreased with increase in adsorbent dose. At higher PP to solute concentration ratios, there is a very fast superficial adsorption onto the adsorbent surface that produces a lower solute concentration in the solution than when the adsorbent to solute concentration ratio is low. This is because a fixed mass of PP can only adsorb a certain amount of metal ions [22]. However, the removal of Cu(II) increased with an increase in adsorbent dosage. This may be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increase dose of the adsorbent. Additionally, it was observed from Fig. 3 that the decrease in the amount of Cu(II) adsorbed with increasing adsorbent dose is due to the split in the concentration gradient between solute concentration in the solution and the solute concentration on the surface of the adsorbent.

3.2.2. Effect of initial pH

The initial pH of metal ions solutions is the major parameter controlling metal adsorption processes. This is because hydrogen ions have a great affinity for many complexing and ion exchange sites [23]. On the other hand, the hydrogen ion may compete with the positively charged metal ions on the active sites of the adsorbent. The effect of pH on the adsorption of Cu(II) ions on PP has been studied by varying it in the range of 2–5 as shown in Fig. 4. This pH range was chosen (pH <6) in order to avoid metal precipitation [24,25]. As shown in Fig. 4, the uptake of Cu(II) ions depends on initial pH; it increases with the increase in pH reaching the maximum adsorption at pH 5 (natural pH of Cu(II) solution). It is speculated that the ion exchange and hydrogen bonding may be

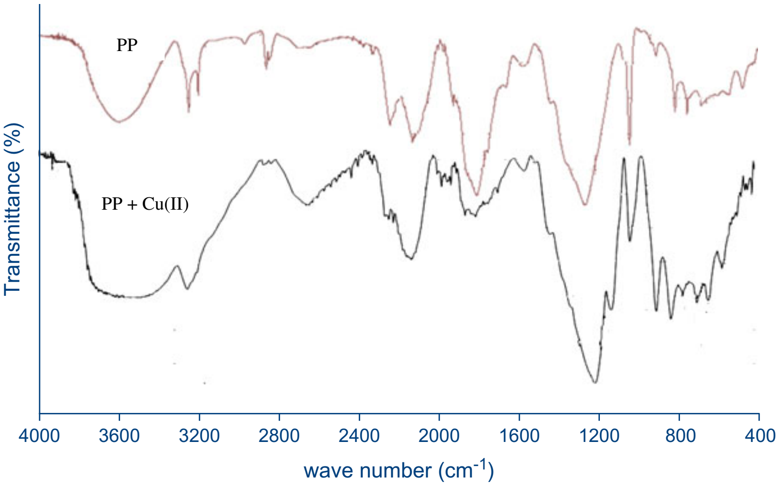

Fig. 1. FTIR spectra of PP before and after Cu(II) adsorption.

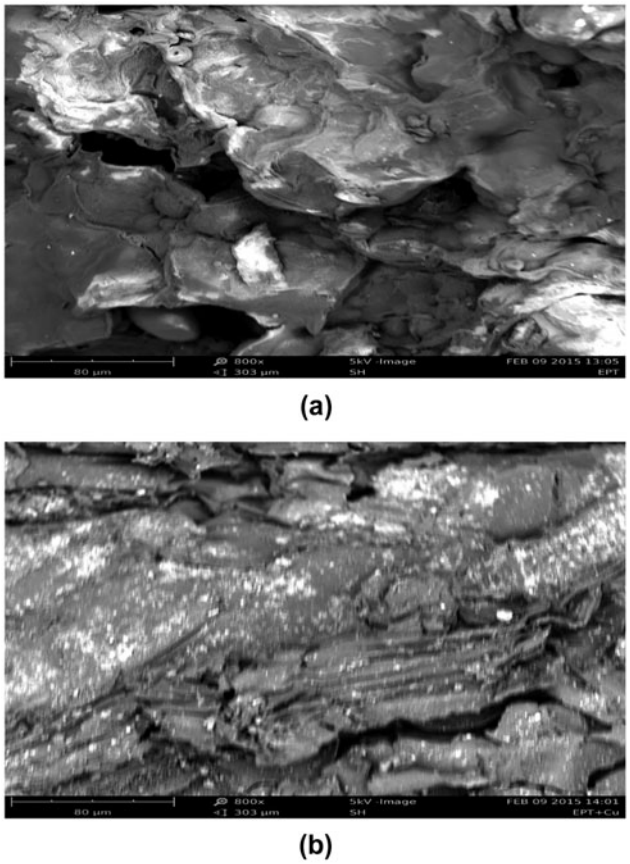

Fig. 2. SEM micrograph (×800) of PP before (a) and after (b) Cu(II) adsorption.

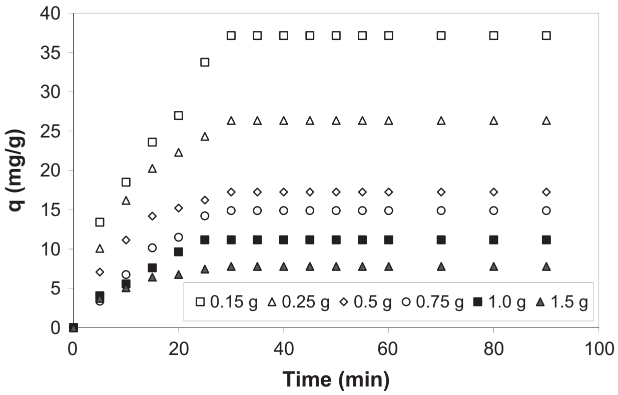

Fig. 3. Effect of adsorbent dosage on the adsorption of Cu(II) by PP (conditions: solution volume = 400 mL; initial metal concentration = 200 mg/L; stirring speed = 400 rpm; *T* = 25°C; pH 5).

the principal mechanism for the removal of heavy metals [4]. There are a number of parameters to support this speculation, including the components and complexing properties of the adsorbent (PP). At lower pH values (2–3), the adsorption capacities were found to be low due to the competitive adsorption of H^+ ion and metal ions for the same active adsorption site. At higher pH values (4–5), the lower number of protons and greater number of negative charges results in higher Cu(II) adsorption. The effect of pH on the adsorption kinetics is attributed to electrostatic attraction existing between the adsorbent surface and the Cu(II) ions in solution. Similar results were reported using different adsorbents for the removal of Cu(II) [17,18,26].

3.2.3. *Effect of stirring speed*

Fig. 5 shows a plot of Cu(II) uptake by PP against time at various stirring speeds (0, 60, 100, 200, 400,

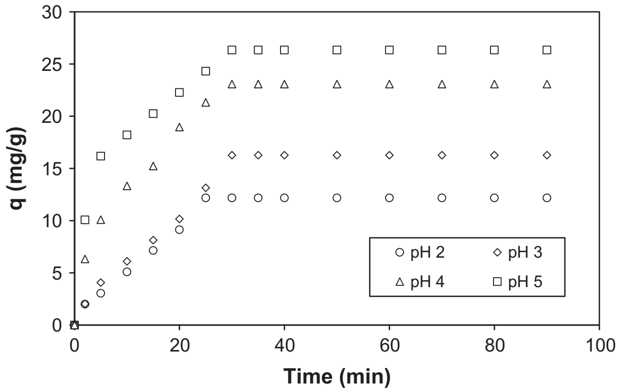

Fig. 4. Effect of initial pH on the adsorption of Cu(II) by PP (conditions: initial metal concentration = 200 mg/L; sorbent dosage = 0.25 g/400 mL; stirring speed = 400 rpm; T = 25℃).

600, and 800 rpm). The adsorption of Cu(II) by PP was studied by changing the stirring speed, while maintaining the initial metal ions concentration (200 mg/L), temperature (25℃), contact time (35 min), and pH (5) constant. The amount of Cu(II) adsorption increases from 7.20 to 30.41 mg/g with an increase in stirring speed from 0 (without stirring) to 800 rpm, respectively. This can be explained by the fact that increasing stirring speed reduced the film boundary layer surrounding particles, thus increasing the external film transfer coefficient, and hence the fixation of metal ions [27]. The change in the adsorbed amount was insignificant compared to the dissipated energy, when the stirring speed increased from 400 to 800 rpm, the amount of Cu(II) adsorption increases from 26.34 to 30.41 mg/g. Therefore, all subsequent experiments were conducted at a stirring speed of 400 rpm.

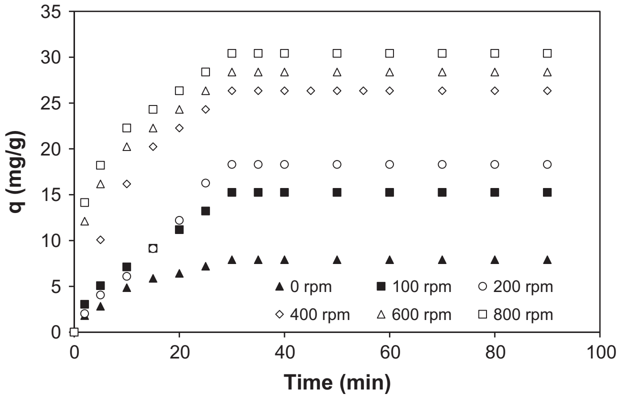

Fig. 5. Effect of stirring speed on the adsorption of Cu(II) by PP (conditions: initial metal concentration = 200 mg/L; adsorbent dosage = 0.25 g/400 mL; pH 5; T = 25℃).

3.2.4. Effect of temperature

Temperature is a highly significant parameter in the adsorption processes. Fig. 6 shows the adsorption of Cu(II) on PP. It was found that the adsorption kinetics of metal ions decreased with the increase in temperature from 25 to 55℃. This indicates that the adsorption process is exothermic in nature. The amount of Cu(II) fixed at equilibrium decreased from 26.34 to 10.15 mg/g with the increasing of temperature from 25 to 55℃, respectively. This may be explained by the fact that as the temperature increased, the solubility of metal ions increased which caused the interaction forces between the solute and the solvent to become stronger than solute and adsorbent, and thus, the solute was more difficult to adsorb [28]. Similarly, the removal of Cu(II) by cedar sawdust [29] was indicated as exothermic.

3.2.5. Effect of ionic strength

In water, salt is present in a wide range of concentrations depending on the source and the quality of the water. The presence of salt or co-ions in solution can affect the adsorption of metal ions. The effect of salt concentration (ionic strength) on the amount of Cu(II) adsorbed by PP was investigated over the NaCl concentration range of 0.25–5 g/400 mL. The obtained results are shown in Fig. 7. It was observed that the increase in salt concentration resulted in a decrease in Cu(II) adsorption by PP. This may be due to the following two reasons:

- The electrostatic attraction seems to be a significant mechanism, as indicated by the results, where at high ionic strength, the increased

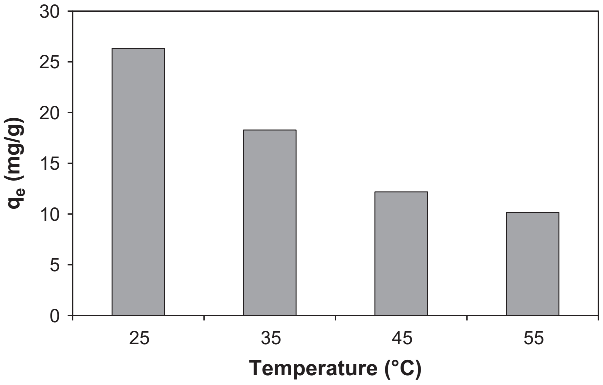

Fig. 6. Effect of temperature on the adsorption of Cu(II) by PP (conditions: initial metal concentration = 200 mg/L; adsorbent dosage = 0.25 g/400 mL; stirring speed = 400 rpm; pH 5).

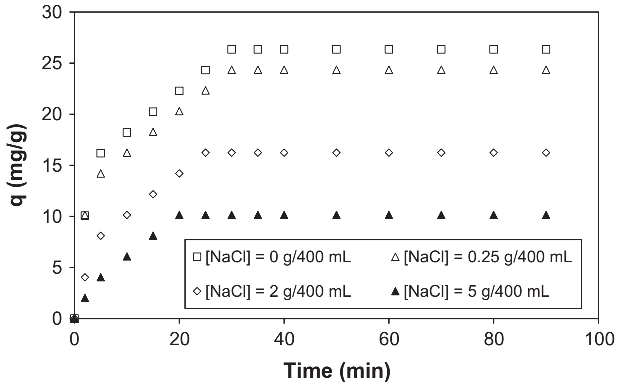

Fig. 7. Effect of salt (NaCl) concentration on the adsorption of Cu(II) by PP (conditions: initial metal concentration = 200 mg/L; adsorbent dosage = 0.25 g/400 mL; stirring speed = 400 rpm; T = 25°C; pH 5).

- amount of NaCl can help to render the surface of the adsorbent not easily accessible to Cu^{2+} ions and hence decreasing the adsorption rate. In fact, according to the surface chemistry theory developed by Guoy and Chapman [30], when solid adsorbent is in contact with adsorbate species in solution, they are bound to be surrounded by an electrical diffused double layer, the thickness of which is significantly expanded by the presence of electrolyte. Such expansion inhibits the adsorbent particles and Cu(II) from approaching.
- The relative competition between sodium ions and Cu(II) species for the active sites of adsorbent can also be an explaining factor. As the concentration of salt was increased from 0 to 5 g/400 mL, the amount of Cu(II) adsorbed on PP decreased from 26.34 to 10.15 mg/g.

3.2.6. Effect of adsorbent particle size

The effect of adsorbent particle size on the Cu(II) removal was studied. Fig. 8 shows the adsorption kinetics of the Cu(II) at three different particle sizes (0.16–0.63, 0.63–1, and 1–1.5 mm). The adsorption rate and capacity increase with decreasing particle size of PP. The relationship between the effective surface area of the adsorbent particles and their sizes is that the effective surface area increases as the particle size decreases and, consequently, the adsorption capacity per unit mass of the adsorbent increased. Therefore, the smaller adsorbent particle sizes for a given mass of adsorbent have more surface area, and therefore, the number of available sites is more for adsorbing the metal ions.

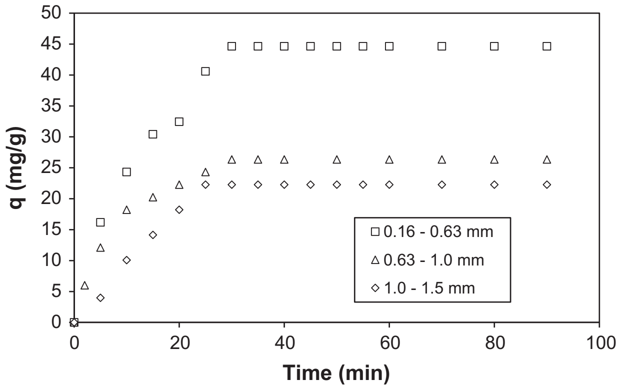

Fig. 8. Effect of adsorbent particle size on the adsorption of Cu(II) by PP (conditions: initial metal concentration = 200 mg/L; adsorbent dosage = 0.25 g/400 mL; stirring speed = 400 rpm; T = 25°C; pH 5).

3.2.7. Effect of initial concentration of Cu(II)

The effect of initial metal ions concentration on the adsorption of Cu(II) by PP at 25°C is shown in Fig. 9. It can be observed that the adsorption capacity increased with time and, at some point in time, reached a constant value where no more ions of Cu(II) were removed from the solution. It was observed that an increase in initial metal ions concentration leads to an increase in the adsorption of Cu(II) by PP. Equilibrium uptake increased with the increase in initial metal ions concentration at the range of experimental concentration. The amount of metal adsorbed at equilibrium increased from 4.99 to 37.55 mg/g as the concentration was increased from 25 to 300 mg/L. It was also shown in Fig. 9 that the adsorption of Cu(II) by PP was carried out using contact times ranging from 15 to 35 min and it was observed that metal

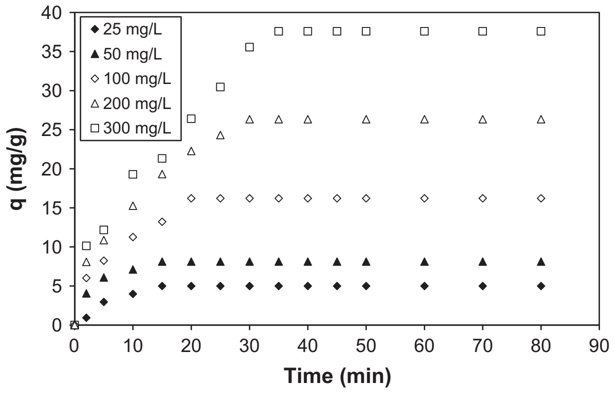

Fig. 9. Kinetics of Cu(II) uptake by PP for various initial metal concentrations (conditions: adsorbent dosage = 0.25 g/400 mL; stirring speed = 400 rpm; pH 5; T = 25°C).

adsorption occurred rapidly. Equilibrium uptake increased with the increase in initial metal ions concentration. This is a result of the increase in the driving force of the concentration gradient [27,31], as an increase in the initial Cu(II) concentrations. This effect can be explained as follows: At low metal/adsorbent ratios, there are a number of adsorption sites in PP structure. As the metal/adsorbent ratio increases, adsorption sites are saturated, resulting in a decrease in the adsorption efficiency.

3.3. Adsorption kinetic studies

The effect of initial Cu(II) concentration and time on adsorption by PP was shown in Fig. 9. Preliminary experiments showed high initial rates of adsorption of Cu(II) ions followed by lower rates near equilibrium. To gain a better understanding adsorption kinetics and rate-limiting step, three kinetic models were used. These kinetic models are Lagergren's first-order model, pseudo-second-order kinetic model, and intraparticle diffusion model.

Lagergren equation was used to investigate the suitability of pseudo-first-order kinetic model to describe the adsorption process. This equation can be written as [32]:

$$\ln(q_{\mathrm{e}} - q_t) = \ln q_{\mathrm{e}} - k_1 t \tag{1}$$

where q_{e} (mg/g) and q_t (mg/g) are the amount of Cu (II) adsorbed at equilibrium and at any time t, respectively, and k_1 (min^{-1}) is the rate constant for Lagergren's first-order model. The straight line plots of ln $(q_{\mathrm{e}} - q_t)$ against t were made at different initial Cu(II) concentrations (25, 50, 100, 200, and 300 mg/L). The plot of $\ln(q_{\mathrm{e}} - q_t)$ vs. t gives a straight line for the pseudo-first-order adsorption kinetics (Figure not shown). The values of the pseudo-first-order rate constant k_1 were obtained from the slopes of the straight lines. The k_1 values, the correlation coefficients r, and the predicted and experimental q_{e} values are given in Table 1. It was observed that Lagergren's equation does not represent a good fit with the experimental data.

The pseudo-second-order model can be expressed as follows [33,34]:

$$\frac{t}{q} = \frac{1}{k_2 q_{\mathrm{e}}^2} + \frac{1}{q_{\mathrm{e}}} t \tag{2}$$

where k_2 (g/mg min) is the rate constant for the pseudo-second-order kinetics and $h = k_2 q_{\mathrm{e}}^2$, where h is the initial adsorption rate (mg/g min). The slopes of the plots t/q_t vs. t (Fig. not shown) give the value of q_{e}, and from the intercepts, k_2 can be calculated. The pseudo-second-order rate constants k_2, the predicted q_{e} values, and the corresponding correlation coefficients r were given in Table 1. The calculated or predicted q_{e} values agree with experimental values, and also, the correlation coefficients for the pseudo-second-order kinetic plots at all the studied concentrations were higher ($r \geq 0.993$). It was seen that the pseudo-second-order kinetics equation adequately fits the adsorption of Cu(II) by PP.

Table 1
Parameters of the kinetic models for the adsorption of Cu(II) by PP at different concentrations

	Initial Cu(II) concentration				
Model	25	50	100	200	300
Pseudo-first order					
$q_{\mathrm{e,\ exp}}$ (mg/g)	4.98	8.12	16.22	26.34	37.58
$q_{\mathrm{e,\ cal}}$ (mg/g)	5.32	1.23	7.53	34.66	9.55
k_1 (1/min)	0.169	1.111	0.052	0.067	0.072
r	0.989	0.978	0.998	0.986	0.961
Pseudo-second order					
$q_{\mathrm{e,\ exp}}$ (mg/g)	4.98	8.12	16.22	26.34	37.58
$q_{\mathrm{e,\ cal}}$ (mg/g)	5.25	9.80	18.18	29.15	37.17
k_2 (g/mg min)	0.0636	0.0371	0.0082	0.0076	0.0032
h (mg/g min)	1.75	3.56	2.74	6.53	4.40
r	0.997	0.997	0.994	0.999	0.996
Intraparticle diffusion					
k_{d} (mg/g $\mathrm{min}^{1/2}$)	1.59	1.94	2.97	4.01	5.66
C_{d}	1.03	1.41	1.56	4.16	1.97
r	0.984	0.986	0.996	0.998	0.991

The pseudo-first-order and pseudo-second-order kinetic models could not identify the diffusion mechanism. An intraparticle diffusion model was used to predict the rate-controlling step. In adsorption systems where there is the possibility of intraparticle diffusion being the rate-limiting step, the intraparticle diffusion approach described by Weber and Morris is used. The rate constants for intraparticle diffusion (k_{d}) are determined using equation given by Weber and Morris [35]:

$$q_t = k_{\mathrm{d}} \cdot t^{1/2} + C_{\mathrm{d}} \tag{3}$$

where k_{d} is the intraparticle diffusion rate constant (mg/g $\mathrm{min}^{1/2}$). If intraparticle diffusion is rate-limited, then plots of adsorbate uptake q_t vs. the square root of time ($t^{1/2}$) would result in a linear relationship, and k_{d} and C_{d} values can be obtained from these plots

(Fig. 10 and Table 1). C_d is the intercept, which represents the thickness of the boundary layer. A larger intercept means a greater effect of the boundary layer [36]. Fig. 10 shows two consecutive linear steps during the adsorption of Cu(II) on PP, indicating the different stages in adsorption. The first, sharper portion can be attributed to the rapid use of the most readily available adsorbing sites on the adsorbent surface. This portion is the gradual adsorption stage where intraparticle diffusion is rate-limiting. The second portion is the final equilibrium stage where intra-particle diffusion starts to slow down due to the extremely low adsorbate concentration left in the solution. The lines do not pass through the origin ($C_d \neq 0$); therefore, intraparticle diffusion is not the only rate-limiting step, and then other processes may control the rate of adsorption of Cu(II) on PP and boundary layer control may be involved in the process.

3.4. Adsorption isotherms studies

In general, an adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid phase at a constant temperature and pH [37,38]. An adsorption isotherm describes the relationship between the amount of adsorbate adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium. Several mathematical models can be used to describe experimental data of adsorption isotherms of Cu(II) on PP. In this study, equilibrium isotherms at different temperatures for adsorption of Cu(II) on PP were presented in Fig. 11. The shape of the curves q_e vs. C_e clearly indicated that the isotherms for all temperatures belong to L type according to the classification of equilibrium isotherm in solution by Giles et al. [39]. The adsorption of Cu(II) by PP decreases progressively with the increase in temperature from 25 to 55°C, indicating that the adsorption process of Cu(II) on PP is exothermic. The increase in temperature decreases the physical forces responsible for adsorption [28]. On the other hand, the temperature has two main effects on the adsorption process. An increase in temperature is known to increase the diffusion rate of the adsorbate across the external boundary layer and within the pores. This could be the result of decreasing solution viscosity. Furthermore, changing the temperature will modify the equilibrium capacity of the adsorbent for a particular adsorbate [29].

3.4.1. Langmuir model

The Langmuir model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane.

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{4}$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration of the solute in the bulk solution (mg/L), q_m is the maximum adsorption capacity (mg/g), and b is the constant related to the free energy of adsorption (L/mg). The linear form of the Langmuir isotherm is given by the following equation:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{b \cdot q_m} \times \frac{1}{C_e} \tag{5}$$

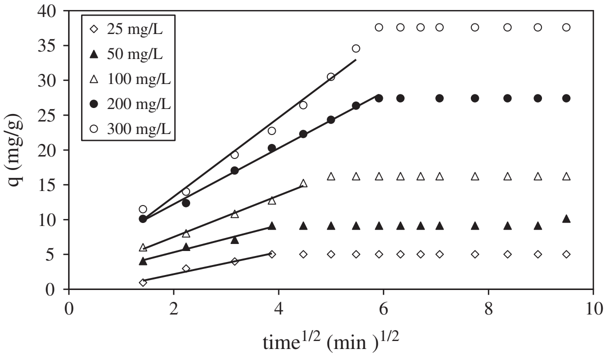

Fig. 10. Intraparticle diffusion kinetics for adsorption of Cu(II) onto PP at 25°C.

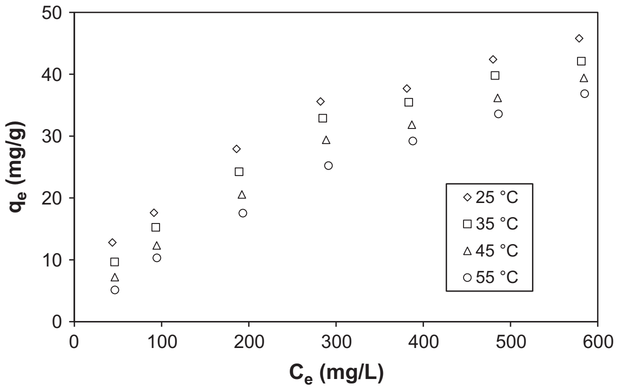

Fig. 11. Equilibrium isotherms of Cu(II) adsorption by PP at different temperatures.

The linear plot of $1/q_e$ vs. $1/C_e$ shows that the adsorption obeys to the Langmuir model (Figure not shown). The values of constants q_m and b were calculated and reported in Table 2. The maximum monolayer adsorption capacities (q_m) for the adsorption of Cu(II) on PP were 84.74, 60.60, 56.18, and 50.76 mg/g at 25, 35, 45, and 55℃, respectively.

3.4.2. Freundlich model

The Freundlich model can be applied to non-ideal adsorption on heterogeneous surfaces as well as multilayer adsorption and expressed by the following equation:

$$q_e = K_F C_e^{1/n} \tag{6}$$

where n is a constant indicative of the intensity of the adsorption and K_F is a constant indicative of the relative adsorption capacity of the sorbent ($\text{mg}^{1-\frac{1}{n}}\text{L}^{\frac{1}{n}}\text{g}^{-1}$). The fit of adsorption data to Freundlich isotherm indicates the heterogeneity of the sorbent surface. $1/n$ is the heterogeneity factor, and it is a measure of the deviation of adsorption from linearity. The n value indicates the degree of nonlinearity between solution concentration and adsorption as follows: If the value of $n = 1$, the adsorption is linear; if $n < 1$, the adsorption process is chemical; if $n > 1$, the adsorption is a favorable physical process. Eq. (6) can be linearized in the form of Eq. (7) and the constants can be determined by the following equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{7}$$

The linear plot of ln q_e vs. ln C_e at different temperatures (Fig. not shown) shows that the adsorption obeys to the Freundlich model. The correlation coefficients, $r \geq 0.994$, obtained from the Freundlich model, were comparable to that obtained from Langmuir model (Table 2). This result indicates that the experimental data fit to the Freundlich model and $n > 1$, indicating that adsorption for Cu(II) onto PP is a favorable physical process.

3.4.3. Temkin isotherm model

Temkin [40] isotherm equation assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions and that the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy. Temkin model is given by the following equation:

$$\theta = \frac{RT}{\Delta Q} \ln K_0 C_e \tag{8}$$

where θ is the fractional coverage, R *is* the universal gas constant (kJ/mol K), T *is* the temperature (K), ΔQ is the variation of adsorption energy (kJ/mol), and K_0 is the Temkin equilibrium constant (L/mg).

If the adsorption obeys Temkin equation, the variation of adsorption energy and the Temkin equilibrium constant can be calculated from the slope and the intercept of the plot θ vs. ln C_e by the relation:

$$\theta = \frac{RT}{\Delta Q} \ln K_0 + \frac{RT}{\Delta Q} \ln C_e \tag{9}$$

Temkin equilibrium constant and the variation of adsorption energy together with the correlation coefficient values were listed in Table 2. This model may

Table 2
Isotherms constants for the adsorption of Cu(II) by PP at different temperatures

Temperature (℃)		25	35	45	55
Langmuir	q_m (mg/g)	84.74	60.60	56.18	50.76
	$b \times 10^3$ (L/mg)	7.3	4.38	2.86	1.39
	r	0.999	0.998	0.997	0.996
Freundlich	K_F ($\text{mg}^{1-1/n}\ \text{L}^{1/n}\ \text{g}^{-1}$)	1.88	1.03	0.55	0.28
	n	1.97	1.68	1.50	1.29
	r	0.997	0.997	0.997	0.996
Temkin	$K_0 \times 10^2$ (L/mol)	5.07	4.67	3.11	2.63
	ΔQ (kJ/mol)	14.65	12.60	12.40	12.82
	r	0.990	0.992	0.980	0.985
Elovich	q_m	27.17	33.33	41.32	56.49
	$K_E \times 10^2$ (L/mg)	8.70	1.11	1.32	1.40
	r	0.982	0.985	0.979	0.981

describe the adsorption isotherms of Cu(II) on PP because of the good coefficients of correlation.

3.4.4. Elovich isotherm model

The model of Elovich and Larinov [41] is based on a kinetic principle assuming that the adsorption sites increase exponentially with adsorption, which implies a multilayer adsorption. It is expressed by the relation [42]:

$$\frac{q_e}{q_m} = K_E C_e \exp\left(-\frac{q_e}{q_m}\right) \tag{10}$$

where K_E is the Elovich equilibrium constant (L/mg) and q_m is the Elovich maximum adsorption capacity (mg/g). The linearized form of the Eq. (12) is given below:

$$\ln\frac{q_e}{C_e} = \ln K_E q_m - \frac{q_e}{q_m} \tag{11}$$

The variables of Elovich (K_E, q_m) with the correlation coefficients were regrouped in Table 2. In spite of the good correlation coefficients, the values of maximum adsorption capacity determined using the linear transformation of the Elovich equation are lower than the experimental adsorbed amounts at equilibrium corresponding to the plateaus of the adsorption isotherms. This means that the assumption of the exponential covering of adsorption sites that implies multilayer adsorption is not in agreement with the experiment in the studied concentration range. Therefore, the Elovich model is unable to describe the adsorption isotherms of Cu(II) on PP.

3.5. Thermodynamic studies

In engineering practice, entropy and energy factors should be considered in order to determine what processes will occur spontaneously. The amounts of adsorption of Cu(II) ions by PP were measured in the temperature range of 298–328 K. Thermodynamic parameters, i.e. free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) changes, were determined using the following relations:

$$\ln b = \frac{\Delta S^\circ}{R_g} - \frac{\Delta H^\circ}{RT} \tag{12}$$

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

where T (K) is the absolute temperature, R_g (kJ/mol K) is the ideal gas constant, and b (L/mol) is the Langmuir equilibrium constant.

It appears from Eq. (12) that both ΔH° and ΔS° of adsorption of Cu(II) by PP can be determined from the plot of ln b vs. $1/T$ (Fig. not shown). The Gibbs free energy change (ΔG°) was obtained according to Eq. (13) at different temperatures. The thermodynamic parameters are regrouped in Table 3. The negative values of ΔG° demonstrate the feasibility of the process and the spontaneous nature for the adsorption with a high preference of Cu(II) to PP at lower temperatures. The negative values of enthalpy change (−43.58 kJ/mol) indicated the exothermic nature of the adsorption. The decrease in adsorption capacity with increase in temperature is known to be due to the weakening of adsorptive forces between the active sites on the PP and the metal ions species and also between adjacent Cu(II) ions on the adsorbed phase [28]. The low and the negative value of ΔS° reflects the decreased randomness at the solid–solution interface during adsorption. Similar result was reported for adsorption of mercury onto banana stem [43].

Table 3
Thermodynamic parameters for the adsorption of Cu(II) by PP

T (°C)	ΔH° (kJ/mol)	$-\Delta G^\circ$ (kJ/mol)	ΔS° (J/mol K)
25	−43.58	15.20	−94.86
35		14.37	
45		13.74	
55		12.22	

Table 4
Previously reported adsorption capacities of various low-cost adsorbents for Cu(II) removal

Adsorbent	Adsorption capacity (mg/g)	Refs.
Tea waste	8.64	[3]
Sawdust	1.79	[44]
Wheat shell	8.34	[18]
Sawdust of poplar tree	5.43	[26]
Activated sawdust of poplar tree	13.49	[26]
Peanut hulls	9	[45]
Peanut pellets	12	[45]
Sawdust	8.45	[46]
Meranti sawdust	32.05	[47]
Corncobs	7.62	[48]
Peanut husk	10.15	[46]
Potato peel (PP)	84.74	This work

However, other workers have observed positive value of entropy change for the adsorption of Cu(II) by cedar sawdust and crushed brick [29].

4. Evaluation of PP as adsorbent

Table 4 lists a comparison of the maximum monolayer adsorption capacities of various adsorbents for Cu(II). The value of $q_{\max}$ in this study (84.74 mg/g) is larger than those in most of the previous studies. This suggests that Cu(II) could be readily adsorbed by PP used in this work.

5. Conclusion

The results obtained in this study demonstrated the potential use of PP for the adsorption of Cu(II) ions from aqueous solutions. The FTIR analysis confirmed that many functional groups were present on the PP surface. The amount of Cu(II) ions adsorbed by PP increased with an increase in initial concentration, pH, adsorbent dose, and stirring speed. However, the amount of Cu(II) adsorbed decreases with an increase in temperature, ionic strength, and particle size. The kinetics of the adsorption of Cu(II) ions on PP followed closely the pseudo-second-order kinetic model. For the diffusion mechanism studies, the results obtained reveal that an intraparticle diffusion is not the only rate-limiting step, other processes may control the rate of adsorption of Cu(II) on PP. Equilibrium data were fitted to Langmuir, Freundlich, Temkin, and Elovich isotherm models, and the equilibrium data were best described by both the Langmuir and Freundlich isotherm models. The maximum monolayer adsorption capacity of 84.74 mg/g was obtained at 25°C. The negative value of the change in enthalpy (ΔH°) confirmed the exothermic nature of the adsorption interaction, whereas the low and the negative value of change in entropy (ΔS°) reflects the decreased randomness at the solid–solution interface during adsorption. The negative value of change in free energy (ΔG°) indicated the feasibility and the spontaneous nature for the adsorption of Cu(II) onto PP. Taking into consideration the above results, it can be concluded that the PP is a suitable adsorbent for the removal of Cu(II) ions from aqueous solutions.

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