

Original Research Paper

Enhancing of Copper (II) Adsorption Efficiency by Mixing Plantain and Orange Peelings as Bio-Sorbent Support

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Abstract: The present study focuses on the valorization of plantain and orange peels in the field of water treatment contaminated by heavy metals, especially copper (II). To carry out this study, simplex centroid mixture design was used to determine best mixture from plantain and orange peelings through iodine number, specific surface area and point of zero charge. The influence of contact time, adsorbed amount, bio-sorbent mass, medium temperature and medium pH were equally investigated from best mixture and thermodynamic parameters were also carried out. The results show that R^2 , Absolute Average Deviation (AAD), bias factor and exactitude factor are respectively 89.39%, 0.01, 1.00 and 1.00 for iodine number, 94.13%, 0.03, 0.99 and 0.99 for Specific surface Area (SA) and 97.05%, 0.01, 1.00 and 1.00 for Point of Zero Charge (PZC). These values are in agreement with the interval set to validate the model. Besides, desirability is 1.00, 0.80 and 0.77 respectively for specific surface area, iodine number and zero point of charge and closer to 1. The best mixture from this study is 90% of orange peelings proportion and 10% of plantain peelings proportion. The results also show that contact time is 10 min, adsorbed amount of copper ions (II) increases with initial copper concentration, bio-sorbent mass and medium temperature. Adsorbed amount increases for pH between 3 and 5 and decreases for pH greater than 5. The efficiency of Copper (II) removal is about 88.11% for the native bio-sorbent and 97.04% for activated bio-sorbent. These efficiencies are higher than those obtained from orange and plantain peelings taken individually and are ranged between 70 and 85%. The pseudo second order describes perfectly the adsorption mechanism followed by intra particular diffusion while the isotherm adsorption is well described by Langmuir and Freundlich model. The thermodynamic parameters indicate that adsorption reaction is spontaneous, reversible and endothermic.

Keywords: Plantain and Orange Peelings, Mixture Design, Copper (II) Adsorption

Introduction

Water pollution by toxic heavy metals is the most encountered environmental problem worldwide (Zhang *et al.*, 2017; Duodu *et al.*, 2016). These heavy metals are generated by anthropogenic activities such as mining and smelting, fertilizer production, agriculture and battery manufacturing. Heavy metal contamination is found in aqueous waste stream (Aman *et al.*, 2008; Jiang *et al.*, 2009). The presence of heavy metals in water is responsible for many health

problems and a high risk for environment and ecosystems (Huang *et al.*, 2008). This makes it important to find environmentally friendly and cost effective water purification technologies for the removal of these contaminants (O'Connell *et al.*, 2008).

However, several methods have been developed to eliminate heavy metal in industrial and domestic effluents. They are divided into three groups: Microbiological degradation methods, oxidation methods (electrochemistry, electrocoagulation, catalytic oxidation, ozonation) and physico-chemical methods

(coagulation-flocculation, precipitation, ion exchange, membrane filtration, adsorption) (Lin *et al.*, 2017; Taseidifar *et al.*, 2017; Zewail and Yousef, 2015; Zhu *et al.*, 2017). Among these methods, adsorption is the most promising and suitable method due to its easy implementation, relatively low cost compared to other processes and its great capacity for purification of water contaminated by heavy metals (Liu *et al.*, 2017). The activated carbon is the most commonly used adsorbent in heavy metals removal due to its high specific surface area and its affinity with them. Commercial activated carbon is high cost and bio-sorbent appears to be a promising alternative for less developed country such as Cameroon due to their same characteristics as activated, which is less expensive and widely available in nature (Jakóbk-Kolon *et al.*, 2017; Kumar *et al.*, 2017; Xu *et al.*, 2017). In fact around 1.11 million dry bon tons of biomass are generated in Cameroon per year (Ackom *et al.*, 2013). Moreover, in Cameroon, plantains are produced in great quantity (Inna *et al.*, 2015) and a significant quantity of oranges, approximately 2.595.000 tons is exchanged each year between northern and southern Cameroun (Ndumbe, 2010), which generates enormous quantities of solid waste and can be used as adsorbent materials in the liquid waste processing. They are rich in cellulose and lignin which contains many oxygen functionalities such as phenols and ketones and can serve as adsorption sites for binding heavy metals (Kumar *et al.*, 2017; Xu *et al.*, 2017).

Several studies have been conducted on the use of biomass as bio-sorbents for Copper (II) removal (Sehaqui *et al.*, 2014; Annadurai *et al.*, 2003; Luis *et al.*, 2016). The interest of removing copper in water is that it occurs naturally in rock-forming and ore minerals and is brought to environment through industrial and other domestic processes (Sehaqui *et al.*, 2014). The efficiencies of copper (II) adsorption using biosorbent are often ranged between 70 and 85% (Farnad *et al.*, 2012; Yargıç *et al.*, 2015). However, some experts have shown that the mixture of bio-sorbent as adsorbent improves adsorption properties (Rosales *et al.*, 2015). Their study was done to eliminate Cu (II), Ni(II), Mn(II), Zn(II) and Cr(VI). In their study, simplex-centroid mixture design was used to find the best combination

from fern, oak leaves and rice husk. However, the study reveals that the efficiency of heavy metal removal varies from one heavy metal to another. Thus the best mixture to remove Cu(II) and Ni(II) is different to the best mixture to eliminate Mn(II).

The efficiency of mixing fern, oak leave and rice husk is justified by the fact that, taken individually these bio-sorbents show C-N, C=O, C-H, COOH and N-H as functional group. Their mixture reveals new functional group, in particular C=C/C≡N/N-H/C=O amide/-NO₂ (Ma *et al.*, 2014; Abdolali *et al.*, 2014) which improves adsorbent properties. Concerning oranges and plantains peelings as bio-sorbents, studies showed that the chemical functions present are similar to those present in fern, oak leaves and rice husk (Samomssa *et al.*, 2019; Kamsonlian *et al.*, 2011; Lazim *et al.*, 2015). Orange and plantain peelings as bio-sorbents, to carry out kinetics model, adsorption isotherm and thermodynamic parameters and to investigate influence of stirring time, copper (II) ion concentration, bio-sorbent mass, medium temperature, medium pH.

Materials and Methods

Sampling

Bio-sorbents used in this study are plantain and orange peelings. Plantain and orange were collected from the farm and brought to the laboratory where they were peeled. Peelings were washed several times with tap water follow by distilled water and dried at 50°C until constant mass. Dried samples were ground and sieved with sieve of 500 µm.

Experimental and Calculation Method

Formulation

Formulation was done by mixing plantain and orange peelings in different proportions. This was done according to simplex centroid mixture design based on two variables (plantain and orange peelings proportion). Table 1 shows experimental matrix. Responses are specific surface area, iodine Number and point of zero charge.

Table 1: Experimental design

Experiments N°	Coded matrix		Tests matrix		Responses		
	X ₁	X ₂	M ₁ (g)	M ₂ (g)	Specific area	Iodine number	Point of zero charge
1	1.00	0.00	1.00	00.00	Y1	Y1	Y1
2	0.75	0.25	0.75	0.25	Y2	Y2	Y2
3	0.50	0.50	0.50	0.50	Y3	Y3	Y3
4	0.25	0.75	0.25	0.75	Y4	Y4	Y4
5	0.00	1.00	0.00	1.00	Y5	Y5	Y5

X₁: Plantain peels proportion, X₂: Orange peels proportion, M₁: Plantain peels mass, M₂: Orange peels mass

Determination of Responses (Specific Surface Area, Iodine Number and Point of Zero Charge).

Specific Surface Area

Specific surface area was determined using methylene blue method described by (Yukselen and Kaya, 2008). The goal of this method was to determine the necessary amount of methylene blue to form a monolayer on the surface of the bio-sorbent. 1 g of the grind sample was mixed in a 100 mL beaker with 20 mL of distilled water and stirred for 5 min on a magnetic stirrer. Then, 5 mL of methylene blue (10 g/L) was added and the mixture was stirred for one minute. The drop of solution was deposited on a wattman filter paper. The test is positive if on the filter paper there is a blue drop surrounded by a blue-tinted wet zone and negative if there is a blue drop surrounded by a colorless wet zone. If the test is positive, 1 mL of methylene blue is taken 5 times to confirm the result. If the test is negative, 5 mL of methylene blue are added until the positive test is reached. The volume of corresponding methylene blue is noted and the value is determined according to the Equation (1):

$$VBS = \frac{v}{m}100 \quad (1)$$

Where:

v : Is the volume of methylene blue corresponding to the positive test

m : The mass of bio-sorbent removed

The Specific surface Area (SA) (m^2/g) is calculated according to the formula (2):

$$SA = VBS \times 20.93 \quad (2)$$

Iodine Number

Iodine number (II) was determined according to the method described by (Aricetti *et al.*, 2011). This method consists of mixing in a conical flask 0.05 g of the adsorbent and 15 mL of iodine at 0.1 N. The mixture was stirred for 4 min and then filtered. 10 mL of the filtrate was titrated against a 0.1 N thiosulfate solution in the presence of 2 drops of starch until a clear solution. The iodine number (II) was calculated by the Equation (3):

$$II = \frac{(Vb - Vs) * N * 126.9 * \frac{15}{10}}{M} \quad (3)$$

Where:

$(Vb - Vs)$: The difference between the results of the titration in the blank test and the adsorbent test in (mL of 0.1 N sodium thiosulfate)

N : The normality of the solution of sodium thiosulphate in (mol/L)

126.9: The atomic mass of iodine

M : The mass of the adsorbent in (g)

Point of Zero Charge

The pH drift method described by (Noh and Schwarz, 1989) was used to determine the point of zero charge. This method consists to set 50 mL of 0.01 M NaCl solution in closed vials and adjusting the pH of each by adding NaOH or HCl solution (0.1 M). 50 mg bio-sorbent was added. Suspensions were kept in agitation at room temperature for 24 h and the final pH was determined. Zero point of charge is the point at which the final pH curve as a function of the initial pH intercepts the final pH line = initial pH.

Validation of Model

To validate the model, adjusted R^2 , Absolute Average Deviation (AAD), Exactitude Factor (A_{f1}) and bias factor have to fulfill the following conditions:

- Adjusted R^2 have to be more than 95%
- Absolute Average Deviation (AAD) has to be nearer to zero
- Exactitude Factor (A_{f1}) and bias factor (BF) have to be between 0.75 and 1.25

These parameters were obtained using Equations 4-7:

$$R^2_{aj} = \frac{\sum_{i=1}^n (y_{call} - \overline{y_{exp}})}{\sum_{i=1}^n (y_{exp} - \overline{y_{exp}})} \quad (4)$$

$$ADD = \left[\sum_{i=1}^n \frac{|y_{exp} - y_{cal}|}{y_{exp}} \right] / n \quad (5)$$

$$Af1 = 10^{\frac{1}{n} \sum_{i=1}^n \left| \log \frac{y_{cal}}{y_{exp}} \right|} \quad (6)$$

$$BF = 10^{\frac{1}{n} \sum_{i=1}^n \log \frac{y_{cal}}{y_{exp}}} \quad (7)$$

Where:

Y_{exp} : Experimental value

Y_{cal} : Calculated value

n : Number of experiments

Activation of Bio-Sorbent

Activation was done according to (Gautam *et al.*, 2014) method. 25 g of optimized mixture was mixed

with 250 mL of sulfuric acid 1N. The whole mixture was thermochemical treated at 150°C during 24 h. Then was washed with distilled water to remove excess sulphuric acid. The residue was immersed in sodium bicarbonate solution NaHCO₃ (1%) for one night in order to eliminate remaining sulphuric acid. Finally, the residue was dried at 50°C until a constant mass.

Adsorption

Adsorption was carried out in an agitated reactor and stirring is kept constant throughout the experiments. 20 mL of mixture (solution of copper (II) and bio-sorbents) are introduced into beaker and stirring is started. After this contact time, the solution is filtered on wattman paper. The filtrate is then recovered for analysis by UV-visible spectroscopy to determine the absorbance. The absorbance of each solution was measured at 380 nm of Cu (II), against blank solutions which have the same composition but without Cu (II). This value of wavelength corresponding to the maximum of absorption was established experimental, from absorption spectra.

Adsorbed amounts of copper were determined by formula (8):

$$q = \frac{V(C_0 - C)}{m} (\mu\text{mol} / \text{g}) \quad (8)$$

Where:

- q: Adsorbed amount per gram of adsorbent μmol/g
- C₀: Initial concentration (μmol/L)
- C: Equilibrium concentration (μmol/L)
- m: Mass of bio-sorbent used; V volume of solution L

The percentage of copper removed (E) is determined by the formula (9):

$$\%E = \frac{C_0 - C_e}{C_0} * 100 \quad (9)$$

Evaluation of Impact of Some Parameters on Copper (II) Elimination

The influence of contact time, copper (II) concentration, bio-sorbent mass, temperature of the medium, pH of the medium was investigated on adsorption of copper (II). The Table 2 presents the different variations.

Kinetic, Isotherm and Thermodynamic Studies

Kinetic Studies

Pseudo-first-order, pseudo-second-order and intra particular diffusion models were applied and the mathematical relations are given by equation 10 11 and 12 respectively.

Pseudo-First-Order:

$$\ln(qe - qt) = \ln qe - K_1 t \quad (10)$$

Pseudo-Second Order:

$$\frac{t}{qt} = \frac{1}{qe^2 k_2} + \frac{1}{qe} t \quad (11)$$

Intra Particular Diffusion Model:

$$qt = kdt^{0.5} + C \quad (12)$$

where: k₁ (min⁻¹), k₂ (g mg⁻¹ min⁻¹) and K (g mg⁻¹ min⁻¹) are the rate constants of the pseudo-first-order and pseudo-second-order and intra particular diffusion and qe the copper (II) adsorption amount (mg g⁻¹).

Adsorption Isotherms

To determine the nature of adsorption, data were fitted into Langmuir and Freundlich isotherms. Langmuir isotherm defines a monolayer adsorption according to the mathematical relation given by Equation 13:

$$\frac{ce}{qe} = \frac{1}{qm} ce + \frac{1}{dqm} \quad (13)$$

Table 2: Condition of evaluation of some parameters on adsorption

Stiring time (minutes)	Copper (II) concentration (μmol/L)	Biosorbant mass (g)	Temperature of the medium (K)	pH of the medium
5.0	82.7	0.1	288.0	3.0
10.0	165.5	0.2	298.0	4.0
20.0	248.3	0.3	318.0	5.0
30.0	331.1	0.4	/	6.0
40.0	413.9	0.5	/	7.0
50.0	/	/	/	/
60.0	/	/	/	/

Freundlich isotherm defines a heterogeneous adsorption that involves multiple surfaces of suitable energy. It assumes the uptake of the copper changes with the distribution of adsorption sites and surface energies. It is represented by the mathematical relation presented by Equation 14:

$$\ln q_e = 1/n \ln C_e + \ln k_f \quad (14)$$

Thermodynamic Parameters

Thermodynamic parameters include standard enthalpy (ΔH°), standard entropy (ΔS°) and free standard energy (ΔG°). Enthalpy variations (ΔH°) and entropy (ΔS°) were obtained from slope and interception of Van't Hoff equation of (ΔG°) as function of temperature T by Equation (14):

$$\Delta G = \Delta H - T\Delta S \quad (15)$$

$\ln K_c = f(1/T)$ allow to obtain ΔH (slope) and ΔS (ordinate at origin).

Gibbs free energy variation of adsorption (ΔG°) is given by Equations (15) and (16):

$$\Delta G^\circ = -RT \ln k_c \quad (16)$$

$$\ln k_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (17)$$

K_c is equilibrium adsorption constant and is determined by the relation presented by Equation (17):

$$k_c = \frac{C_a}{C_e} \quad (18)$$

Where:

C_a : Concentration of Cu^{2+} at bio-sorbent surface

C_e : Concentration of Cu^{2+} in solution

ΔG° : Gibbs standard free energy variable (J)

R : Universal constant of perfect gases (8.314 J/mol K)

T : Absolute temperature (K)

Results and Discussion

Analyzing of Mixture Design

The specific surface area, iodine number and point of zero charge of various mixtures of bio-sorbents in the native state are presented in Table 3. It appears from this table that orange and plantain peelings taken individually have the same specific area while orange peeling has a higher iodine number value. The iodine number is 723.33 and 826.12 mg/g for plantain and orange peelings respectively. According to (Cleiton *et al.*, 2011), iodine number in this range offers good adsorption properties and are mainly constituted with micropores and macropores. Thus the investigated bio-sorbents have good adsorption properties. It is better for orange peelings than plantain peelings. This result is in agreement with (Annadurai *et al.*, 2003) who have shown through SEM image that the native orange peels have a highly porous structure while the native plantain peels is non porous. This table also shows that specific surface area and iodine number are higher for mixing ratio 25% Plantain Peelings (PP) +75% Orange Peelings (OP) and lower for mixing ratio 75% PP +25% OP. This table also reveals that the specific surface area and the iodine number increase with addition of orange peelings. Mixture 25% PP +75% OP offers the best adsorption properties.

Table 3 also reveals that Average Absolute Error (AAE) is in the range 0.05 to 0.11, 0.00 to 0.01 and 0.02 to 0.06 respectively for specific surface area, point of zero charge and iodine number. These AAE are closer to zero and can be considered negligible compared to observed responses. This demonstrates the reliability of models. coefficients R^2 are 94.13, 89.39 and 97.05 for specific surface area, iodine number and point of zero charge respectively. These values show that correlation between the two variables is well.

Table 3: Experimental matrix

Experimental design		Responses			AAE		
Experiments	Test Matrix	Specific area (m ² /g)	Point of zero charge	Iodine Number (mg/g)	Specific area (m ² /g)	Zero point of charge	Iodine number (mg/g)
1	100% PO	61.05	5.10	826.12	0.05	0.02	0.03
2	100% PP	20.93	7.40	723.33	0.08	0.01	0.03
3	75% PP +25% PO	31.40	7.20	856.58	0.06	0.03	0.04
	50% PP +50% PO	41.86	6.40	951.75	0.09	0.00	0.02
5	25% PP +75% PO	62.79	5.50	1016.47	0.11	0.04	0.06

AAE: Average absolute error

Table 4: Condition to validate models

Responses	R ²	R ² Adjusted (%)	AAD	Biais factor	Exactitude factor
Specific area	94.13	88.27	0.03	0.99	0.99
Iodine index	89.39	78.78	0.01	1.00	1.00
point of zero charge	97.05	94.10	0.01	1.00	1.00

AAD: Absolute Average Deviation

Validation of Model

Table 4 illustrates that the Absolute Average Deviation (AAD) is closer to zero for the three responses. This is in agreement with the interval set to validate average deviation absolute analysis. Besides it, the bias factor and exactitude factor values are equal to 1. The validation condition is that their values should be between 0.75 and 1.25. In addition, the adjusted R^2 of both is closer to 100%. On these bases, models from specific surface area, iodine index and point of zero charge are validated.

Modeling

The equations 19, 20 and 21 present models from specific surface area (SA), iodine number (II) and Point of Zero Charge (PZC) respectively. These models are linear and quadratic with interaction between variables. For Specific surface Area (SA), model reveals that plantain and orange peelings influence positively. This influence is higher with orange peeling which shows the highest coefficient. Interaction between plantain and orange peelings influence SA also positively but lower compare to Plantain Peeling (PP) and Orange Peeling (OP) taken individually. For the iodine number (II), orange peels, plantain peels and interaction between them have positive effect. This effect is higher for OP follow by interaction between OP and PP. For Point of Zero Charge (PZC), OP, PP and OP*PP have positive influence. PP and OP show the highest influence, while interaction between the both presents the lowest influence:

$$SA = 63.94 * OP + 19.29 * PP + 15.94 * OP * PP \quad (19)$$

$$II = 851.10 * OP + 704.90 * PP + 774 * OP * PP \quad (20)$$

$$PZC = 4.99 * OP + 7.51 * PP + 0.57 * OP * PP \quad (21)$$

Determination of Optimum Area

The optimum area was generated by Minitab. In fact, technical specification of each response was introduced in the software and the optimum was given through Fig. 1. According to this figure, the optimum is obtained by taking 90% proportion of Orange Peel (OP) and 10% proportion of plantain peel. The desirability is the most important parameter which controls mixture design with two parameters. Thus, desirability has to be closer to 0 when response is minimized and closer to 1 when response is maximized. In this study, specific Surface Area (SA), Point of Zero Charge (PZC) and iodine number (II) have to be in their maximum value thus closer to 1. It is clearly seen from Fig. 1 that desirability is 1.000, 0.796 and 0.765 respectively for specific

surface area, iodine number and point of zero charge. According to this it can be concluded that the optimum obtained is reliable.

Analyzing of Kinetic Model, Isotherm Adsorption and Thermodynamic Parameters

Kinetic Model

Kinetic models are presented in Table 5. It appears from this table that the correlation factor from first pseudo order model is the lowest compared to that of pseudo second order and intra particular diffusion. According to (Abadian *et al.*, 2015) the highest correlation factor is favorable to describe adsorption mechanism. Thus, the pseudo second order model describes perfectly the adsorption mechanism followed by intra particular diffusion. Two steps describe these mechanisms (Tsamo *et al.*, 2019). The first is the diffusion of copper (II) solution toward the bio-sorbent surface and the second the fixation of copper (II) in bio-sorbent surface.

Isotherm Adsorption

Table 6 shows correlation coefficient of Langmuir and Freundlich model. The correlation coefficient R^2 of Langmuir and Freundlich model is 0.99 for the activated and non activated bio-sorbent. This reveals that the experimental and theoretical results are close. The adimensional separation RL of Langmuir model is lower than 1, thus according to (Tsamo *et al.*, 2019) adsorption is favorable. The affinity indicator n is higher than 1. Whereas, according to Freundlich model, the adsorption is also favorable.

Thermodynamic Parameters

Table 7 presents thermodynamic parameters. This table reveals that ΔG values are negative for both bio-sorbents and decrease with the increasing of temperature. The negative values of ΔG illustrate that the adsorption is spontaneous. These values are ranged between -20 and 0 kJ/mol, thus the adsorption of Copper (II) is physical (Aderibigbe *et al.*, 2017). An increased of the adsorbed amount with temperature reveals that the medium needs energy to overcome kinetic activation energy. The lower ΔG° shows that bonds are low energy. Thus according to (Kolwa *et al.*, 2019), the adsorption of copper (II) by the mixture 90% orange peels and 10% plantain peels is guided by intermolecular forces. Table 5 also reveals that the ΔH values are positives, thus reaction between Coper (II) and bio-sorbent is endothermic. The increased in temperature enables to increase Copper (II) diffusion towards bio-sorbent surface. This table shows that the ΔS are positive for both bio-sorbents, thus spontaneous transformation increase disorder, affinity between bio-sorbent and Copper (II) (Yargiç *et al.*, 2015).

Analyzing of Behavior of Some Parameters

Influence of Contact Time

Figure 2 shows the adsorption kinetics of copper (II) from mixtures 10% PP +90% OP inactivated and activated. It appears from this figure that the inactivated and the activated bio-sorbent have similar adsorption kinetics plot. The amounts of copper (II) adsorbed per gram of bio-sorbent increase tremendously from the first minutes of adsorption and then stabilize after a certain time. The time required to reach adsorption equilibrium is 10 min. The relatively short equilibrium time obtained for all kinetics is due to greater diffusion of Copper (II) molecules towards bio-sorbent mixtures surface. This equilibrium time is lower compared to the literature (Abadian *et al.*, 2015; Singh *et al.*, 2006). These results can be justified by the efficiency of mixture of bio-sorbent.

Furthermore, it is observed that amounts of copper (II) adsorbed are greater with activated bio-sorbent. This is explained by the fact that the acid treatment applied to material increases adsorption efficiency. Indeed, action of acid treatment causes destruction of organic material (cellulose fiber and lignin granule). This destruction of organic material gives activated bio-sorbent a larger

surface area and increases its porous structure. The results of bio-sorbent characterization showed that acid treatment conferred on the activated bio-sorbent a greater specific surface area and porosity. The same phenomena has been demonstrated in the literature (Vijayaraghavan *et al.*, 2006; Chen *et al.*, 2010).

Influence of Initial Copper (II) Concentration

The influence of copper (II) concentration is presented in Fig. 3. This figure shows that the inactivated and the activated bio-sorbent have similar curves. The adsorption capacity increases with initial copper (II) ion concentration. Indeed, an increase in the adsorption capacity with an increase in the concentration of copper (II) may be due to an increase in the adsorption specific surface area. At high concentrations, the forces are more important and the amount of Cu^{2+} adsorbed per unit mass of bio-sorbent is higher. Figure 3 also reveals that adsorbed amounts of copper (II) for activated bio-sorbent are greater than amounts adsorbed by non-activated bio-sorbent. Indeed, acid treatment applied to activated bio-sorbent increases its specific surface area and its porosity, which reflects a higher removal rate of copper (II) for activated bio-sorbent relative to non-activated (Tsamo *et al.*, 2019).

Table 5: Kinetic models

Kinetic models	Constantes	Non activated bio-sorbent	Activated Bio-sorbent
First order	R^2	0.12	0.14
	k_1	0.0016	0.0234
	q_e	5.69	9.69
Second order	R^2	0.99	0.99
	k_2	16.91	0.38
	q_e	14.04	15.38
Intra particular diffusion	R^2	0.93	0.93
	K_{intt}	4.76	5.15

Table 6: Langmuir and freundlich coefficients

Modele	Constantes	Non activeted Bio sorbent	Activeted Bio sorbent
Langmuir	R^2	0,99	0,99
	q_m	11,75	13.81
	RL	0,02	0,007
Freundlich	R^2	0,99	0,99
	n	5,37	10,75

Table 7: Thermodynamic parameters of the copper (II) adsorption

Samples	T (K)	Ln Kc	ΔG (KJ.mol ⁻¹)	ΔH (KJ.mol ⁻¹)	ΔS (KJ.mol ⁻¹ .k ⁻¹)	R^2
Unactivated mixture	288	0.25	-0.6			
	298	0.7	-1.73	36.13	0.13	0.99
	318	1.67	-4.42			
Activated mixture	288	0.49	-1.17			
	298	1.04	-2.58	36.05	0.13	0.99
	318	1.92	-5.08			

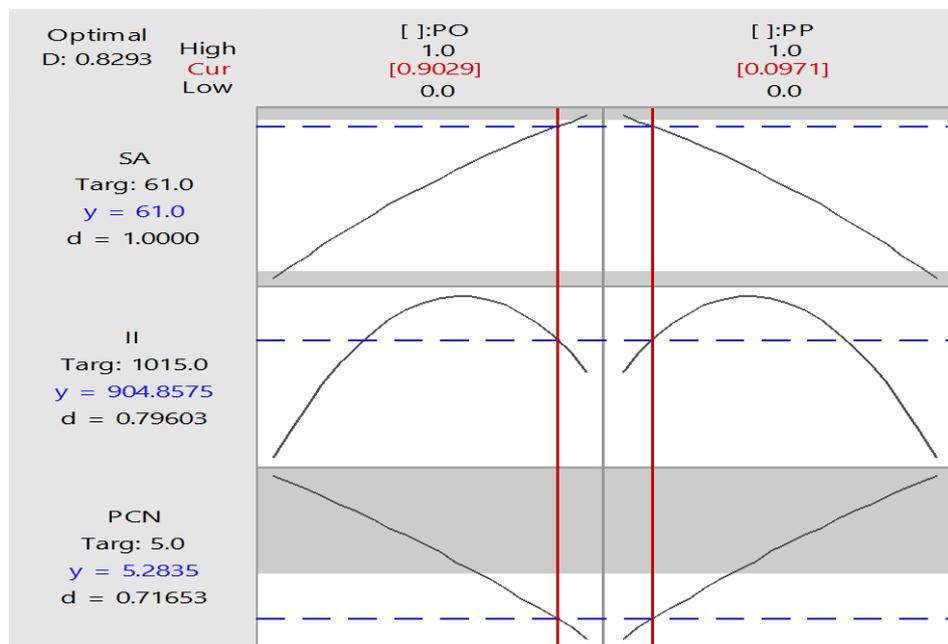


Fig. 1: Optimal area of mixture design

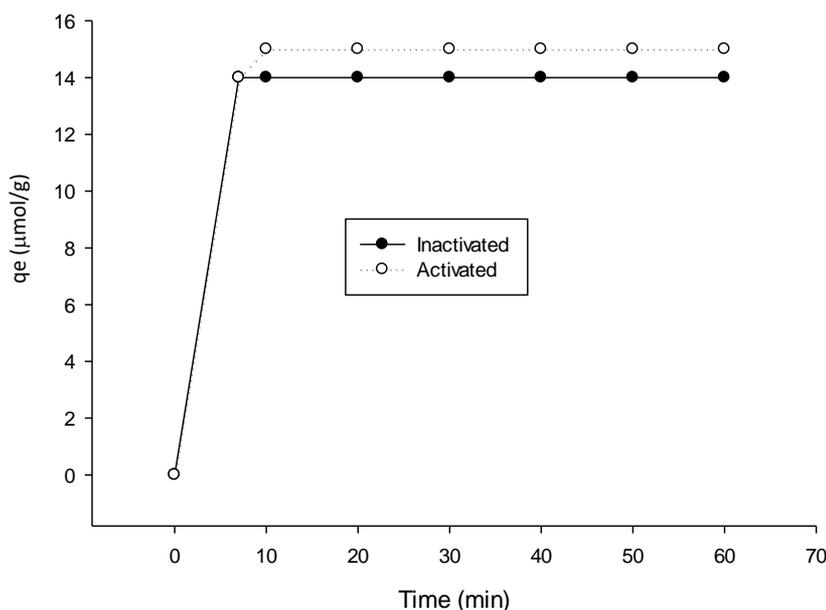


Fig. 2: The influence of contact time of copper (II) on adsorption from biosorbents. $C = 82.7 \mu\text{mol/L}$; $m = 0.1 \text{ g}$; $T = 25^\circ\text{C}$; $\text{pH} = 4$

Influence of Bio-Sorbent Mass

The results of bio-sorbent mass behavior are presented in Fig. 4. It appears from this figure that both have similar curves. The removal rate of Copper (II) increases with the bio-sorbents mass. The largest elimination rate of copper (II) is obtained for bio-sorbents mass equal to 0.5 g. This is because number of

available adsorption sites increases with bio-sorbent mass; which has consequence of the increasing adsorbed amount. Figure 4 also shows that the removal rate on activated bio-sorbent of Copper (II) is greater than removal rate of inactivated bio-sorbent. In fact, action of acid treatment on activated bio-sorbents increases its specific surface area and its porosity (Gupta and Bhattacharyya, 2008).

Influence of Temperature

The influence of temperature on the inactivated and activated bio-sorbent was studied in order to understand thermodynamic phenomenon of the adsorption of copper (II). The results obtained are shown in Fig. 5. This figure shows that inactivated and activated bio-sorbent have similar curves. The adsorbed amount of copper (II) increases linearly with temperature. Hence the adsorption is probably endothermic. Indeed, an increase

in temperature enables the diffusion of the copper (II) through the outer boundary layer of the bio-sorbent, then on its surface and finally towards inside of pores. An increased in the adsorbed amount as a function of temperature could also come from an increased in the adsorption sites created by the breaking of certain bonds on the surface of bio-sorbent (Abadian *et al.*, 2015). Figure 5 also reveals that the adsorbed amount of copper (II) for activated bio-sorbent are larger than the amount adsorbed by inactivated bio-sorbent.

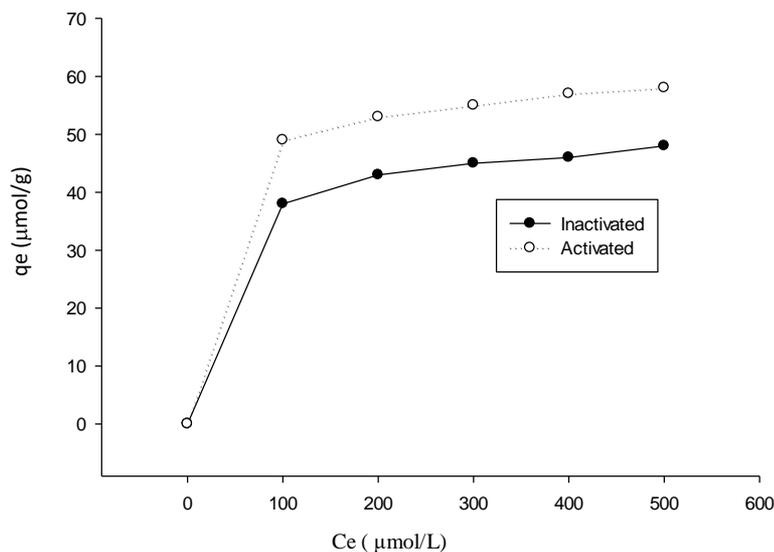


Fig. 3: The influence of copper (II) concentration from biosorbents. M = 0.1g; T = 25°C ; pH = 4

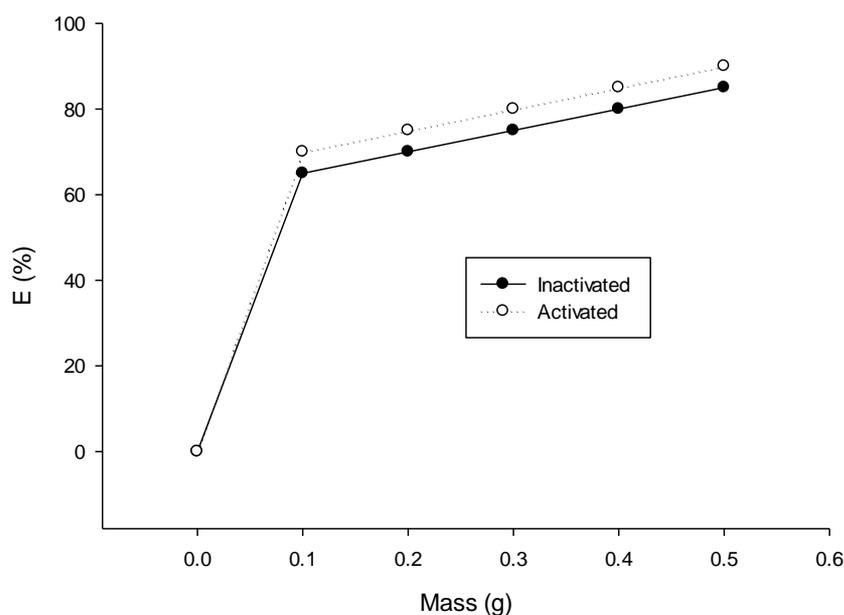


Fig. 4: The influence of the biosorbent mass on the adsorption of copper (II). C = 413.9 µmol/L; T = 25°C ; pH = 4

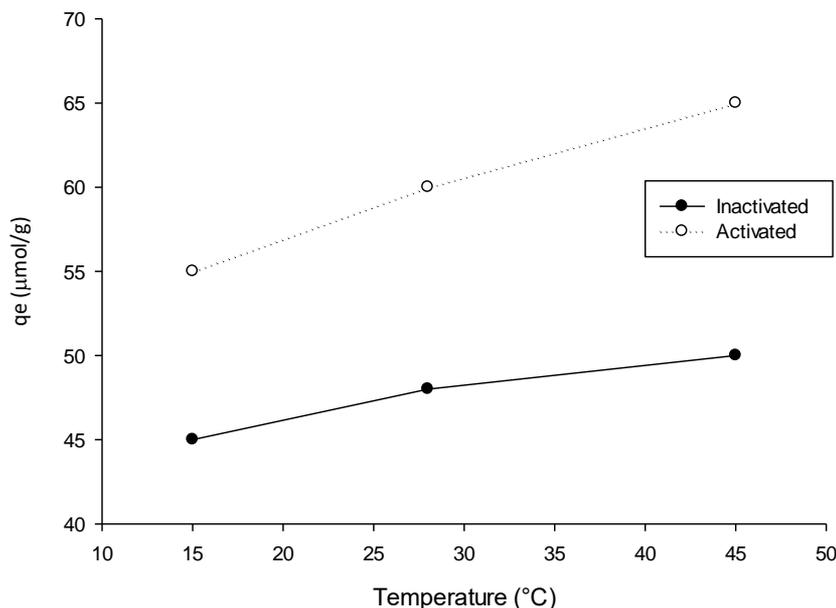


Fig. 5: The influence of temperature on the adsorption of copper (II). C = 413.9 µmol/L; m = 0.1 g; pH = 4

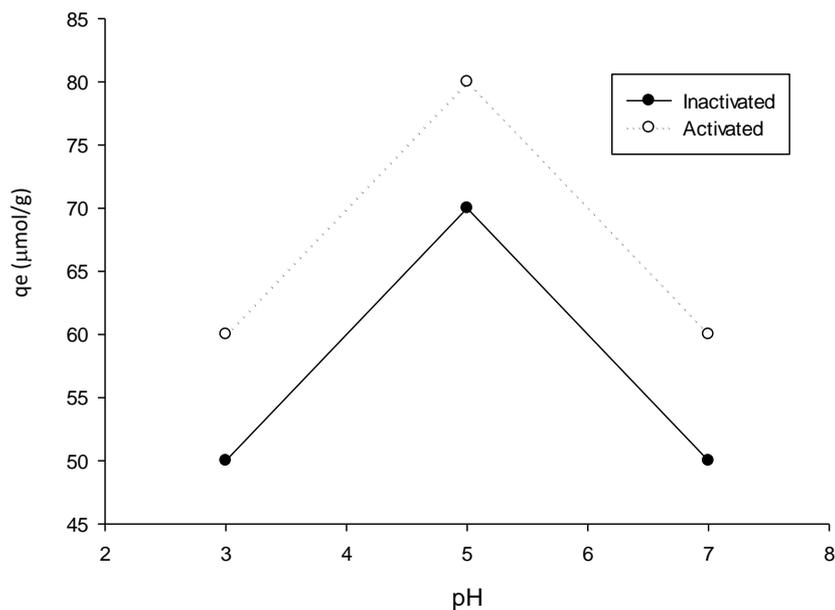


Fig. 6: The influence of pH on the adsorption of copper (II) from biosorbents. C = 413.9 µmol/L; m = 0.1 g; T = 25°C

Influence of the pH

From Fig. 6, curves of activated and inactivated bio-sorbent are similar in shape. The adsorption capacity of activated and non-activated bio-sorbents shows two domains. When the pH is between 3 and 5 the adsorbed amount increases. When the pH is above 5, the adsorbed amount decreases. An increase in the adsorbed amounts of Copper (II) with the pH indicates weak electrostatic interaction during the adsorption. Indeed, if electrostatic

interaction was important, evolution of amount adsorbed at pH_{PZC} bio-sorbent mixtures were broken. Moreover, for the pH lower than pH_{PZC} , copper (II) and bio-sorbent mixtures are all positively charged (Abadian *et al.*, 2015). This situation is therefore unfavorable for electrostatic adsorption. The evolution of adsorbed amount reveals that the adsorption is by surface complexation. The complex formed would therefore be unstable at pH greater than 5, hence the reduction of adsorbed quantities is observed beyond pH equal to 5 (Khan *et al.*, 2013). This result is in

accordance with the previous studies (Abadian *et al.*, 2015; Khan *et al.*, 2013; Singh *et al.*, 2006).

Conclusion

The purpose of this study is to enhance copper (II) adsorption by mixing plantain and orange peelings. The results show AAD, the bias and exactitude factors obtained are in agreement with the interval set to validate the model. The optimum mixture from this study is 90% of orange peelings proportion and 10% of plantain peelings proportion. The results also show that contact time is 10 min, adsorbed amount of copper ions (II) increases with initial copper concentration, mass of bio-sorbent and temperature of medium. Adsorbed amount increases for pH between 3 and 5 and decreases for pH greater than 5. Efficiency of Copper ions (II) removal is about 88.11% for the native bio-sorbent and 97.04 for the activated bio-sorbent. These efficiencies are higher than those obtained when orange and plantain peelings are taken individually and are in the range 70 and 85%. This could justify efficiency of mixture. Thermodynamic parameters indicate that adsorption reaction is spontaneous, reversible and endothermic.

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Author's Contributions

Inna Samomssa: Did an experimental design part of experimental work and the evaluation and calculation part of different parameters.

Ebelle Alvine: Did the experimental work with data collection in the evaluation of the influence of some parameters on adsorption as well as thermodynamic study.

Adjia Zangue Henriette and Sielichi Joseph: Are the supervisors. Their contributions include research planning, organizational designing and framework of the manuscript.

Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and no ethical issues involved.

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