

## Adsorption of Copper from Waste Printed Circuit Boards with Modified Orange Peels

Aysun Özkan,\* Zerrin Günkaya, Ece Yapıcı, and Müfide Banar

Copper adsorption from waste printed circuit boards (PCBs) was studied using biosorbents derived from waste orange peels (OP). The orange peels were modified by different methods including saponification with NaOH (OP-S), crosslinking with sodium trimetaphosphate and sodium tripolyphosphate (OP-C), hydroxypropylation with propylene oxide (OP-H), and acidification with citric acid (OP-A) to increase the adsorption capacity of orange peels. Adsorption tests on the copper (Cu) model solutions were performed by using native and modified orange peels at three different temperatures (25 °C, 40 °C, and 60 °C) to determine the optimum adsorption conditions. The PCB was pyrolyzed in a fixed bed stainless steel reactor to obtain a solid product that contained only inorganic material. Metals were then leached from the solid product, and adsorption studies were realized on the leach solution under optimum adsorption conditions. According to the analyses results, the best adsorption efficiency for the Cu model solution was obtained with OP-S at 25 °C for 30 min. Under these conditions, the Cu adsorption efficiency from pyrolysis solid product was approximately 86%.

*Keywords:* Adsorption; Copper; Modified orange peel; Waste printed circuit boards

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### INTRODUCTION

Large quantities of electrical and electronic equipment (WEEE) are being discarded, and the amount has rapidly increased because of continuous progress of technology. There were 41.8 million tons of electronic waste produced in the world, and in Turkey, 503,000 tons of electronic waste were generated in 2014 (Balde *et al.* 2015). Because of the increase of electronics in recent years, the management of WEEE has gained importance. Legal and technical principles about the management of WEEE have been defined by the European Union's Waste Electrical and Electronic Equipment Directive and the Turkish Regulation on the Control of Waste Electrical Electronic Equipment that came into force on May 22, 2012 (Ministry of Environment and Urbanization 2012). In the hierarchical procedure of these principles for an integrated and sustainable WEEE management, material recovery has a priority importance.

The basic components of electrical and electronic equipment are printed circuit boards (PCBs). The PCBs contain microelectronic components, such as semiconductor chips and capacitors. They provide electrical connections between internal components (Liu *et al.* 2007; Duan *et al.* 2011). Several hazardous materials, such as lead, antimony, beryllium, cadmium, and brominated flame retardants, are found in PCBs (Noon *et al.* 2011). Although PCBs are approximately 6% of the total weight of WEEE (Chao *et al.* 2011), they have high economic value because of their precious material content. The PCB

production uses precious metals that have limited reserves and require sizeable investments to obtain. These metals are comprised of 0.04 wt.% gold (Au), 0.16 wt.% silver (Ag), 0.01 wt.% palladium (Pd), and 18.4 wt.% copper (Cu). The natural sources of these metals are extremely limited, and recovery of these metals from PCB is crucial to protect natural sources and reduce their environmental impact (Petter *et al.* 2014).

Several studies have investigated the recovery of valuable metals found in PCBs by pyrometallurgical, hydrometallurgical, and biometallurgical processing. Pyrometallurgical processing employs either an incinerator, a plasma arc reactor, or a sintering furnace. The significant disadvantages of this method are the high processing cost and the environmental effect due to high temperatures. It is also not a sufficient process alone to recover the precious metal from WEEE. The main steps in the hydrometallurgical process consist of either cyanide, halogen, thiourea, or thiosulfate leaching of WEEE. The leach solutions are separated and purified by the precipitation of impurities, solvent extraction, adsorption, and an ion-exchange. The disadvantages of these processes are the high chemical demand, the toxic effects of the chemicals, and the long processing times (Cui and Zhang 2008). In biometallurgical studies, cellulosic materials (waste paper, wood, *etc.*) and polyphenolic tannin (persimmon tannin) were used as biosorbents (Adhikari *et al.* 2008; Gurung *et al.* 2013). In recent years, studies have been conducted on the use of different biological materials, including algae, bacteria, fungi, and agricultural waste, to remove metals from an aqueous solution through adsorption. Among these materials, and one material from the agricultural waste of the orange juice industry, is the orange peel (OP). The orange peel is attractive, inexpensive, and readily available (Feng *et al.* 2009). It contains pectin, hemicellulose, cellulose, lignin, and other low molecular weight compounds, especially limonene. These compounds contain carboxylic and phenolic acid groups that can form to metal ions complexes (Feng *et al.* 2010). Waste orange peels have a large surface area, high swelling capacity, high adsorption capacity, low cost, and are easily available (Feng *et al.* 2010). The amount of fruit waste generated increases with the fruit juice beverage production rate. This large amount of fruit waste has led to problems with its disposal. In Turkey, about 1,689,921 tons of oranges are produced every year, which means that when squeezed, about 760,000 tons of waste orange peels are generated in the facilities. These waste peels are either discharged to landfill areas or are sent to the farms to be used as animal feed. Therefore, deriving profitable byproducts from these fruit wastes has become a recent matter of concern in the scientific community (Çokaygil *et al.* 2014).

This study aimed to investigate the adsorption of the copper (Cu) from PCB by native/modified waste orange peels. Many studies have shown that the adsorption capacity of these adsorbents may be increased by their treatment with chemical reagents. The diffusion of the metal from the bulk solution to active sites of biosorbents predominantly occurs by passive transport mechanisms and various functional groups such as carboxyl, hydroxyl, amino and phosphate existing on the cell wall of biosorbents which can bind the heavy metals (Ali and Hassaan 2017). For that reason, waste orange peels have been modified by saponification in order to convert methyl ester groups into carboxyl groups. Acidification has been used to remove acid soluble compounds and/or the protonation of the active sites by citric acid treatment, as reported earlier by Dhakal *et al.* (2005) and Izquierdo *et al.* (2013). Differently from the literature, hydroxypropylation and crosslinking method were used in this study. Hydroxypropylation was used to increase swelling power and water absorption capacity of the orange peel, hence metals, and crosslinking was used to reinforces the granule of waste orange peels and activates the phosphate groups. To separate the organic material from the metal components (Hall and

Williams 2007), the PCB was pyrolysed and the pyrolysis solid product was leached with acids. Adsorption studies were performed with the leach solution.

## EXPERIMENTAL

This study includes three stages. In the first stage, the waste orange peels were treated and modified by four different methods to obtain biosorbents. In the second stage, adsorption tests were performed with biosorbent derivatives at different temperatures using a model Cu solution to determine the optimum conditions of adsorption. In the last stage, adsorption studies on the leach solution that were prepared with PCB pyrolysis solid product and acids (nitric and hydrochloric acid) in the optimum conditions were realized. Experimental studies are presented in detail below.

### Materials

Regular and commercially available oranges were used in the study. Propylene oxide, sodium hydroxide, sodium sulfate, citric acid, nitric acid, and hydrochloric acid were provided from Sigma Aldrich (St. Louis, MO, USA). Sodium trimetaphosphate (STMP) and sodium tripolyphosphate (STPP) were purchased from Merck (Darmstadt, Germany). Fluka analytical Cu standard was used for model solution preparation (Ronkonkoma, NY, USA).

### Biosorbent preparation

First, the waste orange peels were washed with ultrapure water and dried at 55 °C in an incubator (Fig. 1a). The dried material was ground in a Retsch grinder (Model GM 200, Retsch GmbH, Haan, Germany) and sieved to the particle size of 0.2 mm to 0.5 mm.



Fig. 1a. Oven-dried orange peels



Fig. 1b. Biosorbent OP

Approximately 20 g of OP was stored in a desiccator, while another approximately 80 g of OP was used for modifications. The OP was chemically modified by saponification (OP-S), crosslinking (OP-C), hydroxypropylation (OP-H), and acidification (OP-A) to improve the metal sorption behavior. For saponification, 10 g of OP was stirred at 200 rpm with 100 mL and 0.1 M sodium hydroxide (NaOH) solution at 25 °C for 2 h. For crosslinking, 10 g of OP was mixed with 100 mL ultrapure water that contained 0.2 g sodium trimetaphosphate (STMP) and 0.5 g sodium tripolyphosphate (STPP). The mixture

was stirred at 200 rpm, at 40 °C for 2 h. For hydroxypropylation, 1.5 g of sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) was dissolved in 100 mL of distilled water, 10 g of OP was added to the mixture, and the pH was adjusted to 10.5 with NaOH. After adding 1 mL of propylene oxide, the mixture was stirred at 200 rpm at 40 °C for 24 h. For acidification, 10 g of OP was stirred at 200 rpm with 100 mL of citric acid solution at room temperature for 2 h. After modifications, all of the solutions that contained OP were filtrated and rinsed with distilled water until a colorless filtrate was obtained. The resulting materials were oven-dried at 55 °C, and stored in sealed bags with the labels of OP-S, OP-C, OP-H, and OP-A.

Biosorbents were characterized by four different analyses. The elemental analysis was completed with a Leco elemental analyser (Leco TruSpec CHN and S, Leco, MI, USA). The specific surface area was measured by the Brunauer–Emmitt–Teller (BET) technique (Quantachrome Autosorb-1 C, Boynton Beach, USA). The morphology and element content of the biosorbents were characterised using a scanning electron microscope (SEM, Zeiss Supra-50 VP, Carl Zeiss, Germany). The functional groups were determined by Fourier transmission infrared spectra (FT-IR) analysis (Perkin Elmer Inc., Wellesley, MA). The elemental analysis system was based on the Dumas method of combustion and provided a result within 7 min for all elements. Before the BET adsorption measurements, the samples were outgassed for 17 h at 60 °C in a vacuum. Before the SEM analysis, to prevent electrical charging, the samples were covered with gold for 40 s under the presence of Argon gas. Gold coating of the specimens was performed using a sputter coater (Model: S150B, Edwards High Vacuum Ltd., Bolton, England). The infrared spectra of the sample were taken with 4  $\text{cm}^{-1}$  spectral resolution between 4000  $\text{cm}^{-1}$  to 500  $\text{cm}^{-1}$ .

#### *Adsorption studies with model Cu solution*

The adsorption studies were carried by a Cu model solution with an initial concentration of 75 mg/L. The pH of the model solution was adjusted to 5 (Feng *et al.* 2009). Optimum adsorption conditions were investigated in terms of equilibrium and isotherms experiments.

#### *Batch equilibrium studies*

For equilibrium experiments, three flasks of 500 mL of a model Cu solution were prepared for the temperatures of 25 °C, 40 °C, and 60 °C in an isothermal shaker. After the desired temperatures were reached, 1 g of OP was added to each flask and vigorously stirred for 120 min. During the stirring, 15 mL of samples were taken every 5 min in the first 30 min, and 15 mL samples were taken every 15 min in last 90 min and filtrated. The same experimental procedure was applied for OP-S, OP-C, OP-H, and OP-A. The concentration of Cu in the supernatant solution before and after adsorption was determined with inductively coupled plasma atomic emission spectroscopy (ICP-OES) (Model 720, Varian, Palo Alto, CA, USA).

#### *Isotherm-kinetic-thermodynamic studies*

For each biosorbent, weight levels of 0.05 g, 0.1 g, 0.15 g, 0.20 g, 0.25 g, 0.30 g, 0.35 g, 0.40 g, and 0.50 g in 200 mL of 75 mg/L Cu solution at optimum conditions were individually evaluated. The solutions were stirred for 2 h and were allowed to settle for 30 min at room temperature. After settling, a 30 mL aliquot of the supernatant was filtered through a 0.45- $\mu\text{m}$  mixed cellulose filter and analyzed for Cu concentrations. The amount of Cu adsorption by biosorbents was calculated from the reduction of Cu concentration in

the solution. Adsorption isotherms were determined using the Langmuir, Freundlich, and Temkin models.

The Langmuir isotherm assumes monolayer adsorption of adsorbate over a homogeneous adsorbent surface, and can be expressed as,

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

where  $C_e$  and  $q_e$  represent equilibrium Cu concentration (mg/L) and adsorbed amount (mg/g), respectively,  $q_{\max}$  represents the maximum uptake of Cu (mg/g),  $K_L$  represents the Langmuir constant (L/mg), and  $C_e/q_e$  versus  $C_e$  was plotted. The  $q_{\max}$  and  $K_L$  were calculated from the slope and intercept of the plot.

The Freundlich isotherm supposes a heterogeneous surface with a nonuniform distribution of heat of adsorption over the surface and multilayer adsorption can be expressed. The linear form of the Freundlich equation is given as Eq. 2,

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

where  $K_F$  is Freundlich constant (L/g) and  $1/n$  is the heterogeneity factor. According to this equation,  $\ln(q_e)$  versus  $\ln(C_e)$  was plotted. The  $K_F$  and  $1/n$  were calculated from the slope and intercept of the plot.

The Temkin isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage. The Temkin isotherm equation is expressed as Eq. 3,

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (3)$$

where  $B_1$  and  $K_T$  are the constants related to the heat of adsorption and the maximum binding energy, respectively. A plot of  $q_e$  versus  $\ln(C_e)$  was prepared,  $B_1$  and  $K_T$  can be detected from the plot.

The pseudo first order, diffusion, and pseudo second order models were used for analysis of the exchange kinetics and the models are represented as Eqs. 4 through 6, respectively.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (4)$$

$$q_t = k_d t^{1/2} + C \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

Moreover, standard free energy ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ), and entropy ( $\Delta S^0$ ) were determined to interpret the thermodynamic properties of the copper adsorption. The following equations were used for these calculations.

$$K_C = \frac{C_{Ae}}{C_{Se}} \quad (7)$$

$$\Delta G^0 = -RT \ln K_C \quad (8)$$

$$\ln K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

where  $K_C$  is the equilibrium constant,  $C_{Ae}$  is the amount of Cu uptake on the biosorbent per L of the solution at equilibrium (mg/L),  $C_{Se}$  is the equilibrium concentration of Cu in the solution (mg/L),  $T$  is the solution temperature (K), and  $R$  is the gas constant (8.31 J/mol.K). In Eq. 8, the standard free energy was determined using the temperature, the ideal gas constant, and  $K_C$ . A graph was prepared according to  $K_C$  and  $1/T$  and  $\Delta H^\circ$ , and  $\Delta S^\circ$  were calculated from the slope and intercept of this graph.

#### Adsorption studies with leach solution

In the second part of the adsorption studies, crushed waste printed circuit boards (PBCs) were pyrolysed under an atmospheric pressure of 500 °C with a 35 °C/min heating rate in a fixed bed (380 stainless steel) 240-cm<sup>3</sup> reactor (Fig. 2a). About 5 g of pyrolysis solid product (Fig. 2b) was dissolved with 50 mL aqua regia, and adsorption was performed with a leach solution under the optimum conditions (temperature, biosorbent, and weight of biosorbent). The pyrolysis solid product yield was obtained as 68.44 wt.% (Fig. 3).



Fig. 2a. Pyrolysis system



Fig. 2b. Pyrolysis solid product of PCB

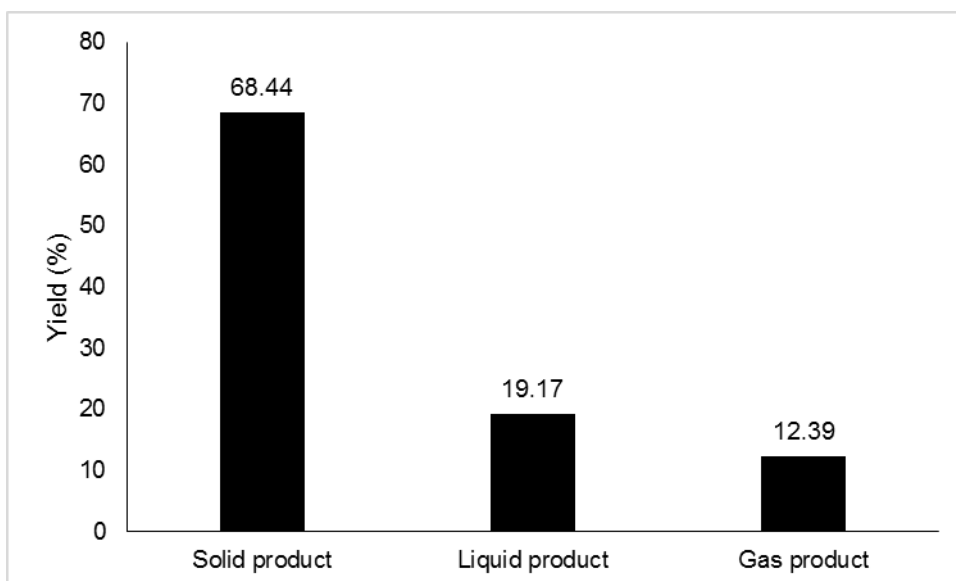


Fig. 3. Pyrolysis product yields

The chemical composition of solid product is given in Table 1.

**Table 1.** Chemical Composition of Pyrolysis Solid Product

Metals	(mg/kg)
Fe	2705.42
Co	4.86
Ni	259.91
Cu	17607.60
Zn	62.58
Al	400.20
Pb	3604.42
Sn	502.21
Cd	0.37
Ag	4.21
Sb	2.45
Au	0.37
Pd	0.64
Ti	5.08

## RESULTS AND DISCUSSION

The elemental and BET analysis results of waste orange peels are given in Table 2. The elemental analysis results of OP had similar results of modified OP. According to the BET results, modified OP-S had the largest surface area, while OP had the smallest surface area. According to the SEM images of biosorbents in Fig. 4, OP-S had a more porous and stratified structure than the others.

**Table 2.** Elemental and BET Analysis Results

Adsorbent Type*	Elemental Analysis				BET (m <sup>2</sup> /g)
	C (%)	H (%)	N (%)	S (%)	
OP	41.52	5.39	1.21	<0.01	0.627
OP-S	38.69	4.96	0.65	<0.01	2.532
OP-C	40.69	5.17	0.79	<0.01	1.049
OP-H	41.12	5.22	0.93	<0.01	2.099
OP-A	43.29	6.20	0.69	<0.01	0.660

Note: \* OP: orange peel, OP-S: modified orange peel with saponification, OP-C: modified orange peel with cross linking, OP-H: modified orange peel with hydroxypropylation, and OP-A: modified orange peel with acidification

EDX spectra of OP, OP-S, OP-C, OP-H, and OP-A are given in Fig 5. In the OP EDX spectrum (Fig. 5a), the Ca and K elements belonged to the orange peel structure. Different from Ca and K in OP, the Na, Na-P, and Na-S elements occurred in the spectrums of OP-S, OP-C, and OP-H, respectively. The Na peak resulted from the NaOH saponification in OP-S. After saponification with NaOH (OP-S), an additional peak of sodium confirmed the ion exchange between K<sup>+</sup> and Na<sup>+</sup> in the solution (Fig. 5b). The Na and S peaks were attributed to crosslinking by STMP and STPP for OP-C (Fig. 5c.). In the OP-H spectrum (Fig. 5d.), the Na and P peaks resulted from hydroxypropylation and Na<sub>2</sub>SO<sub>4</sub>. After a citric acid treatment (OP-A), the only peak of Ca was observed while K was not detected (Fig. 5e.).



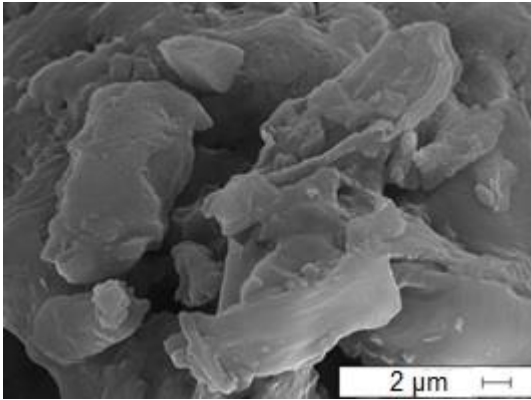


Fig. 4a. SEM image of OP

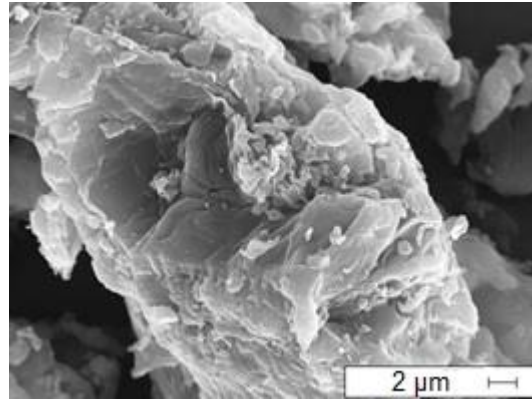


Fig. 4b. SEM image of OP-S

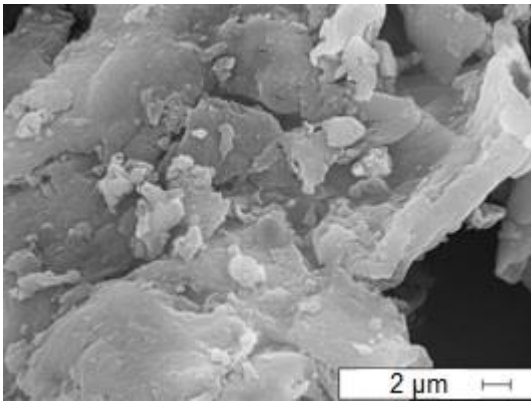


Fig. 4c. SEM image of OP-C

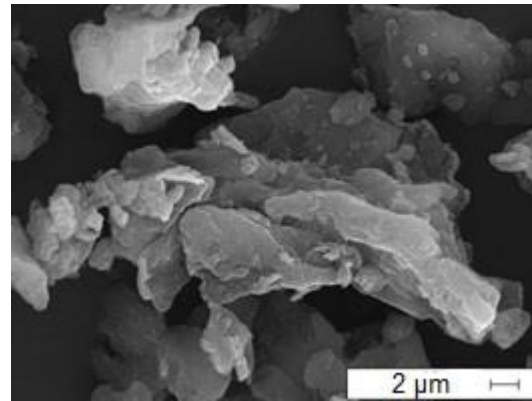


Fig. 4d. SEM image of OP-H

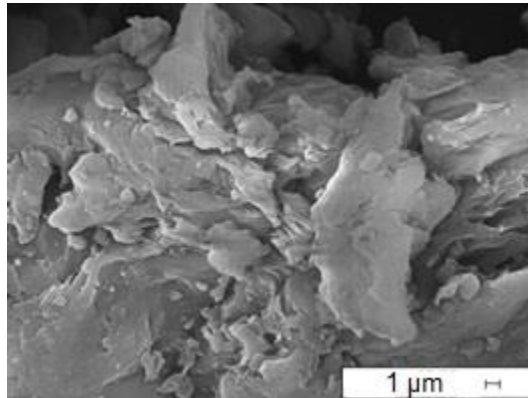


Fig. 4e. SEM image of OP-A

**Fig. 4 (a-e).** SEM images of orange peel and various modified forms of orange peel: OP means unmodified orange peel; OP-S means saponified with NaOH; OP-C means cross-linked using sodium trimetophosphate and sodium tripolyphosphate; OP-H means hydroxypropylated with propylene oxide; and OP-A means acidified with citric acid



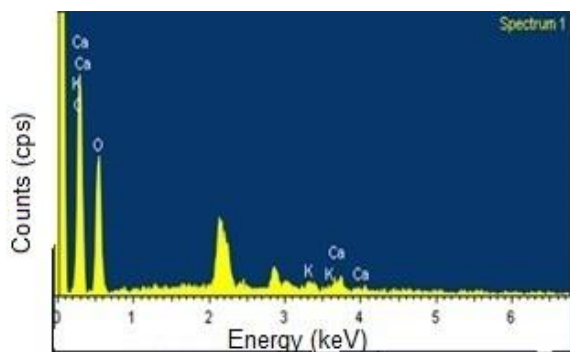


Fig. 5a. EDX spectrum of OP

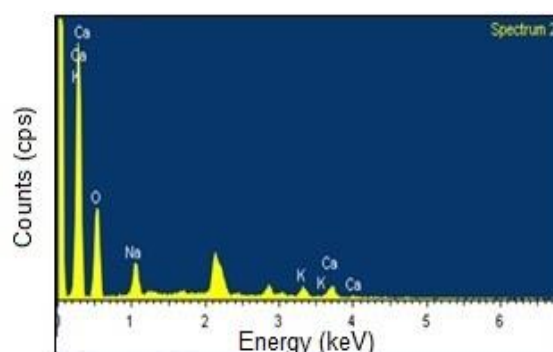


Fig. 5b. EDX spectrum of OP-S

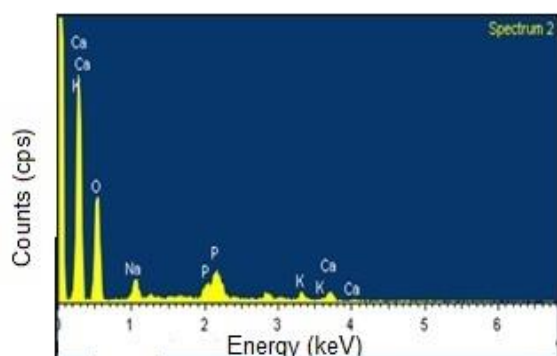


Fig. 5c. EDX spectrum of OP-C

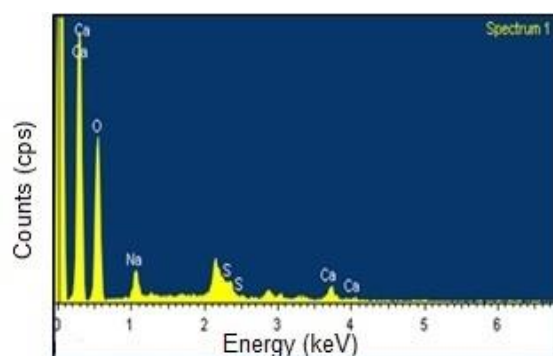


Fig. 5d. EDX spectrum of OP-H

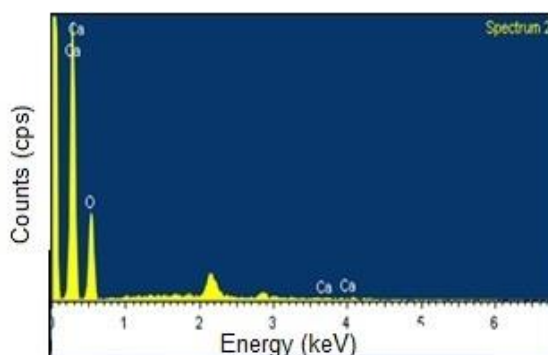


Fig. 5e. EDX spectrum of OP-A

FT-IR spectra of OP, OP-S, OP-C, OP-H, and OP-A were obtained with  $4\text{ cm}^{-1}$  spectral resolution between  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$  (Fig. 6). The broad peaks at  $3100\text{ cm}^{-1}$  to  $3410\text{ cm}^{-1}$  indicated the O-H stretching vibrations of cellulose, pectin, hemicellulose, and lignin. The peak at  $2920\text{ cm}^{-1}$  corresponded to the C-H stretching vibrations of aliphatic structures. The peak at  $1732\text{ cm}^{-1}$  represented the carbonyl (C=O) stretching vibration of the carboxyl groups in the waste orange peels. The peak at  $1641\text{ cm}^{-1}$  was due to an aromatic C=C stretching and/or asymmetric C=O stretching of carboxylate (COO<sup>-</sup>). The peak at  $1000\text{ cm}^{-1}$  to  $1100\text{ cm}^{-1}$  indicates the combination of C-O stretching and O-H deformation of polysaccharide structures (Feng *et al.* 2009, 2010; Izquierdo *et al.* 2013).

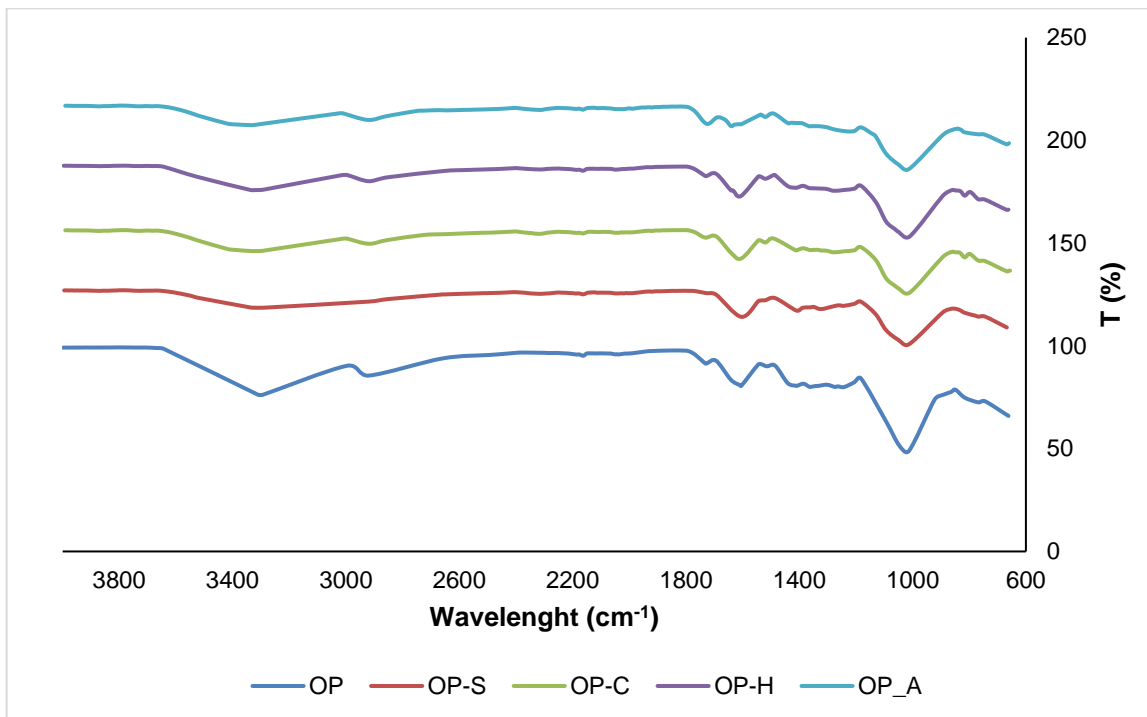


Fig. 6. FT-IR spectra of OP, OP-S, OP-C, OP-H, and OP-A

**Effect of Contact Time on the Adsorption**

The effect of contact time on the adsorption of the three batches for temperatures of 25 °C, 40 °C, and 60 °C are given in Figs. 7 through 9. The plots show that OP-S was the most effective adsorbent with the copper adsorption ranging from 70% to 85% at the equilibrium of approximately 30 min. The temperature of 25 °C was the optimum value that provided the higher copper adsorption onto OP-S. This result was also supported by the highest BET analysis result of OP-S among the biosorbents.

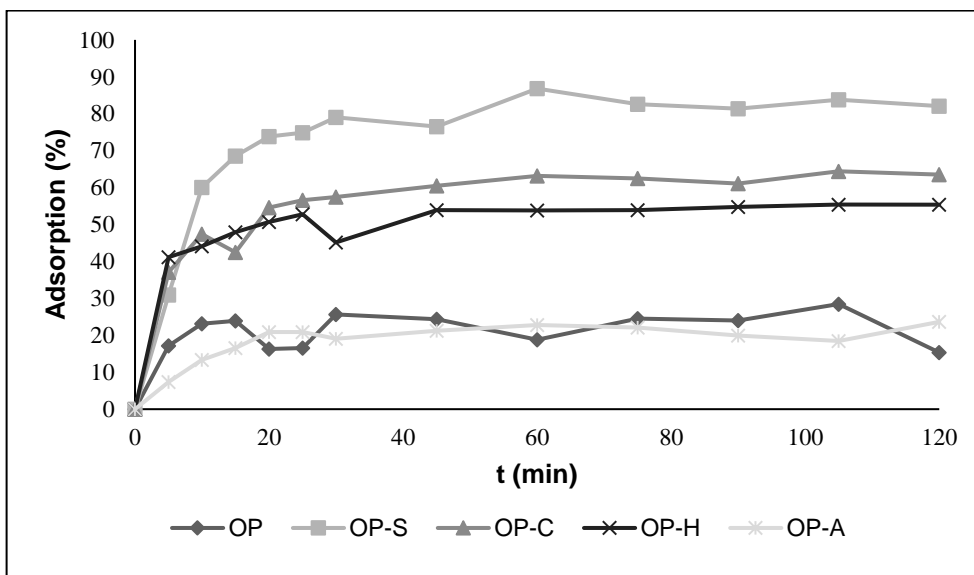


Fig. 7. Adsorption at 25 °C

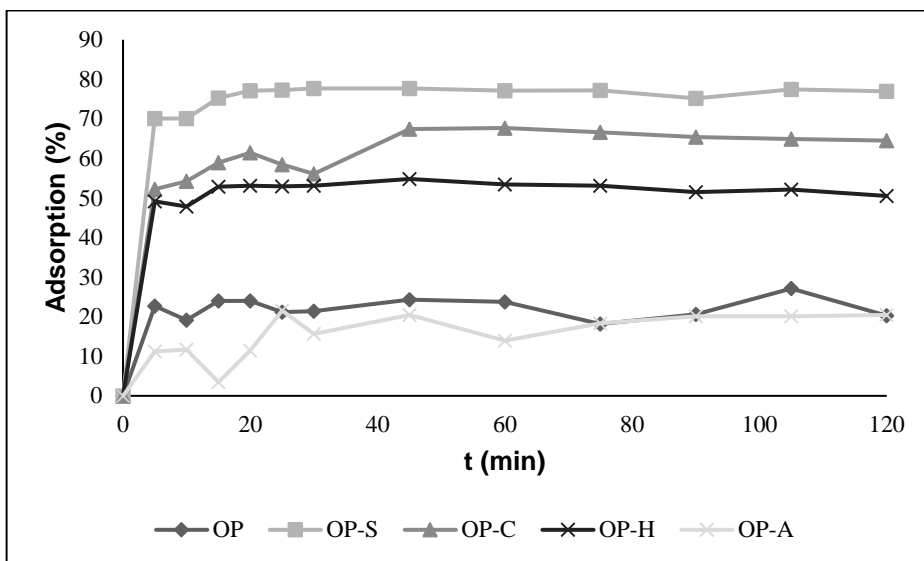


Fig. 8. Adsorption at 40 °C

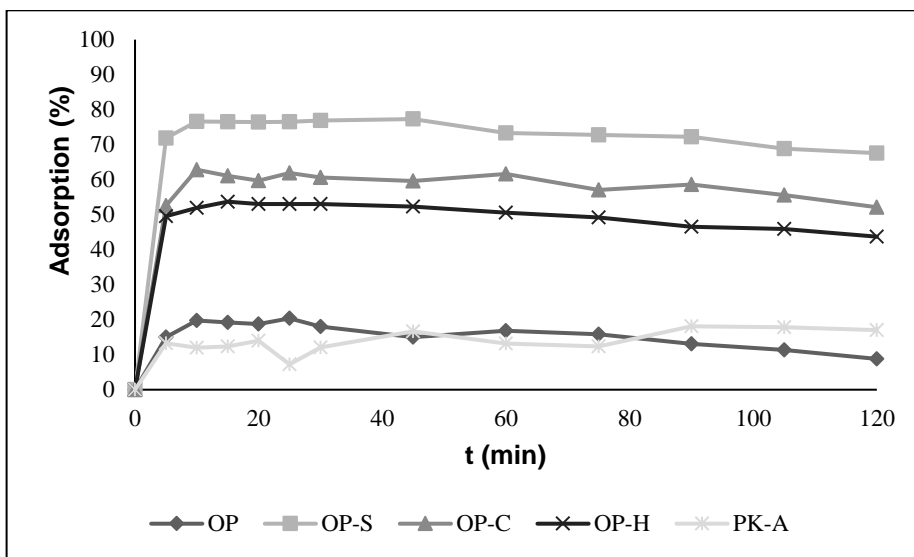


Fig. 9. Adsorption at 60 °C

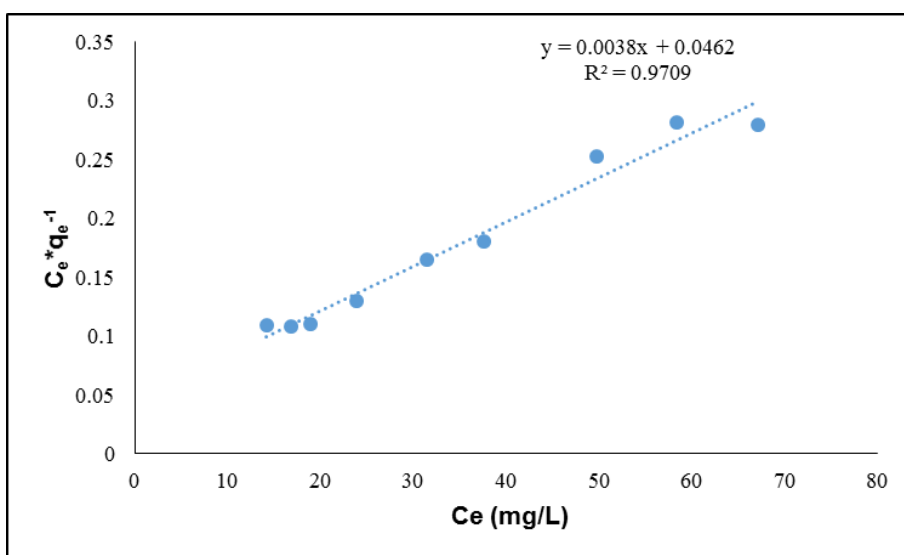
### Isotherm Results

The isotherm experiments were conducted with OP-S at 25 °C, corresponding to the optimum condition. The Langmuir, Freundlich, and Temkin isotherms plots according to final Cu concentrations of different weights of OP-S are given in Figs. 10 through 12, and the adsorption constants are listed in Table 3. A comparison of the correlation coefficients reflects that the Langmuir model yielded a better ( $R^2 = 0.9709$ ) fit than that of the others (Freundlich and Temkin). The adsorption on the surface of OP-S was a monolayer adsorption. According to the equation, the maximum adsorption capacity ( $q_{max}$ ) was 270.27 mg/g, which was higher than those reported in the literature presented in Table 4. Also, the large value of  $K_L$  (0.0754) indicated a strong bond between Cu and OP-S. This was the result of sodium hydroxide modification (saponification), which converted the methylated ester groups that consisted of pectin into carboxyl groups. These functional

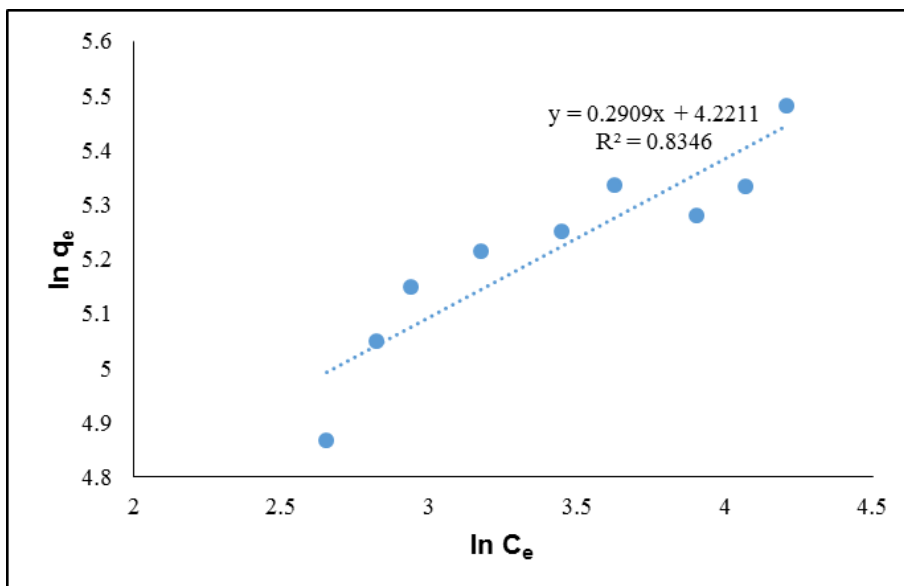
groups contain exchangeable cations that take part in the complexation with each divalent metal ion according to the cation exchange mechanism. Here, the oxygen atom in the pyranose ring of pectic acid plays an important role in the adsorption of cationic metal ions cooperating with carboxylic group to form a stable five-membered chelate ring (Dhakal *et al.* 2005).

**Table 3.** Isotherm Constants for Cu Adsorption onto OP-S

Langmuir	$q_{\max}$ (mg/g)	$K_L$ (L/mg)	$R^2$
	270.27	0.0754	0.9709
Freundlich	$n$	$K_F$ (mg/g)	$R^2$
	3.45	68.11	0.8346
Temkin	$B_1$	$K_T$	$R^2$
	52.588	1.1415	0.8559



**Fig. 10.** Langmuir isotherm for the Cu adsorption



**Fig. 11.** Freundlich isotherm for the Cu adsorption

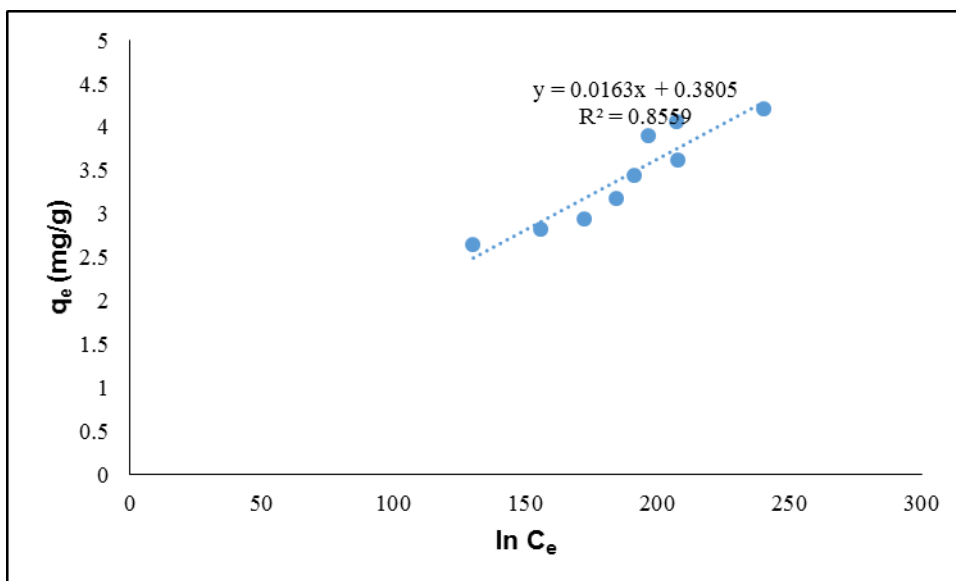


Fig. 12. Temkin isotherm for the Cu adsorption

Table 4. Comparison of Adsorption Capacity of Various Biosorbents for Cu Removal

Biosorbent	Adsorption Capacity (mg/g)	Adsorption Constant (L/mg)	Reference
Shells of Rice	2.95	0.018	Aydın <i>et al.</i> (2008)
Chitosan	8.76	-	Wan <i>et al.</i> (2010)
Modified Orange Peel	50.25	0.045	Feng <i>et al.</i> (2010)
Banana Peel	8.24	-	Liu <i>et al.</i> (2012)
Sugarcane Bagasse	9.48	-	Liu <i>et al.</i> (2012)
Watermelon Rind	5.73	-	Liu <i>et al.</i> (2012)
Untreated Orange Peel	22.10	0.028	Izquierdo <i>et al.</i> (2013)
Activated Grape Bagasse	43.47	0.28	Demiral and Güngör (2016)
Chitosan-EDTA Powder	110	0.302	Labidi <i>et al.</i> (2016)
Pomegranate Peel	30.12	0.058	Ben-Ali <i>et al.</i> (2017)
Thiosemicarbazide Chitosan	140.8	0.0105	Lin <i>et al.</i> (2017)
Saponified Orange Peel	270.27	0.0754	This study

### Kinetic Results

Kinetic model results for OP-S at 25 °C are given in Figs. 13 through 15. The higher coefficient correlation of values confirmed that the Cu uptake followed the pseudo second-order model ( $R^2 > 0.995$ ). The value of  $k_2$  obtained from the plot was 0.0078 g/(mg.min), and  $q_e$  was calculated as 28.49 mg/g.

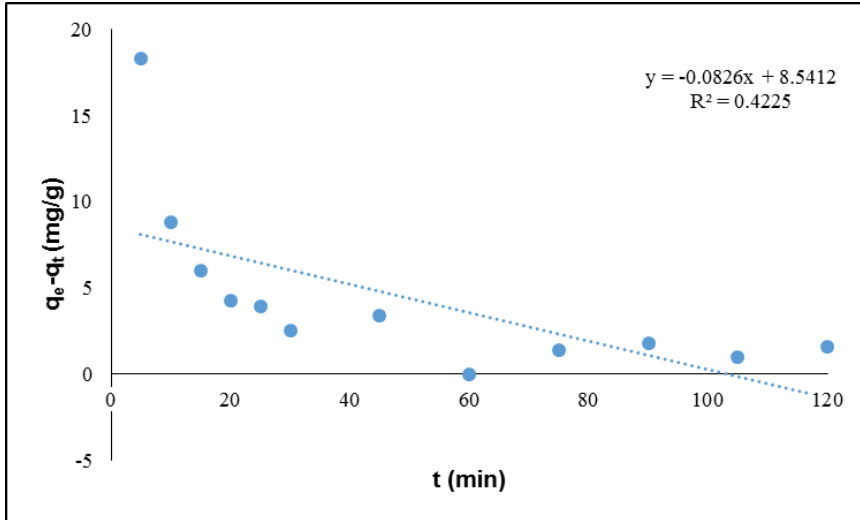


Fig. 13. Pseudo first-order model plot

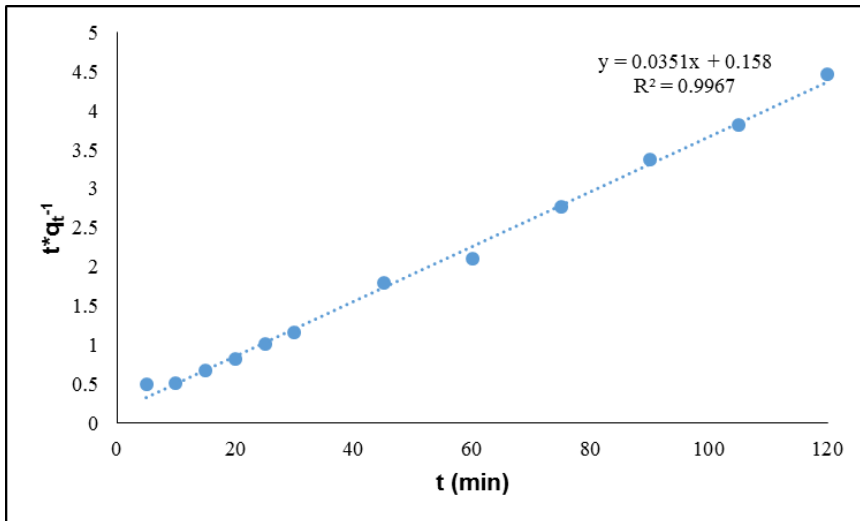


Fig. 14. Pseudo second-order model plot

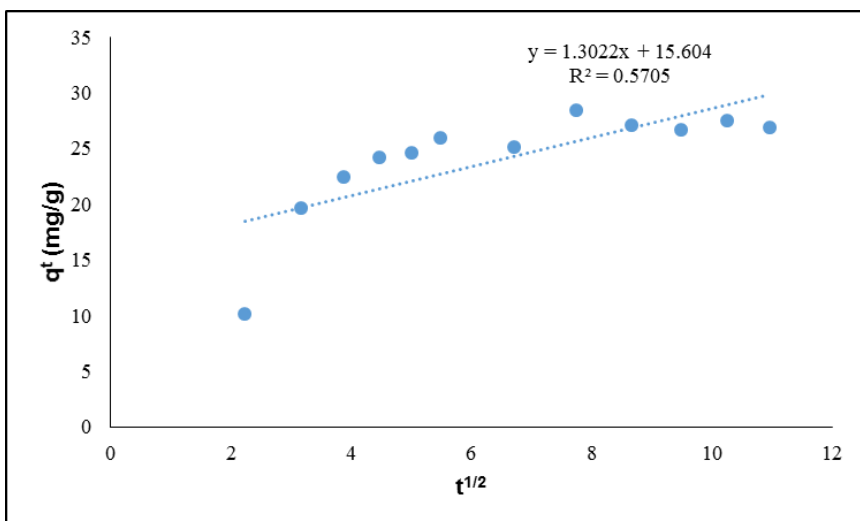


Fig. 15. Diffusion model plot

## Thermodynamic Results

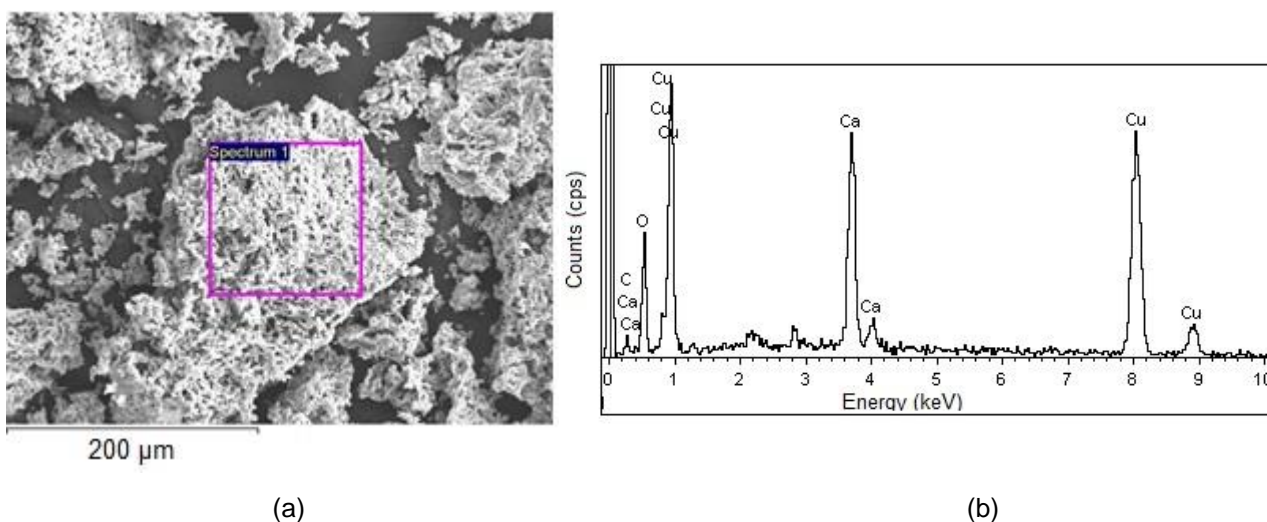
The thermodynamic parameters are summarized in Table 5. Standard free energies ( $\Delta G^0$ ) had negative values in all temperatures. Thus, it can be considered that Cu adsorption was spontaneous. Copper adsorption is an endothermic process because the change in the standard enthalpy ( $\Delta H^0$ ) had a positive value. The negative value of the standard entropy change ( $\Delta S^0$ ) suggested that the randomness decreased at the solid-solution interface during adsorption.

**Table 5.** Thermodynamic Properties for Copper Adsorption with OP-S

Temperature (°C)	$K_c$	$\Delta G^0$ (kJ/mol)	$\Delta H^0$ (kJ/mol)	$\Delta S^0$ (J/mol.K)
25	6.582	-4.666	15.046	-35.841
40	3.485	-3.091		
60	3.407	-3.036		

## Adsorption Results from Solid Product of PCB Pyrolysis

The ICP-OES determined that the Cu content of the PCB waste was 18.1%. The adsorption experiment on a 500 mL sample, that was obtained by diluting (100 times) the leach solution of the pyrolysis solid product, was performed at optimum conditions (30 min, OP-S, 25 °C). The remaining Cu concentration in the leach solution was measured and the copper from the PCB was adsorbed with 85.77% efficiency. The remaining biomass after adsorption studies was burned in 900 °C, and SEM-EDX analysis (Fig. 16) was carried out to the residues after combustion. According to EDX results, the residue have 65 % Cu content from PCB adsorption and 12 % Ca content from waste orange peel. The other metals were very lower concentration (<0.5%) from copper and calcium and so, there were not seen in the EDX graph.



**Fig. 16.** (a) SEM (b) EDX results of the remaining biomass



## CONCLUSIONS

1. Results of this work clearly suggested that orange peel waste could be easily converted to a valuable biosorbent. Saponification is the most effective modification method to obtain high adsorption efficiencies with orange peels. With efficiency and cost taken into consideration, the orange peel modified by saponification with NaOH (OP-S) could be considered as an alternative adsorbent to conventional adsorbents.
2. The Cu adsorption from printed circuit boards (PCBs) was successfully achieved to 85.8% efficiency.
3. The metal-loaded biomass can be burned at high temperatures and remaining inorganics will be contain adsorbed metals. Also, this biomass can be used as feed materials at non-ferrous metals smelters.

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