Evaluation of agricultural waste as a novel biosorbant on the sorption of copper from aqueous solutions: Equilibrium, kinetic and thermodynamic studies

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Abstract

In this study Potato peel (PP) was evaluated for its ability to remove copper ions from a synthetic aqueous solution under various operating conditions in a batch process**.** The FTIR analysis was applied on the PP to determine the surface functional groups and the surface functionalities were investigated by the usual method of Boehm demonstrated that the total acidic sites are higher than the total basic sites. The effect of the experimental parameters such as biosorbent dose (0.25-1.5), initial pH (2-5), stirring speed (0-800rpm), temperature (25-55 °C), ionic strength (0-5g/400mL), biosorbent particle size (0.16-1.5mm) and initial copper concentrations (25-300mgL^{-1}) was investigated through a number of batch sorption experiments. The sorption kinetic uptake for copper by PP at various initial copper concentrations was analyzed by linear method using pseudo-first order, pseudo-second order and Intraparticle diffusion models. It was found that the pseudo-second order kinetic model was the best applicable model to describe the sorption kinetic data. The experimental data were analyzed by six sorption isotherms namely the Langmuir, Freundlich, Temkin, Elovich, Dubinin–Radushkevich and Flory- huggins models. Equilibrium data fitted well both to the Langmuir and Freundlich models with a maximum sorption capacity of PP was 84.74 mg g^{-1} at 25 °C. The dimensionless separation factor R_L revealed the favorable nature of the isotherm of the copper-Potato Peels system. Thermodynamic parameters such as free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy($\Delta S°$) of sorption have also been calculated. The negative values of the change in free energy, enthalpy and entropy indicated that the sorption is spontaneous in nature, exothermic and a greater order of reaction during the sorption of copper onto PP, respectively. These results demonstrate that the Potato Peels is a suitable biosorbent for the removal of copper ions from aqueous solution in terms of low cost, natural and abundant availability.

Keywords: Sorption; agricultural waste; Copper (II); Potato Peels; Batch process; Kinetics; Isotherm; Modeling.

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), Pb(II) etc., have long 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 are important to protect public health and wildlife. Copper and its compounds are ubiquitous in the environment and thus copper is found frequently in surface water [4]. The primary sources of copper in industrial wastewaters are metal-process pickling baths and plating baths. Copper may also be present in wastewater from a variety of chemical manufacturing processes employing copper salts or copper catalyst [5]. Copper is essential to human life and health but, like all heavy metals, is potentially toxic as well. Copper is highly toxic as it is carcinogen and mutagen in nature [6]. The maximum allowable limit for copper in discharged water was set by the Environmental Protection Agency (EPA) to be 1.3 mg L^{-1} [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, but, 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 sorption techniques [8]. In contrast, 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 such as fly ash 10, lignite 11, tree fern 12, etc**.** There are many studies for removing Cu (II) ions from aqueous solutions by using adsorption. It has been reported that sago processing waste 13, algae [14], wheat shell [15], seafood processing waste sludge [16] and sawdust [3,4] have been studied to define the adsorption capacity of copper ions. The study of biosorption 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 biomaterials, which can sorb copper. Undoubtedly, agricultural waste biomass is presently one of the most challenging topics, which is gaining stern considerations during the past several decades. In perspective, potato peel has emerged to be an invaluable source.

Potato peel (PP), agricultural and easily available waste, could be an alternative for more costly wastewater treatment processes. Losses caused by potato peeling range from 15 to 40% their amount depending on the procedure applied, i.e. steam, abrasion or lye peeling. Plants peel the potatoes as part of the production of French fries, crisps, puree, instant potatoes and similar products. In the interest of the environment, we propose this agricultural waste as a low-cost sorbent to remove copper from aqueous solution.

The aim of this work was to investigate the potential of PP as a novel sorbent in the removal of the copper (II), from synthetic aqueous solutions. Batch sorption studies were conducted to investigate the effects of various parameters such copper initial concentration, biosorbent dose, pH, temperature, ionic strength and particle size on Cu (II) sorption. The sorption kinetics tested with pseudo-first-order, pseudo-second-order and Intra-particle diffusion models. The sorption kinetics of copper on PP was found to follow closely the pseudo-second-order kinetic model. Equilibrium kinetic and isotherm data are analyzed and modeled using six different models, Langmuir, Freundlich, Temkin , Elovich, Dubinin–Radushkevich and Flory- huggins isotherms by linear regression technique. Additionally, thermodynamic parameters for the sorption of copper ions were determined.

2. Materials and methods

2.1. Sorbate

Copper (II) solutions of desired concentration have been prepared by dissolving the appropriate amount of copper sulfate pent hydrate ($CuSO_4 \cdot 5H_2O$, analytical grade) purchased from Merck in distilled water. Test samples of various concentrations range between 25–300 mgL^{-1} were prepared from this stock solution. For pH adjustments, analytically pure H_2SO_4 and NaOH, purchased from Prolabo, were used. Initial pH of the Cu (II) solutions was around 5 before addition biosorbent.

2.2. Preparation and characterization of Biosorbent

The 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 days and stored in a desiccator until use. The principal characteristics of PP were collected in Table 1. Fourier Transform Infrared (FTIR) (SHIMADZU FTIR-408) analysis was applied on the PP to determine the surface functional groups, where the spectra were recorded from 4000 to 400 cm^{-1} on the hand.Also on the other hand the surface functionalities were investigated by the usual method of Boehm [17] consisting in pH-metric titration of acidic and basic surface groups by aqueous solutions.

*2.3. Bath **sorption** kinetic and equilibrium studies*

The effects of experimental parameters, biosorbent dose (0.25–1.5g/400ml), pH (2–5), stirring speed (0-800rpm), and ionic strength (0–5g/400ml), particle size (0.16-1.5mm), temperature

(25-55°C) and initial metal ions concentration (25-300 mg L^{-1}) on the sorption of copper were studied in a batch operation mode.

The initial concentration of copper (II) solution was 200 mg L^{-1} for all experiments, except for those carried out to examine the effect of the initial concentration ion. For copper (II) removal kinetic experiments, the batch method was used because of its simplicity: 0.25 g of biosorbent was contacted with 400 mL of ion solution in a sealed flask agitated vigorously by a magnetic stirrer using a water bath maintained at a constant temperature at 25 C°, except for those carried out to examine the effect of the temperature. The stirring speed was kept constant at 400 rpm. The experiments were performed at the pH that resulted from solving the ion copper (II) in water (around 5) without further adjustment, except for those conducted to examine the effect of solution pH.

To study the effect of solution pH on copper (II) sorption, 0.25 g of PP was agitated with 400 mL of copper (II) solution of concentration 200 mg L^{-1} at 25°C. The experiment was conducted at different pH values ranging from 2 to 5. The solution pH was adjusted using 0.1N H_2SO_4 or NaOH aqueous solutions. Agitation was provided for a period which is sufficient to reach equilibrium with a constant agitation speed of 400 rpm.

The effect of temperature on the sorption of copper (II) was studied by contacting 0.25 g of biosorbent with 400 mL of ions solution of 200 mg L^{-1} initial concentration at different temperatures (25–55 °C).

The influence of ionic strength on the sorption of copper (II) by PP was studied with a constant initial concentration of 200 mg L^{-1}, biosorbent mass of 0.25 g, solution volume of 400 mL, and temperature of 25°C. The ionic strength of the copper (II) solution was modified using different dosages of NaCl (0.25–5 g)/ 400 mL. The amount of sorption at time t, q_t (mg g^{-1}), was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{W} \qquad (1)$$

Where C_0 and C_t (mg L^{-1}) are the liquid phase concentrations of copper (II) at initial and any time, respectively, V (L) is the volume of the solution and W (g) is the mass of biosorbent used.

The procedures of equilibrium experiments were basically identical to those of kinetic tests. sorption 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^{-1}) of copper (II) solution without changing pH. 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. The amount of sorption at equilibrium, q_e (mg g^{-1}), was calculated by:

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad (2)$$

Where C_0 and C_e (mg L^{-1}) are the liquid phase concentrations of copper (II) at initial and equilibrium time, respectively, V (L) is the volume of the solution and W (g) is the mass of biosorbent used.

After agitating the beakers for 2h, the reaction mixtures were filtered through filter paper, and then the filtrates were analyzed for the remaining copper (II) concentration). 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 sorbed amount was ±2%.

The equilibrium data were modeled by the Langmuir, Freundlich, Elovich, Temkin, Dubinin-Radushkevich and Flory-Huggins. This part aims to find the models that can describe with precision the experimental results of sorption isotherms of copper by PP, specify the parameters that can be determined and compared. The Freundlich and Langmuir isotherms are the most commonly used to describe the adsorption characteristics of adsorbent used in water and wastewater.

3. Resultats and discussions

3.1. Characterization of PP

The principal characteristics of Potato peel (PP) were given in Table 1. Fourier Transform Infrared (FTIR) (SHIMADZU FTIR-408) analysis was applied on the waste agricultural, Potato peel (PP), to determine the surface functional groups, where the spectrum was recorded from 4000 to 400 cm^{-1}. FTIR spectrum for Potato peel is shown in Fig. 1. It can be seen from this figure that a strong peak at 3450 cm^{-1} represents the –OH stretching of phenol group of cellulose and lignin, and a peak at 2930 cm^{-1} corresponds to –CH and $-CH_2$ stretching of aliphatic compound. The peaks at 1735 and 1636 cm^{-1} were attributed to C=O stretching of aldehyde group and C=C stretching of phenol group, respectively [18]. The peaks at 1507.78, 1370.20, 892, and 660 cm^{-1} in the spectrum of PP can be du to NH deformation, C–O–H bend, C–N stretch, and C–O–H twists, respectively [19]. It is clear that the biosorbent displays a number of sorption peaks, reflecting the complex nature of the biomaterial.

3.1.1. *Surface functionalities of PP*

As far as liquid adsorption on solids is concerned, surface chemistry is known to be at least as important as the pore texture; the role of surface functionalities indeed increases significantly relative to the pore size distribution or BET surface area, and in many cases dominates [20]. The acid–base properties may have two separate origins: chemical composition of ashes and surface functions (moieties) [21]. The acidic/basic character of a PP depends on delocalized electrons and on surface functionalities, the latter being based on surface-bound hetero atoms, especially oxygen but also nitrogen, sulphur, etc. Acidic properties originate from oxygen moieties such as carboxyls, lactones, carbonyls and phenols. Basic properties are due to other oxygenated groups, especially pyrones, chromenes and ethers, nitrogen-containing moieties, and grapheme layers behaving as Lewis base due to their available π electrons for forming donor–acceptor complexes with protonated molecules [22, 23].

In this study the chemical nature of the Potato Peel surface was estimated as follows. The surface functionalities were investigated by the usual method of Boehm, consisting in pH-metric titration of acidic and basic surface groups by aqueous solutions [17, 24]. The total acid sites matching the carboxylic, phenolic, lactonic and carbonylic and quinonic sites were neutralized using alkaline solutions (0.1N NaOH, 0.1N $NaHCO_3$, 0.1N Na_2CO_3, and 0.1N $NaOC_2H_5$) while the basic sites were neutralized with a 0.1N HCl solution.

The acidic and basic sites were determined by adding 50mL of 0.1N titrating solution and 1 g of Potato Peel to a 50mL volumetric flask. The flask was slowly agitated at room temperature and it was left there for 72h. Afterward, a sample of 10mL was titrated with 0.1N HCl or NaOH solution. The concentrations of surface functionalities (total acid and basic sites) of Potato Peel are collected in Table 2. The result of Table 2 shows that of the four types of acid sites, the carbonylic sites are the dominant acidic oxygenated sites. Also the total acidic sites are higher than the total basic sites.

3.2. Effect of operational parameters

The influence of several operational parameters such as biosorbent dosage, pH, stirring speed, temperature, ionic strength, particle size and initial concentration of copper (II) on the sorption of copper by PP was investigated.

3.2.1. Effect of biosorbent dose

The effect of a variation of biosorbent mass on the kinetics of sorption of copper on PP is reported in Fig.2, which shows a series of contact time curves for variation of mass of PP in the range of 0.15–1.5 g. The sorption of copper increased with an increase in biosorbent dosage. This may be attributed to increased biosorbent surface area and availability of more sorption sites resulting from the increase dose of the biosorbent. But amount of metal sorbed per unit mass of biosorbent decreased with increase in biosorbent dose. At higher PP to solute concentration ratios, there is a very fast superficial sorption onto the biosorbent surface that produces a lower solute concentration in the solution than when the biomaterial to solute concentration ratio is lower. This is because a fixed mass of PP can only sorb a certain amount of metal [25]. Also from Fig.2 it was observed that the decrease in amount of copper sorbed (26.34 to 7.77) mg g^{-1} with increasing sorbent mass (0.25 to 1.5)g respectively, is due to the split in the concentration gradient between solute concentration in the solution and the solute concentration in the surface of the sorbent.

3.2.2. Effet of pH

The pH of metal solutions is the major parameter controlling metal sorption processes. This is because hydrogen ions have a great affinity for many complexing and ion-exchange sites [26]. On the other hand, the hydrogen ion competing with the positively charged metal ions on the active sites of the adsorbent. The effect of pH on the sorption of Cu (II) ions on Potato Peel has been studied by varying it in the ranges of 2–5 as shown in Fig. 3. This pH range was chosen (pH <6) in order to avoid metal solid hydroxide precipitation and so adsorption studies at these pH values could not be performed because the adsorbent was deteriorated with the accumulation of metal ions[27,28]. As shown in Fig. 3, the uptake of Cu (II) ions depends on pH, it increases with the increase in pH reaching the maximum sorption at pH 5, natural pH of copper. It is speculated that the ion exchange and hydrogen bonding may be 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 biosorbent (PP).
At lower pH value (2-3), the sorption capacities were found to be low due to the competitive sorption of H^+ ions and metal ions for the same active sorption site. At higher pH values (4-5), the lower number of protons and greater number of negative charges results in greater copper sorption. The effect of pH on the sorption kinetics is attributed to electrostatic attraction existing between the biosorbent surface and the Cu^{+2} ions in solution. As seen in Fig. 3, copper the maximum sorption efficiency at pH 5 may be due to the interaction of the metal ions , M^+, $M(OH)^+$, $M(OH)_2$ with surface functional groups present in the PP. Similar results were reported using different sorbents for the removal of copper adsorbent for the removal of copper [14, 15, 29].

***3.2.3**. Effect of stirring speed*

Fig. 4 shows a plot of copper uptake against time at various stirring speeds for the sorption of Cu (II) on Potato peel at different stirring speeds of 0, 60,100, 200, 400, 600, and 800 rpm.

The sorption of copper by Potato peel was studied by changing the stirring speed while maintaining the initial metal ion concentration (200 mg L^{-1}), temperature (25 °C), contact time (35 min) and natural pH (5) constant. The amount of copper sorption increases from 7.20 to 30.41 mgg^{-1} with an increase of stirring speed between 0 and 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 [30]. The change in the sorbed amount was insignificant compared to the dissipated energy when the stirring speed increased from 400 to 800 rpm, the amount of copper sorption increases from 26.34 to 30.41 mg/g. So, all subsequent experiments conducted at a stirring speed of 400 rpm.

3.2.4. Effect of temperature

Temperature is a highly significant parameter in the adsorption processes. Fig 5 shows the sorption of Cu (II) on PP. It was found that the sorption kinetics of metal decreased with the increase in temperature (25 to 55 °C). This indicates that the sorption process is exothermic in nature. The amount of copper fixed at equilibrium decreased from 26.34 to 10.15 mg $g^{-1}$with the increasing of temperature from 25 to 55 ◦C, respectively. It was explained that as temperature increased, the solubility of copper (sobat) increased which caused the interaction forces between the solute and the solvent to become stronger than solute and adsorbent, therefore the solute was more difficult to adsorb [31]. In literature, the removal of Cu (II) by cedar sawdust [32] was indicated the exothermic nature of the process. However others investigates were reported that adsorption of the copper and others heavy metal ions from aqueous solution the endothermic [33].

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 sorption of metal ions. The effect of salt concentration (ionic strength) on the amount of copper sorbed by PP was analyzed over the NaCl concentration range from 0 to 5 g/400 mL. The obtained results are shown in Fig 6. It was seen that the increase in the salt concentration resulted in a decrease of copper sorption by PP. This may be due to the following two reasons: (a) the electrostatic attraction seems to be a significant mechanism, as indicated by the results where at high ionic strength, the increased amount of NaCl can help to render the surface of the sorbent 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 [34], when solid adsorbent is in contact with sorbate 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^{2+} from approaching, and (b) the relative competition between sodium ions and copper species for the active sites of adsorbent, can also be an explaining factor. As the concentration of salt is increased from 0 to 5 g/400mL, the amount of copper sorbed on PP decreased from 26.34 to 10.15 mg g^{-1}.

3.2.6. Effect of biosorbent particle size

The effect of biosorbent particle size on the copper removal was studied using the diameter of biosobent was varied from 0.16 mm at 1.5 mm. Fig. 7 shows the sorption kinetics of the copper at three different particle sizes (0.16–0.63, 0.63–1 and 1–1.5 mm) . The sorption rate and capacity increase with decreasing particle size of PP. The relationship between the effective surface area of the biosorbent particles and their sizes is that the effective surface area increases as the particle size decreases and as a consequence, the sorption capacity per unit mass of the biosorbent increased. So the smaller biosorbent particle sizes for a given mass of biosorbent have more surface area and therefore the number of available sites is more for sorbing the metal ions.

3.2.7. Effect of initial concentration of Cu (II)

The effect of initial ions concentration on the sorption of copper (II) by PP at 25°C is shown in Fig 8. It can be observed that the sorption capacity increased with time and, at some point in time, reached a constant value where no more ions of copper (II) was removed from the solution. It was observed that an increase in initial ion concentration leads to an increase in the sorption of copper (II) by PP. Equilibrium uptake increased with the increase of initial metal concentration at the range of experimental concentration. The amount of metal sorbed at equilibrium increased from 4.99 to 37.55 mg g^{-1} as the concentration was increased from 25 to 300 mg L^{-1}. It is also shown in Fig. 8 that the contact the sorption of Cu (II) by PP was carried out using contact times ranging from 15 to 35 min and it was observed that metal sorption occurred rapidly. The sorption efficiency of Cu (II) increased gradually with increasing contact times and reached a plateau afterwards. Equilibrium uptake increased with the increase of initial metal concentration at the range of experimental concentration. This is a result of the increase in the driving force the concentration gradient [30, 35], as an increase in the initial copper concentrations. This effect can be explained as follows: at low metal/biosorbent ratios, there are a number of sorption sites in Potato peel structure. As the metal/biosorbent ratio increases, sorption sites are saturated, resulting in decreases in the sorption efficiency.

3.3. Sorption kinetics studies

The effect of initial copper concentration and time on sorption by potato peel (PP) was shown in Fig.8. Preliminary experiments showed high initial rates of sorption of copper ions followed by lower rates near equilibrium. To gain a better understanding sorption kinetics and rate limiting step, three kinetic models were used. These kinetic models are Lagergren-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 and obtain rate constants .This equation can be written as [36, 37]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (3)$$

Where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amount of Cu^{+2} sorbed at equilibrium and at any time t, respectively, and k_1 (min^{-1}) is the rate constant for Lagergren-first-order sorption. The straight line plots of ln ($q_e - q_t$) against t of Eq. (3) were made at different initial copper concentrations (25, 50,100,200, and 300 mg L^{-1}). The plot of ln ($q_e - q_t$) versus t gives a straight line for the pseudo-first-order sorption kinetics (Fig. 9). 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 3, it is seen that Lagergren equation does not represent a good fit with the experimental data.

Pseudo-second-order kinetic model can be expressed as follows [38, 39]:

$$\frac{t}{q} = \frac{1}{k_2 q^2{}_e} + \frac{1}{q_e} t \qquad (4)$$

Where k_2 (min gmg^{-1}) is the rate constant for the pseudo-second-order adsorption kinetics and $h=k_2q_e{}^2$, where h is the initial adsorption rate (min mg g^{-1}). The slopes of the plots t/q_t versus t give the value of q_e, and from the intercept k_2 can be calculated. Fig. 10 shows the pseudo-second-order plots for Cu^{+2} onto Potato peel at 25 ℃ . The pseudo-second-order rate constants k_2, the predicted q_e values and the corresponding linear regression correlation coefficients values r are given in Table 3. The calculated or predicted q_e^2 values agree with experimental q_e,exp 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 is seen that the pseudo-second-order kinetics equation in sorption of copper by the PP does represent a good fit with the experimental data. In other systems, similar kinetic results were reported [40, 41].

The pseudo-first-order and pseudo-second-order kinetic models could not identify the diffusion mechanism. An intra-particle diffusion model was used to predict the rate controlling step. The half-sorption time, $t^{1/2}$ known as the time required for the sorption to take up half as much PP as its equilibrium value. This time is often used as a measure of the sorption rate. In adsorption systems where there is the possibility of intra-particle diffusion being the rate-limiting step, the intra-particle diffusion approach described by Weber and Morriss is used. The rate constants, for intra-particle diffusion (k_d) are determined using equation given by Weber and Morris [42]:

$$q_t = k_d . t^{1/2} + C_d \qquad (5)$$

Where k_d is intra-particular diffusion rate constant (mg/g min$^{1/2}$). If intra-particle diffusion is rate-limited then plots of adsorbate uptake q_t versus 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. 11) and see in (Table 3). C_d is the intercept, which represents the thickness of the boundary layer. A larger intercept means a greater effect of the boundary layer [43]. Fig. 11 shows two consecutive linear steps during the sorption of copper on Potato peel, indicating the different stages in sorption. The first, sharper portion represents the copper ions were adsorbed within a $t^{1/2}$ value of about first minute (around to 6 min); this can be attributed to the rapid use of the most readily available sorbing sites on the biosorbent surface [42, 44]. This portion is the gradual sorption stage where intra-particle 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 sorbate concentrations (copper) left in the solutions. The lines do not pass through the origin ($C_d \neq 0$), therefore, intra-particle diffusion is not the only rate-limiting step, then other processes may control the rate of sorption the copper on PP and boundary layer control may be involved in the process [45, 46]. The values of k_d and C_d were determined from the slopes of the first linear portion, and the constants of intra-particle diffusion model are given in Table.3. Similar mechanism results were reported in other systems [37, 41, 47].

3.4. Sorption 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 [48, 49]. 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 sorption isotherms of copper on PP. In this study, equilibrium isotherms at different temperatures of sorption the copper on PP were determined in (Fig.12). The shape of the curves q_e versus 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. [50]. The sorption of copper by PP decreases progressively with the increase in temperature from 25 to 55°C, as shown in Fig. 12 indicated that the sorption process on Potato Peel is exothermic. The increase in temperature decreases the physical forces responsible for sorption [31]. On the other hand, the temperature has two main effects on the sorption process. An increase in temperature is known to increase the diffusion rate of the sorbate 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 sorbent for a particular sorbate [32].

3.4.1. Langmuir model

The Langmuir (1916) [51] model assumes uniform energies of sorption onto the surface and no transmigration of sorbate in the plane.

$$q_e = \frac{q_m b C_e}{1 + b C_e} \qquad (6)$$

Where q_e is the amount of solute sorbed per unit weight of sorbent at equilibrium (mg g^{-1}), C_e is the equilibrium concentration of the solute in the bulk solution (mg L^{-1}), q_m is the maximum sorption capacity (mg g^{-1}) and b is the constant related to the free energy of sorption (L mg^{-1}). The linear form of the Langmuir isotherm is given by the following equation [52]:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{b \cdot q_m} \times \frac{1}{C_e} \qquad (7)$$

The linear plot of $1/q$e versus $1/C$e shows that the adsorption obeys to the Langmuir model (Fig. 13). The values of constants q_m and b were calculated and reported in Table 4. The results obtained from Langmuir model for the removal of copper onto PP were confirmed that the correlation coefficients at different temperatures (25, 35, 45, and 55°C) were $r \geq 0.993$ and the maximum monolayer capacities (q_m) obtained were 84.74, 60.60, 56.18 and 50.76 mg g^{-1}, respectively (Table 4).

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L also known as the separation factor, given by [53]:

$$R_L = \frac{1}{1 + b \times C_0} \qquad (8)$$

Where b is the Langmuir constant and C_0 is the initial concentration of the sorbate in solution. The value of R_L lies between 0 and 1for favorable adsorption, while $R_L > 1$ represents unfavorable adsorption, and $R_L = 1$ represents linear adsorption while the adsorption process is irreversible if $R_L = 0$. The calculated R_L values versus initial copper concentration at four different temperatures were represented in Fig. 14. From this figure, it was observed that sorption was found to be more favorable at lower temperature and at higher concentrations. Also the value of R_L in the range of 0–1 at all initial metal concentrations and the four studied temperatures confirms the favorable uptake of copper process.

*3.4.2. Freundlich **model(1906)***

The empirical model can be applied to non-ideal sorption on heterogeneous surfaces as well as multilayer sorption and is expresses by the following equation [54]:

$$q_e = K_F C_e^{1/n} \qquad (8)$$

Where n is a constant indicative of the intensity of the sorption and K_F is a constant indicative of the relative sorption capacity of the sorbent ($\mathrm{mg}^{1-\frac{1}{n}}\,\mathrm{L}^{\frac{1}{n}}\,\mathrm{g}^{-1}$).The fit of 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 from linearity of adsorption. The n value indicates the degree of non-linearity between solution concentration and adsorption as follows: if the value of n = 1, the adsorption is linear; $n < 1$, the adsorption process is chemical; if $n > 1$, the adsorption is a favorable physical process [55, 56]. Eq. (8) can be linearized in the form of Eq. (9) and the constants can be determined [57]:

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \qquad (9)$$

Fig.15 shows the plot of ln (q_e) versus ln (C_e) with the intercept value of ln K_F and the slope of $1/n$. The correlation coefficients, $r \geq 0.994$, obtained from the Freundlich model, were comparable to that obtained from Langmuir model (Table 4). This result indicates also that the experimental data fit to the Freundlich model and $n > 1$, indicating that biosorption for Cu^{+2} onto PP is a favorable physical process. Also the linear plot of ln q_e versus lnC_e at different temperatures (Fig. 15) shows that the adsorption obeys to the Freundlich model.

*3.4.3. Temkin **isotherm model***

Temkin and Pyzhev [58] 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 excellent for predicting the gas phase equilibrium (when organization in a tightly packed structure with identical orientation is not necessary), conversely complex adsorption systems including the liquid-phase adsorption isotherms are usually not appropriate to be represented [59]. Temkin model is given by:

$$\theta = \frac{RT}{\Delta Q}\ln K_0 C_e \qquad (10)$$

Where θ is the fractional coverage, R the universal gas constant (kJ $\mathrm{mol^{-1}}$ $\mathrm{K^{-1}}$), T the temperature (K), ΔQ the variation of adsorption energy (kJ $\mathrm{mol^{-1}}$), and K_0 is the Temkin equilibrium constant (L $\mathrm{mg^{-1}}$).

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 versus $\ln C_e$ by the relation:

$$\theta = \frac{RT}{\Delta Q}\ln K_0 + \frac{RT}{\Delta Q}\ln C_e \qquad (11)$$

Fig. 16 shows a plot of θ versus ln C_e. Temkin equilibrium constant and the variation of adsorption energy together with the *r* values were listed in Table 4.

3.4.4. *Elovich* ***isotherm model***

This model [60] 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 [61]:

$$\frac{q_e}{q_m} = K_E\, C_e \exp(-\frac{q_e}{q_m}) \qquad (12)$$

Where K_E is the Elovich equilibrium constant (L $\mathrm{mg^{-1}}$) and q_m is the Elovich maximum adsorption capacity (mg $\mathrm{g^{-1}}$). The linearized form of the Eq. (12) is given below:

$$\ln \frac{q_e}{C_e} = \ln K_E\, q_m - \frac{q_e}{q_m} \qquad (13)$$

Fig.17 shows a plot of ln q_e/C_e versus q_e. The variables of Elovich (K_E , q_m) with the correlation coefficients *r* values were regrouped in Table 4.

3.4.5. *Dubinin-Radushkevich (D-R)* ***isotherm model***

Another model for the analysis of isotherms of a high degree of rectangularity is Dubinin–Radushkevich isotherm [61,62]. Radushkevich [63] and Dubinin [64] have reported that the characteristic sorption curve is related to the porous structure of the sorbent. In general, the Dubinin– Radushkevich isotherm equation has been often used to determine the mean adsorption energy (*E*) that may provide useful information with regard to whether or not biosorption is subject to a chemical or physical process[65,66]. For a magnitude of *E* between 8 and 16 kJ/mol, the adsorption process follows chemical ion-exchange [67], while values of E below 8 kJ/mol characterize a physical adsorption process [68]. The model has often successfully fitted high solute activities and the intermediate range of concentrations data well, but has unsatisfactory asymptotic properties and does not predict the Henry's law at low pressure [69]. The approach was usually applied to distinguish the physical and chemical adsorption of metal ions, with its mean free energy, E per molecule of adsorbate (for removing a molecule from its location in the sorption space to the infinity) can be computed by the relationship [70]:

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

The linearized form of the Dubinin–Radushkevich (D–R) model is given below:

$$\ln q_e = \ln q_s - \beta\varepsilon^2 \qquad (15)$$

Where β was the activity coefficient related to mean sorption energy and ε the Polanyi potential given by:

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \qquad (16)$$

Where R, T and C_e represent the gas constant (8.314 J mol^{-1} K), absolute temperature (K) and adsorbate equilibrium concentration (mg L^{-1}), respectively. Fig. 18 shows the plot of ln q_e versus ε^2 of the experimental data for the sorption of copper onto PP. The slope gives β (mol^2/J^2) and the ordinate intercept yields the sorption capacity q_s (mg/g). Calculated D–R constants for the sorption of copper by PP are shown in Table 4; the values of correlation coefficients $r \geq 0.865$ indicate that the D–R does not represent a good fit with the experimental data comparable with the both to the Langmuir and Freundlich isotherm models. The maximum capacity q_s obtained using D-R isotherm model at 25, 35, 45, and 55°C for sorption of copper is 35.79, 33.17, 29.60, and 26.66 mg g^{-1} on PP, respectively (Table 4).

3.4.6. Flory–Huggins isotherm *model*

The original Flory–Huggins isotherm describes the behaviour of a two-dimensional lattice of non-interacting particles of different sizes, i.e., it accounts for the effect of the surface coverage on adsorption [66, 71]:

$$\frac{\theta}{C_0} = K_{FH}(1-\theta)n^{FH} \qquad (17)$$

Eq.(17) can be further translated to the following linearized form :

$$\ln(\frac{\theta}{C_0}) = \ln K_{FH} + n_{FH}\ln(1-\theta) \qquad (18)$$

Where θ the degree of surface coverage, K_{FH} is is the indication of Flory–Huggins equilibrium constant, and n_{FH} is constant model exponent. Also, Flory–Huggins isotherm model [71], which occasionally deriving the degree of surface coverage characteristics of adsorbate onto adsorbent, can express the feasibility and spontaneous nature of an adsorption process. K_{FH} that used for the calculation of spontaneity free Gibbs energy is related to the equation [72]:

$$\Delta G^{\circ} = -RT \ln (K_{FH}) \qquad (19)$$

Vijayaraghavan et al. [66, 72] applied the Flory–Huggins isotherm equation to determine the equilibrium constant (K_{FH}), which was further used to estimate the change in the Gibbs free energy during Ni^{2+} biosorption.

A plot of $\ln \left(\frac{\theta}{C_0}\right)$ versus $\ln (1- \theta)$ (Fig. 19) enables the constants K_{FH} and n_{FH} to be determined with the correlation coefficients $r \geq 0.955$ (Table 4). In the literature, Horsfall and Spiff [71] also used this model to study the equilibrium sorption of Al^{3+}, Co^{2+} and Ag^{+} by fluted pumpkin waste biomass.

The parameters of the six isotherms were computed and listed in Table 4. The Langmuir and Freundlich isotherm fitted quite well with the experimental data (correlation coefficient $r \geq 0.993$), compared to the other four isotherm models which had lower correlation coefficients.

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 sorption of copper ions by potato peel were measured in the range temperature 298–328 K. Thermodynamic parameters i.e., free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), changes were determined using the following relations [30]:

$$\ln b = \frac{\Delta S^{\circ}}{R_g} - \frac{\Delta H^{\circ}}{RT} \qquad (20)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \qquad (21)$$

Where T (K) is the absolute temperature, R_g (kJ mol^{-1} K^{-1}) is the gas constant, and b (L mol^{-1}) is the Langmuir equilibrium constant.

It appears from Eq. (20) that both ΔH^0 and ΔS^0 of sorption of Cu^{+2} by PP can be determined from the plot of $\ln b$ to $1/T$ (Fig. 20). The Gibbs free energy change (ΔG°) was obtained according to Eq. (21) at different temperatures. The thermodynamic parameters are collected in Table 5. The negative values of ΔG° (-15.31 to -12.46) demonstrate the feasibility of the process and the spontaneous nature for the sorption with a high preference of Cu^{+2} onto PP by lower temperatures. The negative values of enthalpy change (-43.58 $Kjmol^{-1}$**)** indicated the exothermic nature of the adsorption interaction. This decrease in sorption capacity with increase in temperature is known to be due to the weakening of sorptive forces between the active sites on the PP and the metal ions (Cu^{+2}) species, and also between adjacent copper molecules on the sorbed phase [31]. The low and the negative value of $\Delta S°$ copper by the biomaterial (PP) reflect the decreased randomness at the solid–solution interface during sorption of the biosorbent toward copper. In addition the negative values of sorption entropy indicated that the adsorption process was reversible [37]. Some researchers have indicated that the positive values of $\Delta S°$ suggested some structural changes in metal and sorbent [73, 74]. Similar result was reported for adsorption of nitrates onto Amberlite IRA 400[37] and mecury onto banana stem [75]. However, other workers have observed positive values of entropy change for the sorption of copper by cedar sawdust and crushed brick [32].

4. Evaluation of potato peel as biosorbent

As seen in Table 6 lists a comparison of the maximum monolayer de sorption capacities of various adsorbents for copper. The value of $q_{\max}$ in this study (84.74 mg/g) is larger than those in most of previous studies. This suggests that copper could be readily sorbed by potato peel used in this work. Furthermore, the agriculture waste residue, potato peel, used in this work could be easily obtained availability with low cost. The results showed that Potato peel is effective for sorption copper ions.

5. Conclusions

The results obtained in this study demonstrated the potential use of Potato Peels for the sorption of Cu (II) ions from aqueous solutions. The FTIR analysis was confirmed that many functional groups on the PP surface. In addition the surface functionalities were investigated by the usual method of Boehm demonstrated that the total acidic sites are higher than the total basic sites.

The amount of Cu (II) ions sorbed by the Potato Peel increased with an increase in initial concentration, pH, dose of biosorbent material and stirring speed. However the amount of Cu (II) ions decreases with an increase the temperature, the ionic strength and particle size. The kinetic studies at different concentrations was indicated that equilibrium in the sorption of Cu (II) ions on PP was reached in 35 min of contact between the PP and the solution of copper. It was found that the kinetics of the sorption of Cu (II) ions on PP followed closely the pseudo-second-order kinetic model.

For the diffusion mechanism studies, the results obtained to reveal that An intraparticle diffusion is not the only rate-limiting step, then other processes may control the rate of sorption the copper on PP. Equilibrium data were fitted to Langmuir, Freundlich, Temkin, Elovich, Dubinin–Radushkevich, and Flory- huggins isotherm models and the equilibrium data were best described both to the Langmuir and Freundlich isotherm models. The maximum monolayer sorption capacity of 84.74 mg/g at 25°C. The negative of change in enthalpy (ΔH°) value confirmed the exothermic nature of the sorption interaction whereas the low and the negative value of change in entropy (ΔS°) reflect the decreased randomness at the solid–solution interface during sorption of the biosorbent toward copper, also indicated that the sorption process was reversible. The negative value of change in free energy (ΔG°) indicated the feasibility and the spontaneous nature for the sorption of copper onto the Potato Peel. Taking into consideration of the above results, it can be concluded that the Potato Peels is a suitable biosorbent for the removal of Cu (II) ions from aqueous solution in terms of low cost, natural and abundant availability.

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Tables

Table 1. Principal characteristics of PP

Porosity (%)	68.14
Apparent specific gravity	0.36
Absolute specific gravity	1.13
Mean diameter (mm)	≤ 2
PZC	5.7

Table 2. The concentrations of surface functionalities of Potato Peel

Concentration of acidic and basic sites on Potato Peel surface	mequiv.g^{-1}
Carboxylic	1.00
Lactonic	0.00
Phenolic	0.00
carbonylic and quinonic sites	0.08
Acidic sites total	1.08
Basic sites total	0.35

Table3. Parameters of the kinetic models for the sorption of Copper by PP at different concentrations

kinetics models	Initial concentration C_0 (mg L^{-1})				
	25	50	100	200	300
Pseudo-first-order					
qe,exp (mg g^{-1})	4.98	8.12	16.22	26.34	37.58
qe,cal (mg g^{-1})	5.32	1.23	7.53	34.66	9.55
k_1 (min^{-1})	0.169	1.111	0.052	0.067	0.072
r	0.989	0.978	0.998	0.986	0.961
Pseudo-second-order					
qe,exp (mg g^{-1})	4.98	8.12	16.22	26.34	37.58
qe,cal (mg g^{-1})	5.25	9.80	18.18	29.15	37.17
k_2(gmg^{-1}min^{-1})	0.0636	0.0371	0.0082	0.0076	0.0032
h(mg g^{-1}min^{-1})	1.75	3.56	2.74	6.53	4.40
r	0.997	0.997	0.994	0.999	0.996
Intra-particle diffusion					
k_d(mg g^{-1} 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

Table4. Isotherms constants for sorption of copper by potato peel at different temperatures

Isotherm	Parameters	T (°C)			
		25	35	45	55
Langmuir	q_m(mg/g)	84.74	60.60	56.18	50.76
	$b * 10^3$ (L/mg)	7.3	4.38	2.86	1.39
	r	**0.999**	**0.998**	**0.997**	**0.996**
Freundlich	K_F ($mg^{1-1/n}$ $L^{1/n}$ 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	$K_0 * 10^2$ (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
	$K_E * 10^2$ (L/mg)	8.70	1.11	1.32	1.40
	r	**0.982**	**0.985**	**0.979**	**0.981**
Dubinin-Raduchkevich	q_s (mg/g)	35.79	33.17	29.60	26.66
	E (kj/mol)	0.037	0.033	0.032	0.031
	r	**0.865**	**0.893**	**0.893**	**0.890**
Flory-Huggins	$K_{FH} * 10^3$	3.86	3.23	2.59	1.92
	n_{FH}	1.58	1.08	0.82	0.61
	r	**0.983**	**0.986**	**0.977**	**0.955**

Table5. Thermodynamic parameters for the sorption of Cu (II) by PP

T (°C)	ΔH° (kJ/mol)	-ΔG° (kJ/mol)	ΔS° (J/molK)
25	-43.58	15.20	-94.86
35		14.37	
45		13.74	
55		12.22	

Table6. Previously reported sorption capacities of various low-cost adsorbents for Cu (II)

Low-cost adsorbents	sorption capacity (mg/g) of Cu(II), *q*m$_{ax}$	Reference
Tea waste	8.64	[3]
Sawdust	1.79	[76]
Wheat shell	8.34	[15]
Sawdust of poplar tree	5.43	[29]
Activated Sawdust of poplar tree	13.49	[29]
Peanut hulls	9	[77]
Peanut pellets	12	[77]
Sawdust	8.45	[78]
Meranti sawdust	32.05	[33]
Corncobs	7.62	[79]
Peanut husk	10.15	[80]
Potato peel (PP)	84.74	this study

Figures

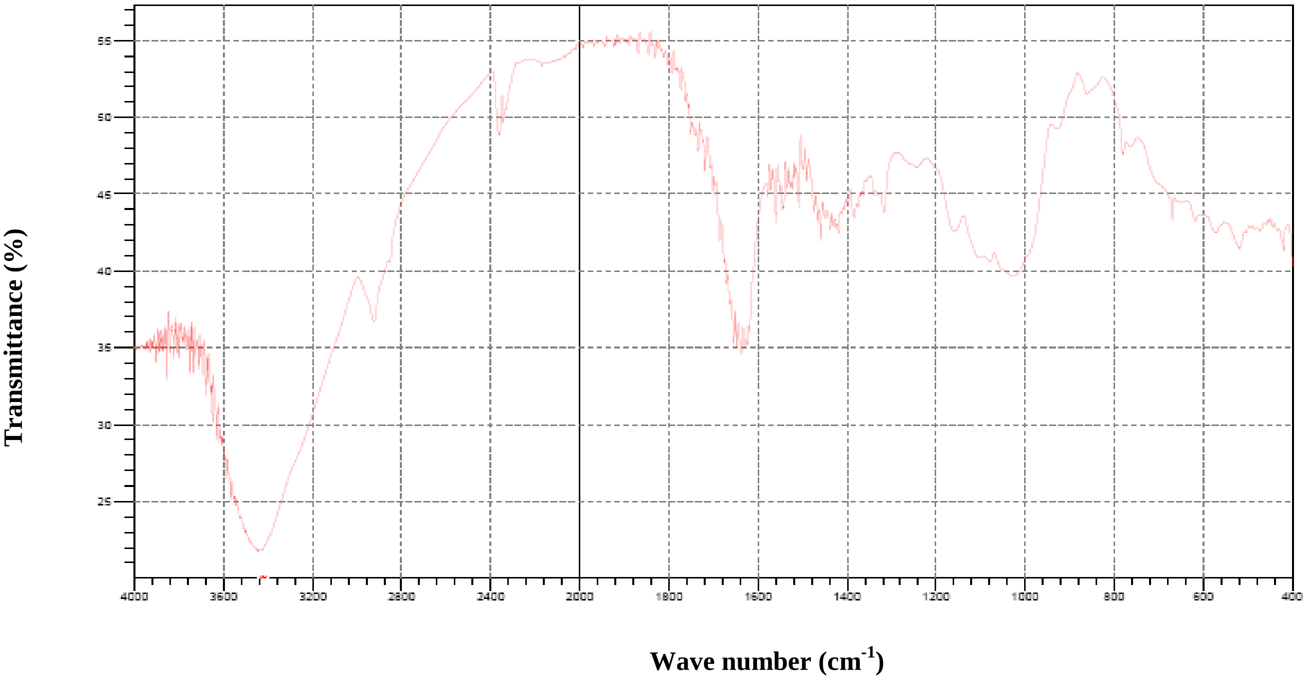

Fig.1. FTIR spectrum of Potato peel

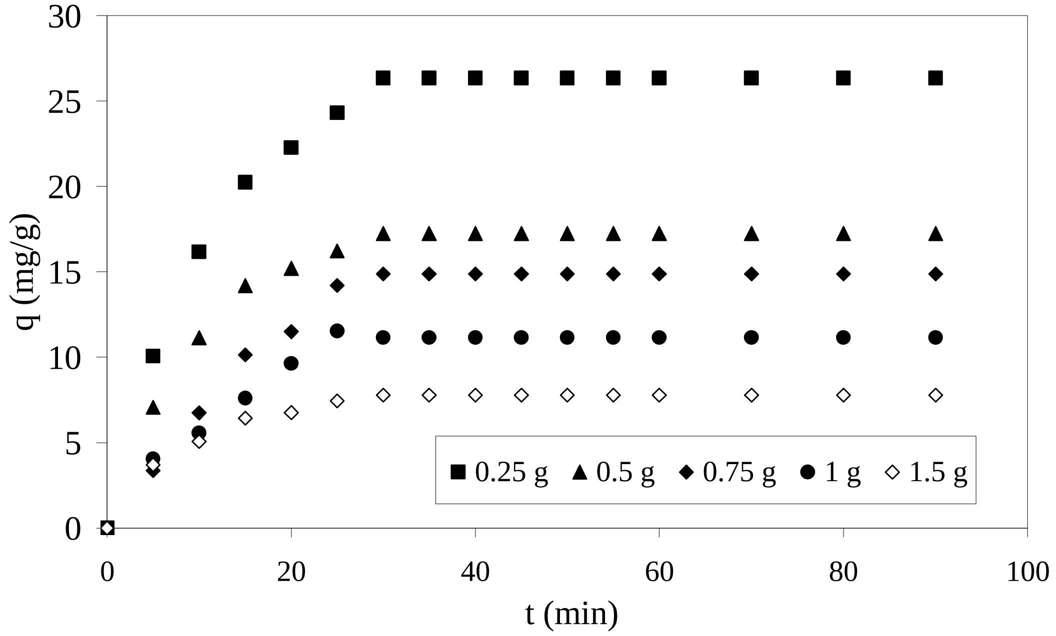

Fig. 2. Effect of biosorbent dosage on the sorption of Cu (II) by PP (conditions: solution volume=400 mL; initial metal concentration=200 mg L^{-1}; stirring speed=400 rpm; T=25°C; pH 5).

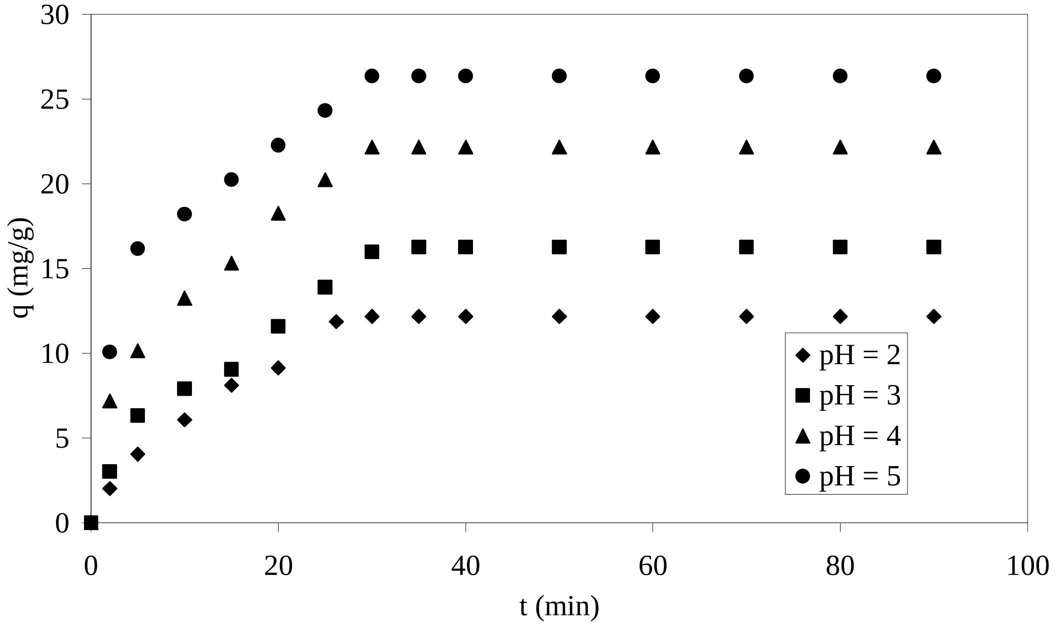

Fig. 3. Effect of initial pH on the sorption of Cu (II) by PP (conditions: initial metal concentration=200 mg L^{-1}; sorbent dosage=0.25 g (400 mL)$^{-1}$; stirring speed=400 rpm; T=25°C).

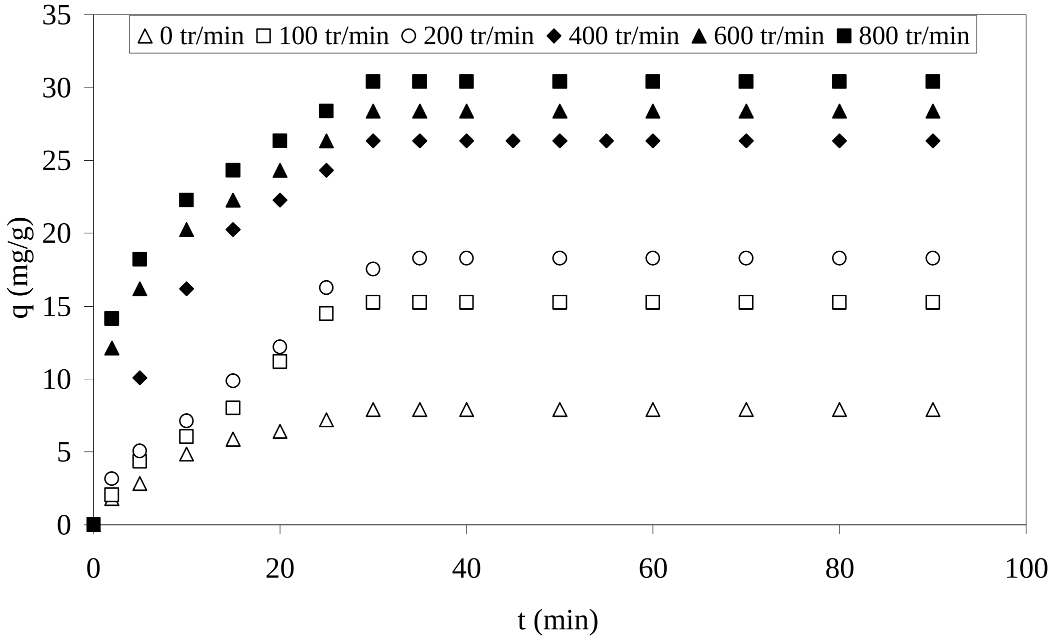

Fig 4. Effect of stirring speed on the sorption of Cu (II) by PP (conditions: initial metal concentration=200 mg L^{-1}; biosorbent dosage=0.25 g $(400\ mL)^{-1}$; pH 5; T=25°C,).

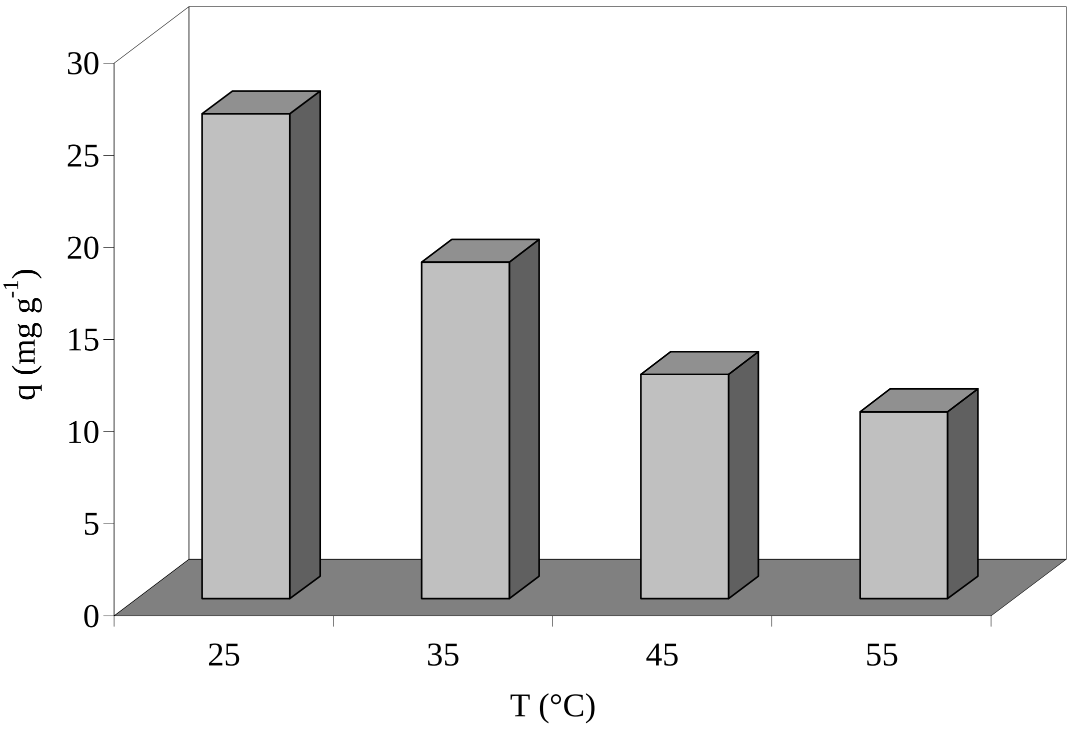

Fig. 5. Effect of temperature on the sorption of Cu (II) by PP (conditions: initial metal concentration=200 mg L^{-1}; biosorbent dosage=0.25 g $(400\ mL)^{-1}$; stirring speed = 400 rpm; pH 5).

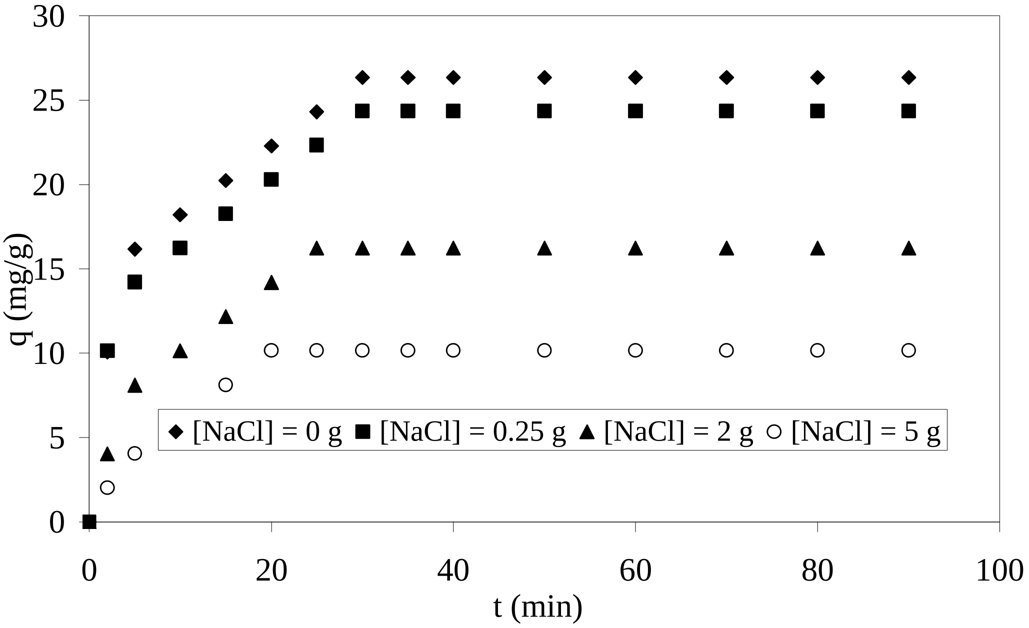

Fig.6. Effect of salt (NaCl) concentration on the sorption of Cu (II) by PP (conditions: initial metal concentration=200 mg L^{-1}; biosorbent dosage=0.25 g (400 mL)$^{-1}$; stirring speed = 400 rpm; T=25°C; pH 5).

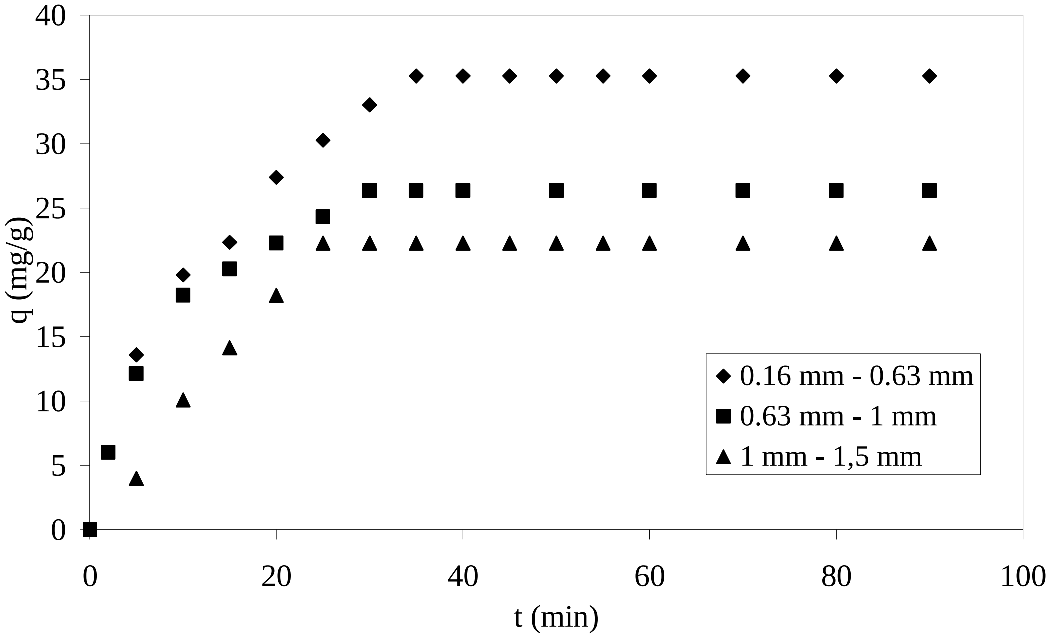

Fig. 7. Effect of biosorbant particle size on the sorption of Cu (II) by PP (conditions: initial metal concentration=200 mg L^{-1}; biosorbent dosage=0.25 g (400 mL)$^{-1}$; stirring speed = 400 rpm; T=25°C; pH 5).

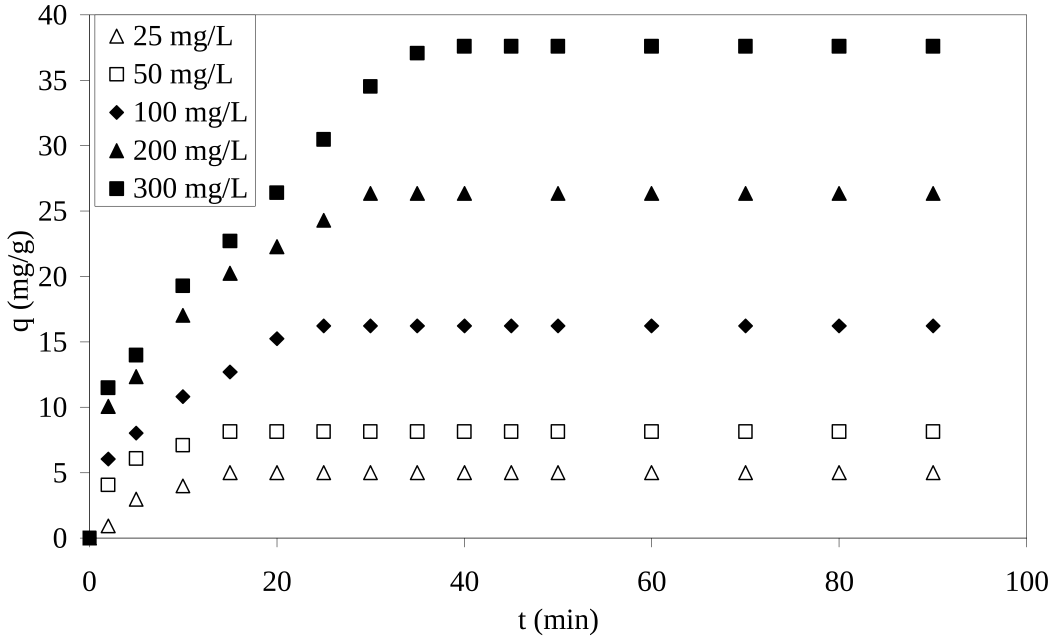

Fig .8. Kinetics of Cu (II) uptake by PP for various initial metal concentrations (conditions: biosorbent dosage=0.25 g (400 mL)$^{-1}$; stirring speed = 400 rpm; pH 5; T=25°C;)

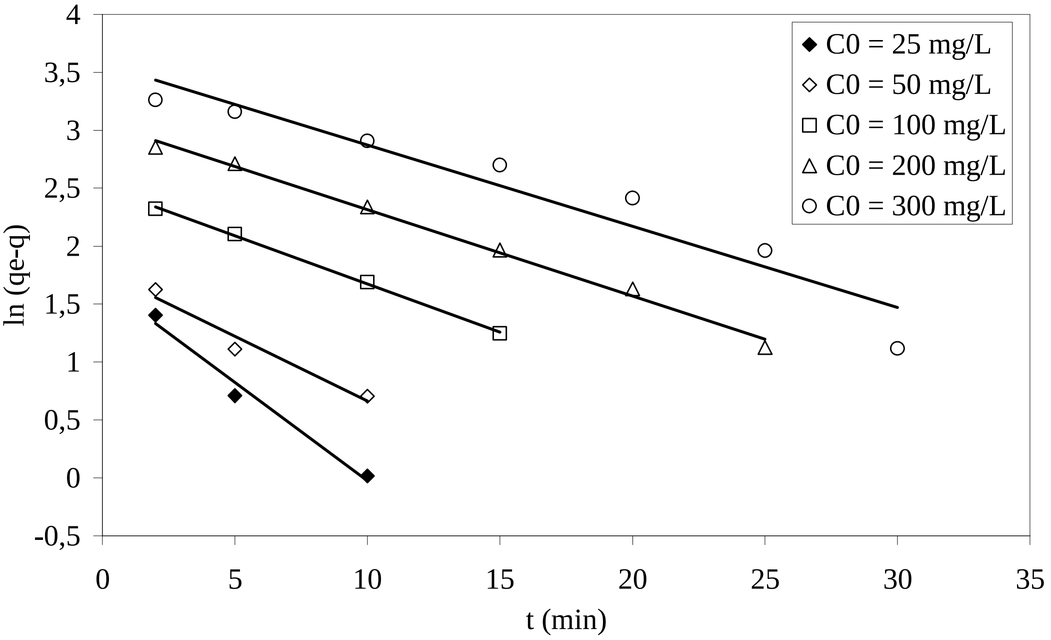

Fig. 9. Pseudo-first-order kinetics for sorption of Cu (II) onto PP at 25 ◦C.

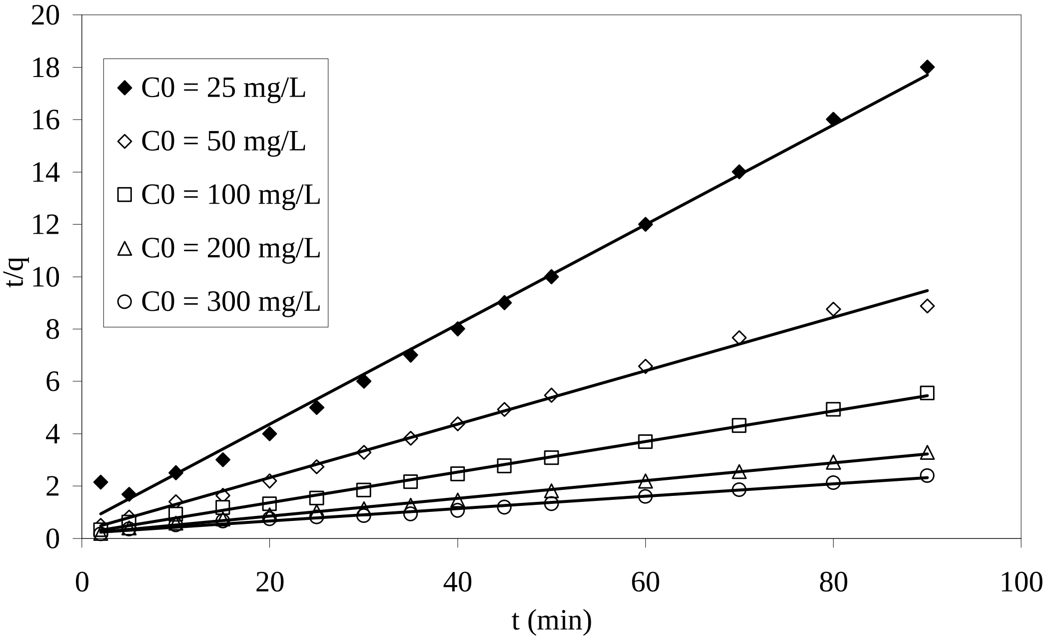

Fig. 10. Pseudo-second-order kinetics for sorption of Cu (II) onto PP at 25 ◦C.

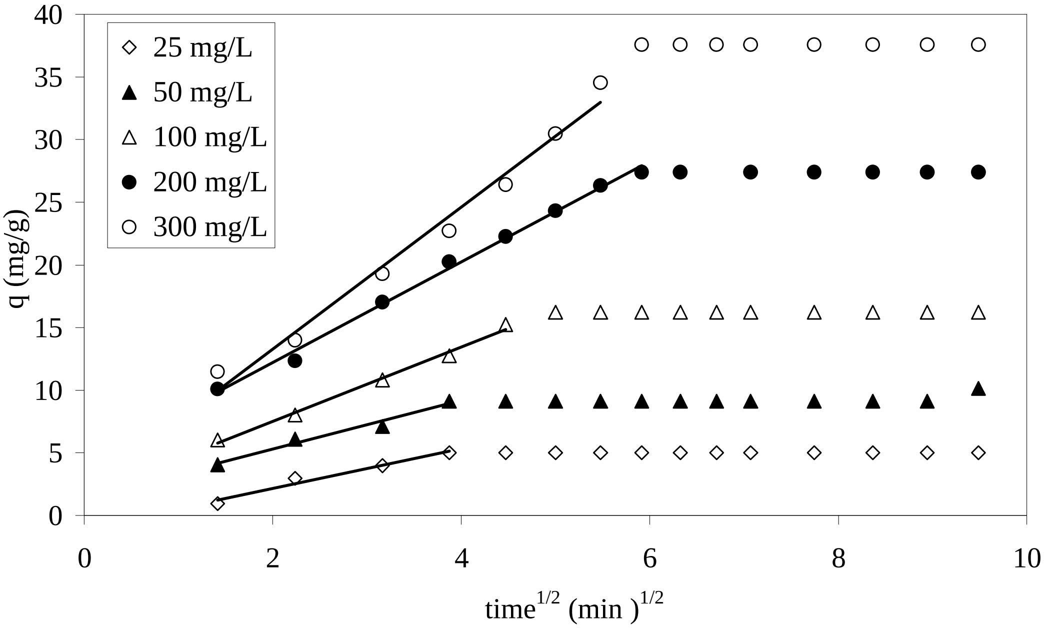

Fig. 11. Intra-particle diffusion kinetics for sorption of Cu (II) onto PP at 25 ◦C.

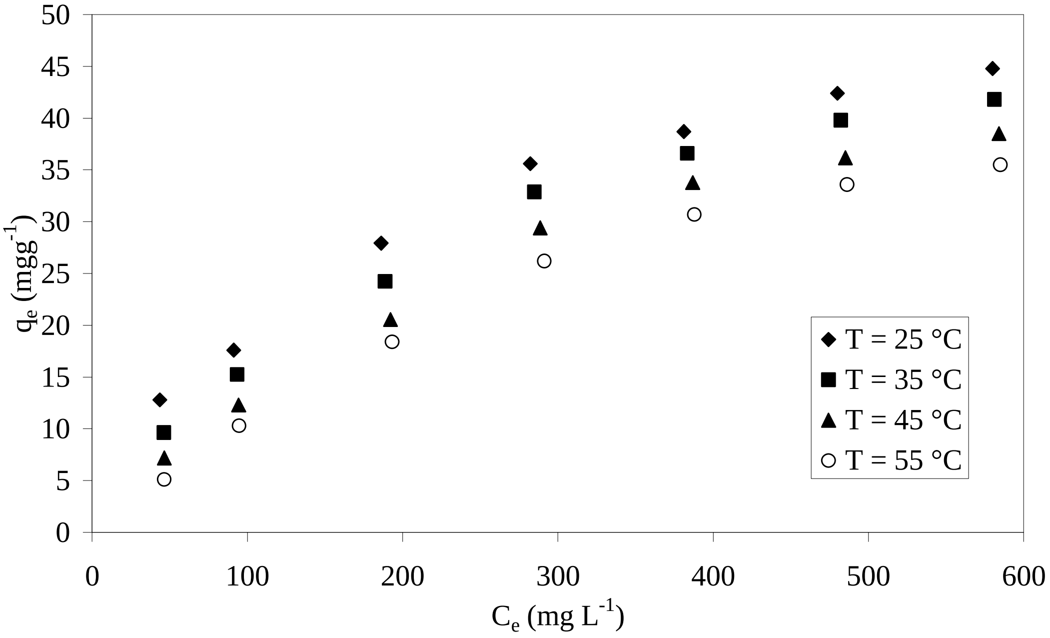

Fig. 12. Equilibrium isotherms of copper sorption by Potato Peel at different temperatures

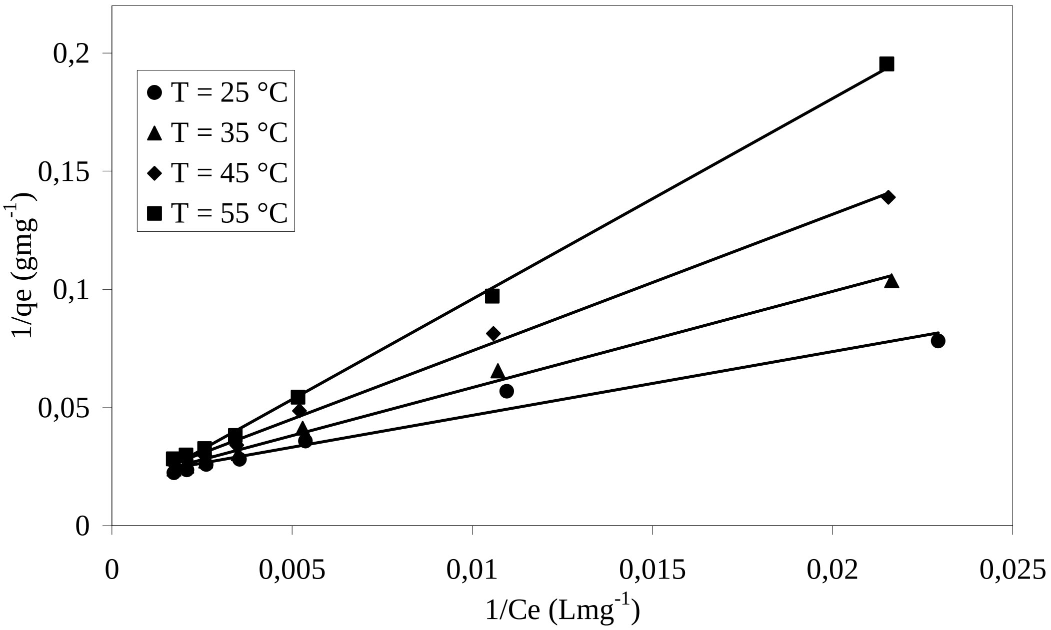

Fig. 13. Sorption isotherms for copper into PP at 25, 35, 45 and 55 ◦C (Langmuir isotherm)

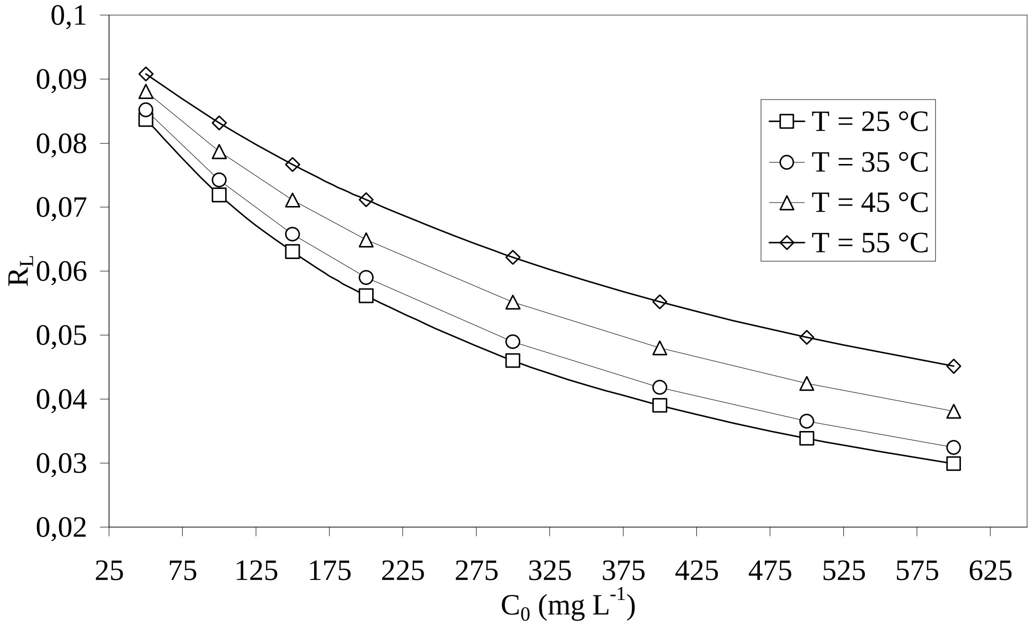

Fig.14. Separation factor (R_L) for the uptake of copper by PP at 25, 35, 45 and 55°C

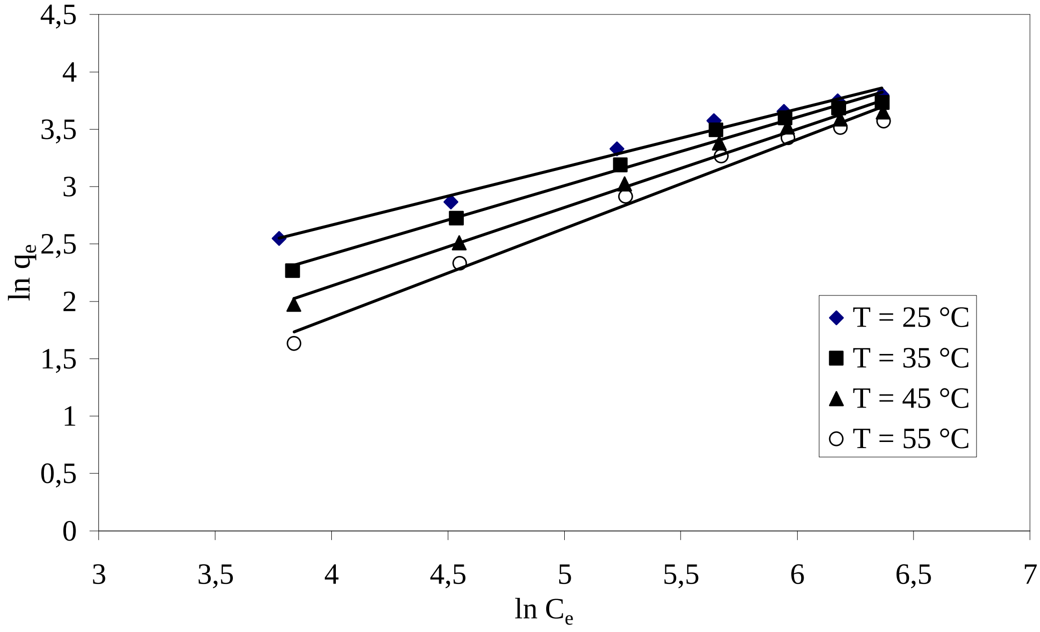

Fig. 15. Freundlich sorption isotherm for copper onto PP at different temperatures.

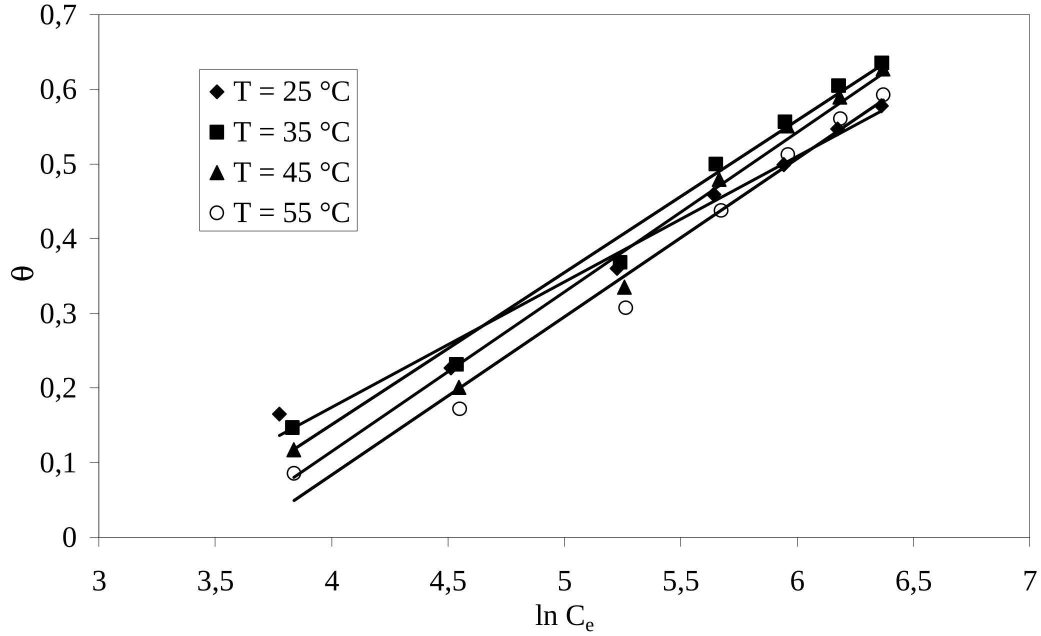

Fig. 16. Temkin sorption isotherm for copper onto PP at different temperatures

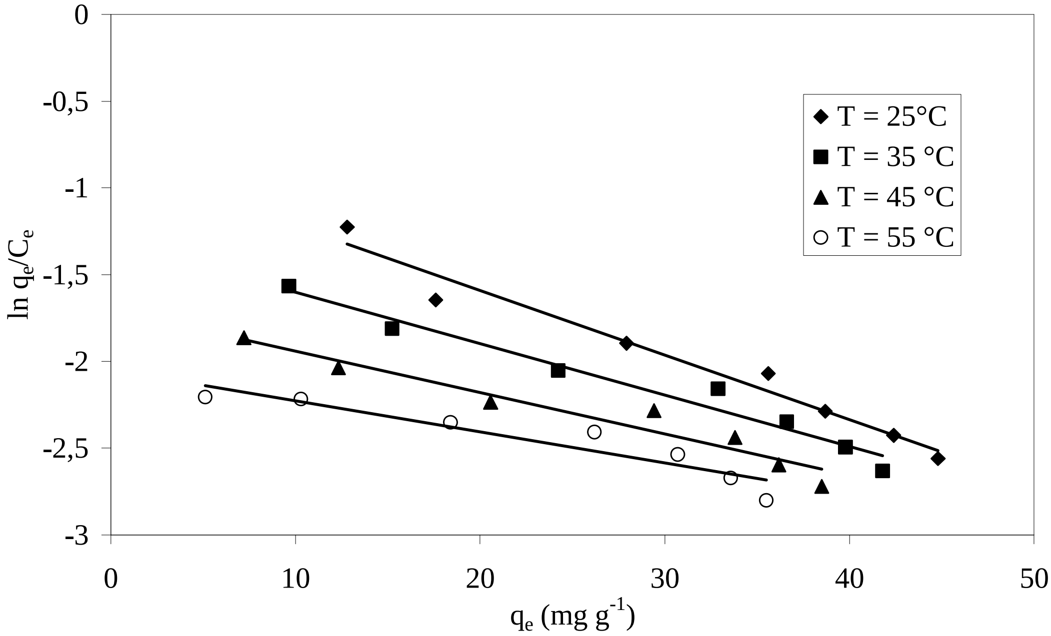

Fig. 17. Elovich sorption isotherm for copper onto PP at different temperatures

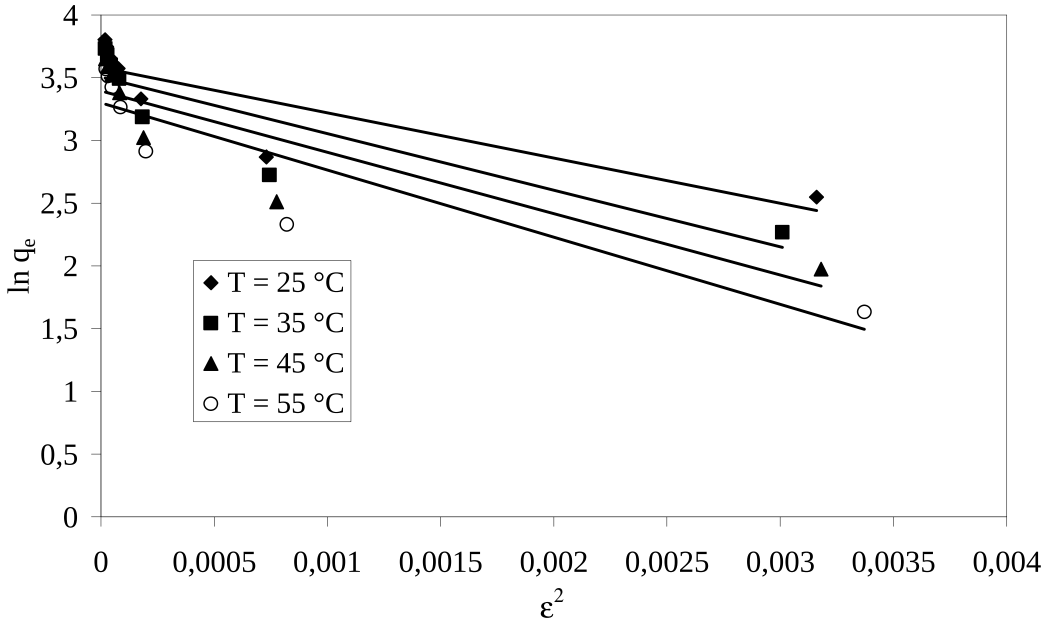

Fig. 18. Dubinin-Radushkevich sorption isotherm for copper onto PP at different temperatures

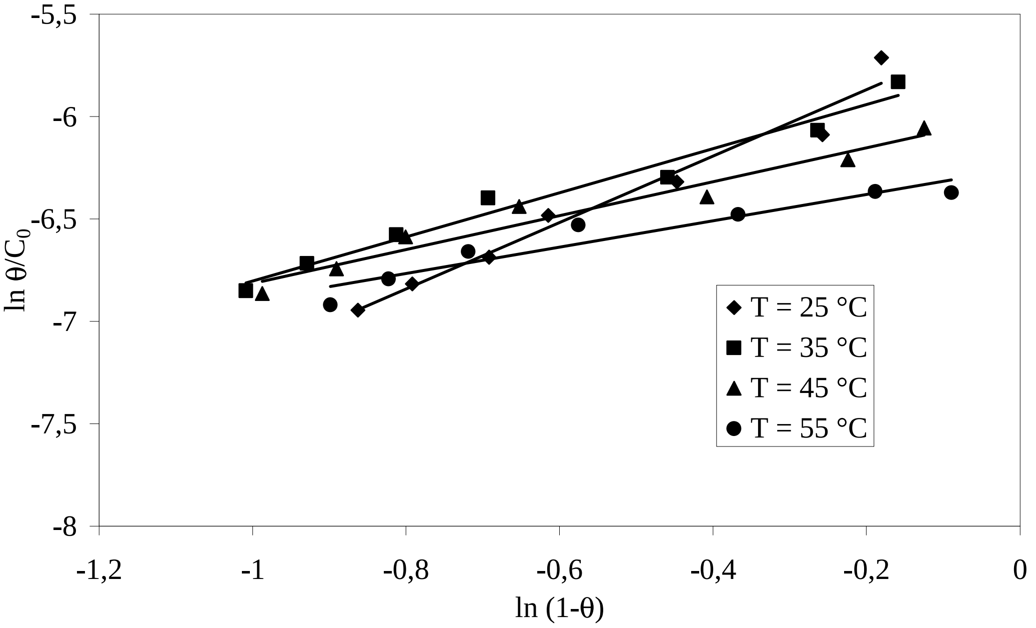

Fig. 19. Flory–Huggins sorption isotherm for copper onto PP at different temperatures

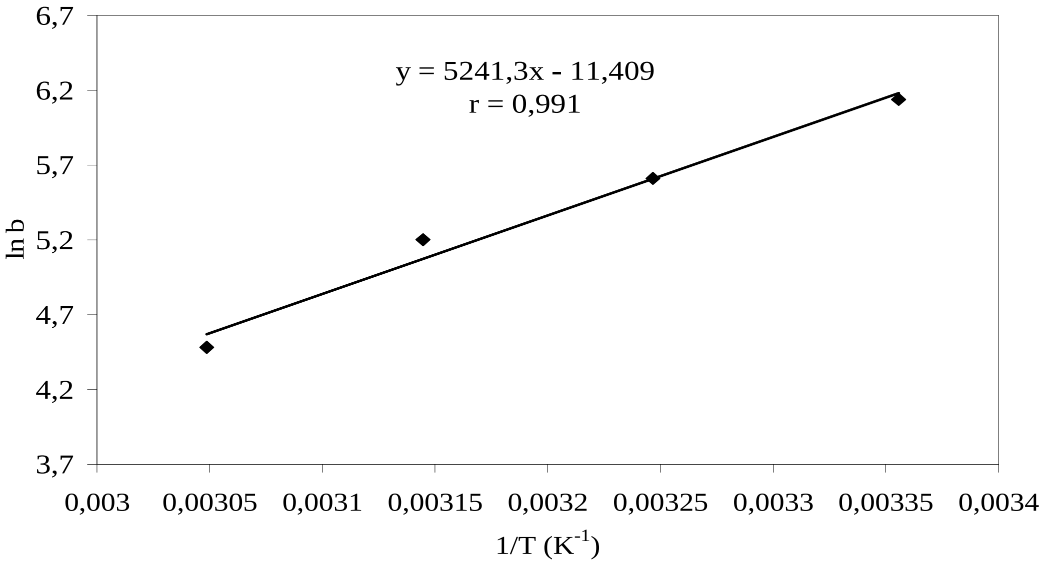

Fig.20. Plot of ln*b* versus 1/*T* for the determination of thermodynamic parameters (Potato peel).