

Bio-sorption of Cu²⁺ and Pb²⁺ Ions onto Citrus Sinensis (Orange) Peels

Felicia O. Afolabi, Paul Musonge and Babatunde F. Bakare

Abstract—Copper and lead ions are the most predominant pollutants found in wastewater in South Africa. The presence of these metals in water is a risk to human life, which results in various diseases. Orange peels powder in its natural form was used for the removal of copper and lead ions from an aqueous solution in a batch system. This work is aimed at the treatment of secondary effluent from a municipal plant. Orange peels powder was characterised before and after adsorption using Fourier transform infrared spectroscopy (FT-IR). The point of zero charge pH_{pzc} of orange peel powder was 3.83. The isotherm and kinetic studies were carried out in the range of pH 5-5.5, concentration of 10-100 mg/L and adsorbent dosage of 0.1 – 1g. A pseudo-second order model fitted the kinetic data while the Langmuir isotherm fitted the adsorption data signifying a monolayer adsorption mechanism. The adsorption of Pb(II) was higher than Cu(II) in both single and binary systems. The adsorption of Cu(II) was sensitive to the coexistence of Pb(II) in binary systems. The adsorption of Cu(II) increased at higher initial concentration which suggests that adsorption of Cu(II) increases after adsorption of Pb(II) had reached equilibrium.

Keywords—Binary system, Bio-sorption, Isotherm study, Orange peels

I. INTRODUCTION

Among toxic heavy metals present in water bodies, copper and lead are the major environmental contaminants [1] generated from industrial activities such as electroplating, leather finishing, battery waste [2]. Wastewater generated from the above activities most times can contain acids, metal plating and hazardous chemical residues with toxic heavy metals being of major concern as they persist for a long time in soil and in the food chain. These heavy metals are non-biodegradable hence, the presence of these heavy metals in the environment, drinking water and food chain pose serious health challenges to humans, animals and plants [3]. Excessive exposure to copper and lead through any means can lead to liver damage, insomnia, kidney disease, endanger the brain, circulatory and nervous system [2],

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4]. The Environmental Protection Agency (EPA) has set the maximum permissible limits of copper and lead in discharged wastewater to 1.3 and 0.05 mg/L respectively [5]. Hence, proper treatment of industrial wastewater containing copper and lead to a bearable minimum before being discharged into the environment is very important, to meet the effluent quality standards and regulations. Aside, the maximum limits for copper and lead in drinking water as stated by the US Environmental Protection Agency (US EPA) is 1.3 and 0.015 mg/L respectively [6]. However, further treatment will be needed for secondary effluent to achieve high quality drinking water as a very low concentration of these metals in water is very toxic. This is important to make the wastewater reusable thereby, combating the water scarcity challenges which has become an epidemic in many developed and developing countries.

Many conventional techniques have been employed for the treatment of wastewater containing heavy metals such as; electrodialysis, reverse osmosis, chemical precipitation, ion-exchange, ultra-filtration, coagulation/flocculation. However, these techniques have disadvantages such as; high operational cost, high chemical usage, membrane fouling through filtration and production of sludge. In addition, these methods are not efficient for low metal ion concentrations [7]. Hence, there is need to develop low-cost and environmentally friendly methods of treating wastewater containing these toxic heavy metals.

Biosorption is a technique employed by researchers in the past few years for removing toxic heavy metals from wastewater as an alternative to the conventional methods due to its efficiency in handling low metal ion concentrations, lower operational cost, locally available raw materials, and generation of little/minimal sludge [6, 8]. Recently, agricultural wastes such as rice husk [9], moringa oleifera seed [6], sawdust, banana peel, lemon peel [10] sugarcane bagasse, maize leaf [11], date palm fibres [12], watermelon rind [13], mango biomass [14] and tea waste [15] have been explored as sorbents for the removal of heavy metals from wastewater.

Oranges are the biggest citrus type in South Africa and account for 60 % of the citrus fruits produced from approximately 45,000 hectares of cultivated land. South Africa produces an average of 1.5 Million mega tonnes of oranges annually from four major cities (Limpopo, Eastern Cape, Western Cape, and Mpumalanga), some of which are exported and used to produce fruit juice. Orange wastes constitute a large fraction of food leftovers generated from households, markets and restaurants. In addition, the domestic orange juice industries generate a huge amount of orange peel wastes which are disposed. These wastes can be used as low-cost, readily

available, and eco-friendly adsorbent for the removal of copper and lead from wastewater thereby reducing environmental pollution. This work is focused on the removal of Cu(II) and Pb(II) from aqueous solution using natural orange peel (OP). The adsorption capacity of orange peel to sequester Cu(II) and Pb(II) in single metal solution and binary solution was studied in batch experiments at lower concentration representing secondary effluent wastewater which has gone through a municipal treatment plant but requires further treatment for higher quality and standards. The kinetic and isotherm studies were compared to determine the effects of metal ion co-existence. All experiments were carried out at room temperature, some operating parameters were varied while keeping others constant.

II. MATERIALS AND METHOD

A. Preparation of bio-sorbent

Orange peels were collected from a local market in Durban, South Africa and washed to remove dirt. The peels were further rinsed with distilled water, allowed to drain, and placed in an oven (Prolab oven and incubator) for drying at 70 °C for 24 hours. Then, the dried peels were crushed using an attrition mill (Retsch GmbH 5657 HAAN, West-Germany) and washed again with distilled water to remove color. The crushed sample was dried again at 50 °C for 24 hr and ground using a coffee blender. The bio-sorbent was then sieved into particle size in the range 75 – 250 µm and stored in an airtight container for use.

B. Determination of the point of zero charge of bio-sorbent (pHpzc)

The pH_{pzc} of orange peel was determined following the procedure proposed by [16]. 50 mL solution of 0.1 N KNO₃ was measured in 11 separate beakers and the pH of the solution was adjusted from 2 to 12 using 0.1 M HCl and 0.1 M NaOH. Then, 0.5 g of bio-sorbent was added to each of the solution and mixed at room temperature for 48 hours. The pH of the solution which denotes the final pH was determined, the changes between the initial and the final pH of the solution were plotted against the initial pH.

C. Preparation of synthetic solution

The stock solution containing mixture of Cu(II) and Pb(II) was prepared in a 1000 mL volumetric flask by dissolving 3.8 g of copper nitrate trihydrate Cu(NO₃)₂ · 3H₂O and 1.6 g of lead nitrate Pb(NO₃)₂ in deionized water. Different initial concentrations ranging from 10 – 100 ppm were prepared from the stock solution by serial dilution. The pH of the solutions was measured using a digital pH meter (edge^{pH} HI 2002, USA), while the solution pH was adjusted using aqueous H₂SO₄ or NaOH (0.1 M each).

D. Analytical instruments

The functional groups present in the bio-sorbent were determined by Fourier transform infrared spectroscopy (FTIR), the data were analyzed using the spectrum 10 software (Perkin Elmer, Frontier, USA). The batch experiments were done using linear shaker (264 R00) and the composition of the metal ions

after adsorption were analyzed using a micro-plasma atomic emission spectrophotometer (MP-AES, MY 18379001, Agilent, USA).

E. Batch experiments

All the batch experiments were done at room temperature (25°C). The kinetic studies were done with single and binary solute of Cu(II) and Pb(II) at a constant pH = 5. A dosage of 1g of bio-sorbent was added to 1 L solution containing Cu(II) or Pb(II) with initial concentration 10 mg/L, 55 mg/L and 100 mg/L. The solution was agitated for 24 hours at 180 rpm while samples were withdrawn at specified intervals (0.25, 0.5, 1, 2, 3, 4, 5, 6 and 24 h). The samples were filtered using Whatman filter paper and syringe filters then, analyzed using MP-AES. The binary solution kinetic experiments of Cu(II) and Pb(II) were prepared with initial concentration in the ratio 1:1 while other procedures remain the same as in single solute. To ascertain the reliability, accuracy and reproducibility of the data obtained, each experiment was repeated in triplicate while the average results were reported.

The single solute isotherm experiments were conducted with initial concentration of Cu(II) or Pb(II) ranging from 10 – 200 mg/L. A dosage of 0.5 g of banana peel was added to the solution and agitated at 180 rpm for 2 hours. The supernatant was filtered using Whatman filter paper and syringe filters then, analyzed using MP-AES. The binary solute isotherm experiments were done with mixture of Cu(II) and Pb(II) containing initial concentration in the ratio 1:1, all other procedures for single solute isotherm study were followed. The amount of Pb(II) and Cu(II) adsorbed was calculated using the equation stated below;

$$q_e = \frac{(C_0 - C_e)}{m} V \quad (1)$$

Where q_e (mg/g) is the quantity adsorbed at equilibrium, C₀ and C_e (mg/L) are the initial and final concentrations respectively, V (L) is the solution volume and m (g) is the mass of the adsorbent used.

F. Adsorption models

1) Adsorption Kinetic Models

The pseudo-first and pseudo-second order kinetic model are used to explain the adsorption process of Pb and Cu onto orange peels. The model for the pseudo-first order is as stated below;

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

The pseudo-second order model is expressed as;

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{K_2} t \quad (3)$$

Where q_e and q_t are respectively the quantities adsorbed at equilibrium (mg/g) and at time t (hr), K₁ is the pseudo-first order rate constant (hr⁻¹) and K₂ is the pseudo-second order rate constant (g mg⁻¹ hr⁻¹).

2) Adsorption Isotherm Models

The Langmuir and Freundlich isotherm models are popularly known adsorption models for describing equilibrium of an adsorption process. The Langmuir isotherm assumes that the surface of an adsorbent is homogenous and adsorption energy is uniform for all sites [17]. The model equation is as stated below;

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \quad (4)$$

The Freundlich isotherm assumes the surface of the adsorbent is heterogenous and adsorption energy is exponentially distributed [17]. The model equation is as shown below;

$$q_e = K_F C_e^{1/n} \quad (5)$$

Where q_e and C_e are the quantity adsorbed (mg/g) and concentration at equilibrium (mg/L) respectively, q_{max} is the maximum quantity adsorbed (mg/g) while b is the Langmuir constant, K_F and n are the Freundlich constant (L/g).

III. RESULTS AND DISCUSSION

A. Characterization Of Bio-Sorbent

1) Physical Properties Of Orange Peels

The point of zero charge (pHpzc) of an adsorbent is the point at which the surface of an adsorbent has zero net charge. The pHpzC of natural orange peel is 3.83 as shown in Fig. 1 below. This means the surface of orange peel is acidic which favors the adsorption of cations. This result is similar to what was reported by [18].

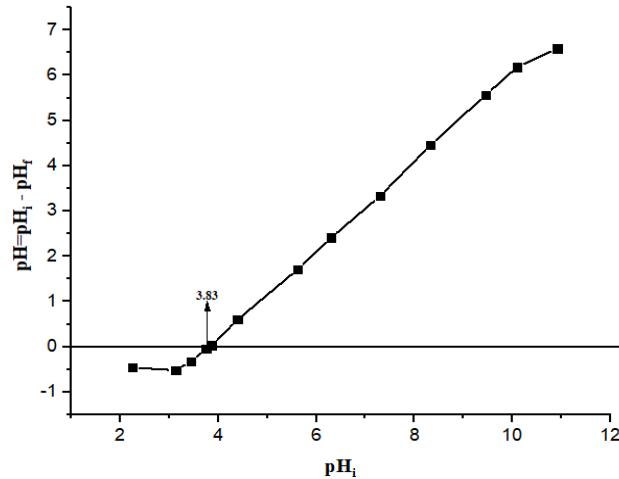


Fig. 1 shows point of zero charge (pHpzc) of orange peel

2) Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR of orange peel before and after adsorption for single and binary solutes were obtained within the range of 500 to 4000 cm⁻¹ wavenumber as depicted in Fig. 2. The FTIR spectra shows different peaks which represent the functional groups present on the surface of an adsorbent. The peaks 3329.98, 1367.4, 1316.4 and 1236.66 cm⁻¹ represent O-H stretching of alcohol, phenol and carboxylic groups, peaks 2920.41 and 2852.1 cm⁻¹ are identified as C-H stretching available in the pulp, the peak 1733 cm⁻¹ is known to be C=O stretching of carboxyl and ester group while the peak at 1607.1 cm⁻¹ stands for C=C stretching which corresponds to amides. These peaks were also observed by [18, 19]. There are similarities in the peaks observed on the FTIR spectra of orange peels before and after adsorption; the hydroxyl, phenol, carbonyl, and carboxyl groups are all represented. However, there was significant shift in the after-adsorption graphs with peaks representing the O-H stretching. The orange peels loaded with Pb(II) was highly influenced as the peak representing hydroxyl and carboxyl groups shifted significantly. This shows

the involvement of the carboxylic groups in the adsorption of Pb(II).

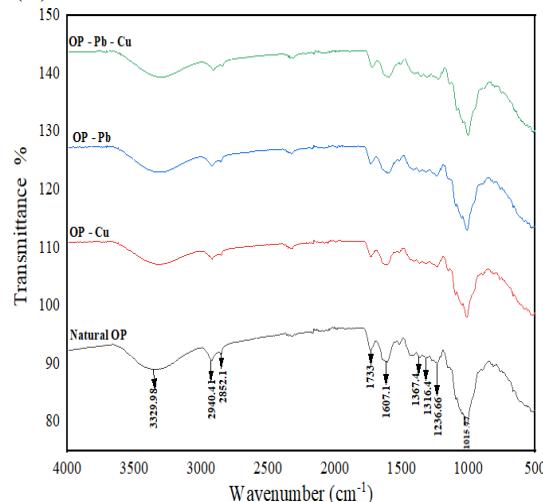


Fig. 2 shows FTIR of orange peel before and after adsorption

B. Single and Binary Adsorption Isotherms

The isotherm studies were performed using a fixed adsorbent dosage and varying initial concentrations. Fig. 3 shows the adsorption isotherm of Cu(II) and Pb(II) for experimental data under single and binary systems as well as the linear fits of the isotherm models. Both the adsorption of Cu(II) and Pb(II) increased with increasing initial concentrations. The adsorption capacity of Pb(II) was higher than Cu(II) in both systems. This suggests that orange peel has higher affinity for Pb(II) than Cu(II). Also, Table 1 shows the Langmuir isotherm constant value 'b' is higher for Pb(II) than Cu(II) in both systems, which suggests that Pb(II) was more adsorbed than Cu(II). Therefore, Pb(II) has higher affinity for the active sites on the surface of orange peels. The Freundlich isotherm constant 'n' which explains the adsorption intensity of the metal ions was found to be greater than 1 in both systems. This implies that the adsorption process is physical. Comparing the correlation value (R^2) for Langmuir and Freundlich isotherm as shown in Table 1, it is obvious that Langmuir isotherm fitted the experimental data well for Cu(II) and Pb(II) in both systems.

In both single and binary adsorption, Pb(II) was more adsorbed on the active sites than Cu(II). In addition, Pb(II) adsorption was not affected by the presence of Cu(II) in binary system while, adsorption of Cu(II) only increased at higher initial metal concentration in binary system. The quantity adsorbed for Cu(II) at initial concentration 125 mg/L increased from 19.72 mg/g in single system to 23.98 mg/g in binary system. This means at the stated initial concentration, Pb(II) reached equilibrium and there was less competition for the active sites. Therefore, at lower initial concentrations, Cu(II) was sensitive to the presence of Pb(II) in binary system.

TABLE 1: LANGMUIR AND FREUNDLICH ISOTHERM PARAMETERS.

Ion	System	Langmuir		Freundlich		
		b (L/mg)	q _m (mg/g)	R ²	K _f	n

Cu	Single	0.16	31.62	0.972	5.40	2.11	0.888
(II)	Binary	0.15	40.18	0.988	5.19	1.56	0.934
Pb	Single	0.59	59.14	0.985	20.18	1.34	0.954
(II)	Binary	4.77	38.05	0.998	24.06	4.29	0.898

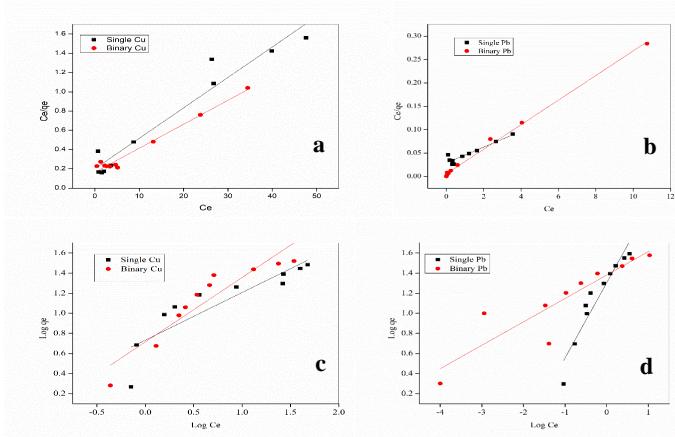


Fig. 3 represents adsorption isotherms of Cu(II) and Pb(II) on orange peel in single and binary systems at pH 5. The symbols represent the experimental results while the solid lines are the linear fittings of (a) Cu Langmuir adsorption, (b) Pb Langmuir adsorption, (c) Cu Freundlich adsorption, (d) Pb Freundlich adsorption

C. Adsorption Kinetics

The linearized form of pseudo-first order and pseudo-second order kinetic models were used to explain the adsorption kinetic experimental data as shown in Fig. 4. The model parameters for the kinetic models are stated in Table 2. The kinetic study for Cu(II) and Pb(II) in single and binary systems were carried out at specified initial concentrations of 10 mg/L, 55 mg/L and 100 mg/L to explain the selectivity of the metal ions in coexistence. The adsorption experimental kinetic data of Cu(II) and Pb(II) in both systems at the specified initial concentrations fitted the pseudo-second order with correlation co-efficient (R^2) equals to 1, which suggests that the adsorption rate is chemically controlled. The quantity adsorbed for Cu(II) and Pb(II) in single system at the different initial concentrations is higher than the quantity adsorbed in the binary system. However, the quantity of Pb(II) adsorbed in both single and binary system is higher than Cu(II) for all the initial concentration. The pseudo-second order constant K_2 value for Pb(II) under binary system is higher than Cu(II) signifying adsorption of Cu(II) is negatively affected in the coexistence of Pb(II).

The adsorption of Cu(II) and Pb(II) in the binary system revealed adsorption capacity of Pb(II) is higher which suggests that Pb(II) could bind with more functional groups on the surface of orange peels.

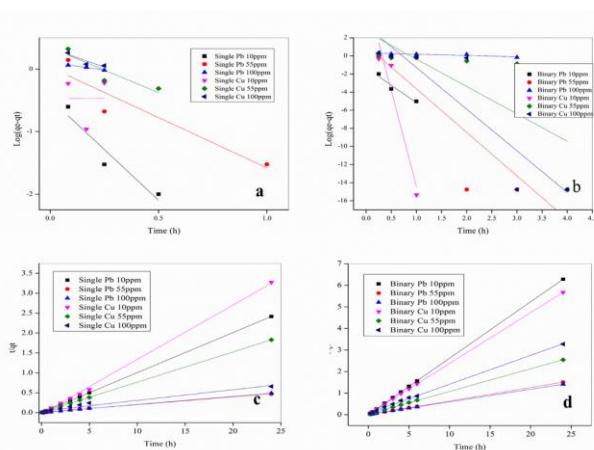


Fig. 4 represents kinetic adsorption model graphs of Cu(II) and Pb(II) at different initial concentrations; (a) pseudo-first order single, (b) pseudo-first order binary, (c) pseudo-second order single, (d) pseudo-second order binary.

TABLE II: KINETIC MODEL PARAMETERS OBTAINED FROM PSEUDO-FIRST ORDER MODEL AND PSEUDO-SECOND ORDER MODEL.

Metal ion Concentratio n	Cu		Pb			
	10	55	100	10	55	100
Pseudo-first order	Single					
q_e	0.34	2.20	2.16	0.34	1.07	1.28
K_1	0.06	3.31	2.81	7.46	3.70	1.13
R^2	0.905	0.903	0.913	0.95	0.94	0.98
Pseudo-first order	Binary					
q_e	6.83E 6	465.2 7	2087.3 7	0.05	14.7 2	2.18
K_1	48.96	6.96	10.59	8.83	11.0 6	0.33
R^2	0.958	0.762	0.897	0.97	0.89 0.92	0.92 4
Pseudo-second order	Single					
q_e	7.32	13.15	3719	9.93	51.4 1	48.9 7
K_2	0.65	0.94	0.02	13.6 9	0.05	0.40
R^2	0.999	0.999	0.991	1.00	0.99 0.99	0.99 9
Pseudo-second order	Binary					
q_e	42.48	9.49	13.39	3.82	15.9 6	17.0 9
K_2	0.02	0.44	0.04	10.7 1	0.55	0.30
R^2	0.999	0.999	0.999	1.00	0.99 0.99	0.99 9

IV. CONCLUSIONS

In this paper, the potential of orange peels for the removal of Cu(II) and Pb(II) was explored in single system and the sensitivity of these metal ions in a binary adsorption process. The isotherm studies showed that the adsorption of Cu(II) and

Pb(II) increased with increasing initial concentration. However, the adsorption of Pb(II) is higher than Cu(II) in both single and binary systems. The Langmuir and Freundlich linearized isotherm models were used to describe the adsorption equilibrium of Cu(II) and Pb(II) in both single and binary systems, the Langmuir isotherm model fitted the experimental data. The adsorption of Cu(II) was sensitive to the coexistence of Pb(II) in binary systems, adsorption of Cu(II) increased at higher initial concentration which suggests that adsorption of Cu(II) increases after adsorption of Pb(II) had reached equilibrium. The kinetic model followed pseudo-second order for both systems. The pH_{pzc} of orange peels was determined to be acidic which favors the adsorption of Cu(II) and Pb(II) since the solution pH was higher than the pH_{pzc}. The FT-IR revealed the presence of acid groups (-OH and -COOH) on the surface of orange peels therefore, the surface of the bio-sorbent becomes negatively charged at a solution pH higher than pH_{pzc}. Hence, Cu(II) and Pb(II) in solution are attracted to the bio-sorbent surface by electrostatic interaction. This study showed that orange peels are an effective bio-sorbent for the removal of Cu(II) and Pb(II) in single and binary systems from aqueous solutions, however orange peels has more affinity for Pb(II) than Cu(II).

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