



## Detoxification of Wastewater by Paw-Paw (*Carica papaya L.*) Seeds Adsorbents

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The present work reports the biosorption studies of metal ions *viz.*, Pb(II) and Cu(II) from aqueous solution onto paw-paw seeds (PPS), acid treated paw-paw seeds (ATPPS) and base treated paw-paw seeds (BTPPS) adsorbents by batch method. A series of tests were carried to evaluate the effect of the system parameters, *i.e.* adsorbent dosage, initial concentration, temperature and contact time. The obtained kinetic data showed that the pseudo first order model best fitted the biosorption of both metal ions with ( $r^2$ ) values of 0.9918, 0.9674 and 0.9463 for Cu(II) onto PPS, ATPPS and BTPPS, respectively and for Pb(II) 0.8513, 0.8686 and 0.9434 onto PPS, ATPPS and BTPPS respectively. Estimated surface adsorption of intra-particle diffusion estimated that surface sorption dominated. Thermodynamic parameter ( $\Delta G^\circ$ ) gave negative values indicating that the biosorption processes were spontaneous and feasible.  $\Delta H^\circ$  gave positive and negative values indicating that some biosorption processes were endothermic and some exothermic. Isotherm data indicated that Langmuir best described the biosorption. The reusability of PPS, ATPPS and BTPPS adsorbents was evaluated up to five cycles without showing significant drop in sorption efficiency.

**Keywords:** Paw-Paw seeds, Lead, Copper, Adsorbent.

### INTRODUCTION

Wastewater containing pollutants create a big problem to the environment and living organisms due to their harmfulness and toxicity. The array of aqueous pollutants is countless; it includes dyes [1], organic pollutants [2], micro (nano) plastics [3], toxic metal ions [4], *etc.* The scope of this study focused on two global environmental metal ions pollutants in water, lead(II) ions and copper(II) ions. Lead(II) is detrimental and linked to neuromuscular weakness and impaired cognitive functions in humans [5]. Copper(II) has been linked to spasms, severe headache, abdominal pain, and hair loss [6].

These two toxic metal ions and their related compounds are amongst the so-called 'black-list' substances in the dangerous substances [7]. They are also classified by the World Health Organization (WHO) as metals of most immediate concern [8]. These toxic metals get introduced into water by industrial activities these include; electroplating, plastic manufacturing, mining, paint pigment production, alloy preparation, batteries manufactures and metallurgical practices [9]. The on-going

issue of toxic metal pollutants removal from aqueous solution has been a matter of great consideration and researched in the last few decades. Several technologies based on adsorption have been applied for the treatment of wastewater due to their advantages; environmental friendliness, ease to conduct, regeneration of used adsorbents and affordability [10] over conventional techniques like membrane technology [11], reverse osmosis [12], electrochemical treatment [13] and ion exchange [14]. A comprehensive review on conventional techniques is reported by Robinson *et al.* [15].

Literature shows agricultural materials are promising adsorbents hence many biosorbent materials have been used applied in wastewater purification these include; banana peel [16], ginger [17], wheat straw [18], coconut husk [19], tea leaves [20], peanut skin [21], hazelnut husk [22], Bengal gram husk [23], *etc.*

Using biosorbent/biomass adsorbents which are available as wastes is of environmental importance. For instance, the top paw-paw producing country in the world is India 5.5 million tons annually, Brazil is second, producing 1.6 million tons

annually. Indonesia is the world's third producing around 900,000 tons. Other countries such as Nigeria and Mexico produce around 800,000 tons every year. The numbers indicate that fairly large amounts of paw-paw fruit are consumed. After consumption, significant amounts of waste are discarded usually peels and seeds. This work reports the use of paw-paw seeds as biosorbent to treat wastewater contaminated with Pb(II) and Cu(II). The paw-paw seeds were pretreated in order to enhance the biosorption capacity. Batch method was applied to evaluate the biosorption capacities.

## EXPERIMENTAL

Fresh ripe paw-paw fruits were bought from a local fruit and veggie market in Johannesburg, South Africa. Hydrochloric acid (32 %), A.R grade, nitric acid (70 %), A.R grade, sodium hydroxide pellets (98.5%) A.R grade, lead nitrate (99.95 %), A.R grade and copper sulfate pentahydrate (98 %) A.R grade. All consumable chemicals were supplied by Merck and used without further purification.

The morphology, chemical features and thermal stability of paw-paw seeds (PPS), acid treated paw-paw seeds (ATPPS) and base treated paw-paw seeds (BTPPS) were affirmed by SEM, FTIR and TGA techniques. Scanning electron microscopy (SEM) images were taken on a Nova Nano SEM 200 from FEI operated at 10.0 kV. Thermogravimetric analyzer (TGA), a Perkin Elmer TGA 4000 was used; analyses were performed from 310 to 900 °C at a heating rate of 10 °C/min under N<sub>2</sub> atmosphere. Perkin-Elmer Fourier transformed

infrared spectroscopy FT IR/ FTNIR spectrometer, spectrum 400 was used. Atomic absorption spectroscopy (AAS) Shimadzu ASC 7000 auto sampler was used to measure the metal ion solutions.

### Preparation of adsorbents

**Untreated paw-paw seeds (PPS) adsorbent:** Wet seeds were isolated from a fresh ripe fruit, soaked and washed in distilled water then dried in the sun for 14 days. Dried seeds were crushed, soaked and washed in distilled water. Ground seeds were dried in oven over night at 30 °C. The powder seeds were labeled untreated paw-paw seeds and used as such for further research studies.

**Acid treated paw-paw seeds (ATPPS) adsorbent:** Untreated paw-paw seeds of 25 g were transferred into a round bottom flask and refluxed with 100 mL of (ratio 1:1) HCl:HNO<sub>3</sub> for 60 min at room temperature. The acid treated PPS were filtered and soaked several times in distilled water to get rid of the acid. The acid treated PPS was dried in an oven at 30 °C.

**Base treated paw-paw seeds (BTPPS) adsorbent:** Untreated paw-paw seeds of 25 g were transferred into a round bottom flask and refluxed with 100 mL of 1M NaOH solution for 60 min at room temperature. The base treated PPS was filtered and soaked in distilled water. The base treated PPS was dried in an oven at 30 °C. The preparation of PPS, ATPPS and BTPPS are depicted in Fig. 1.

**Metal ions sorption:** Batch adsorption experiments (adsorbent dosage effect, time dependent studies, concentration effect and temperature effect) were performed to measure each variable

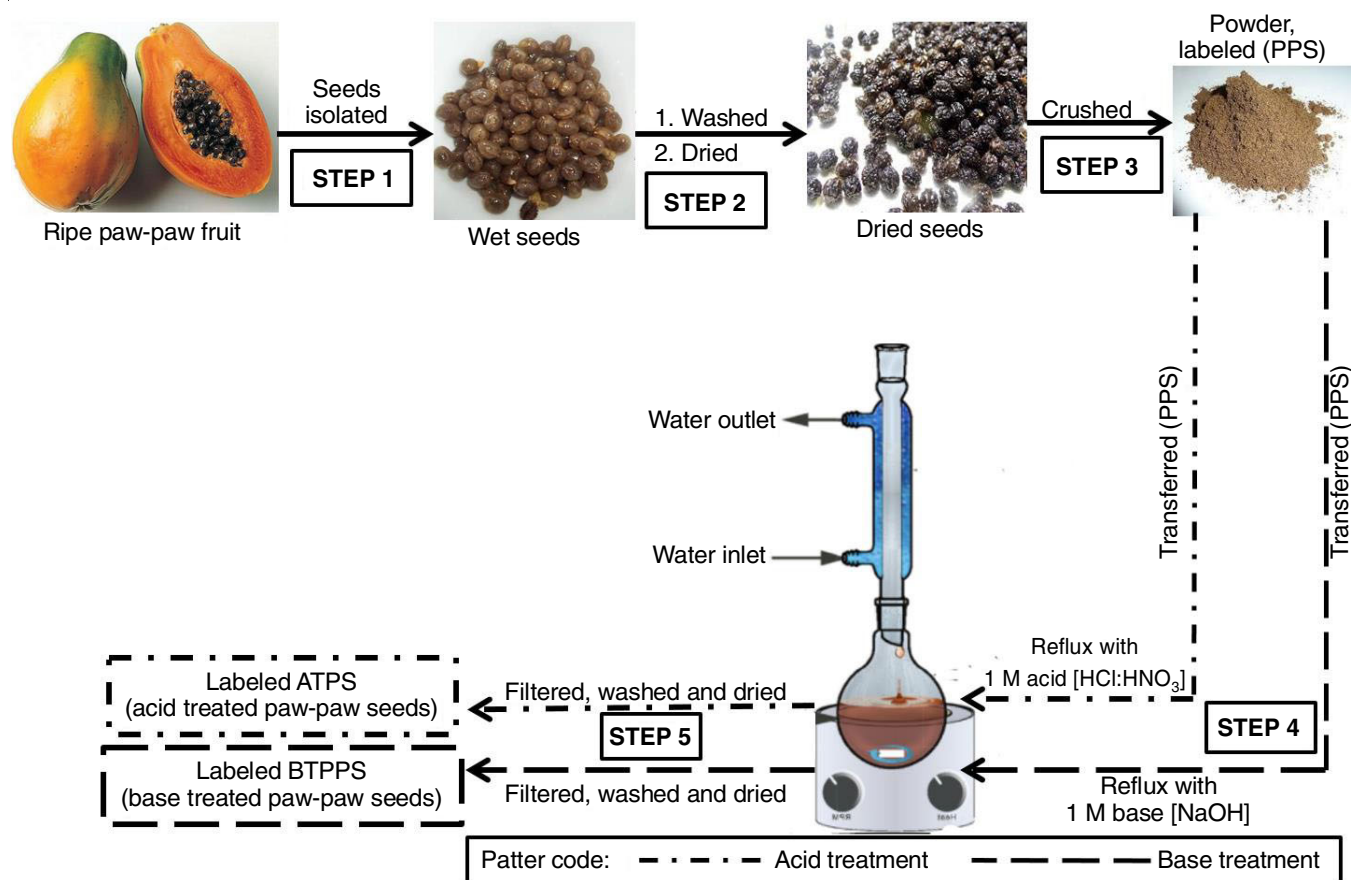


Fig. 1. PPS, ATPPS and BTPPS preparation schematic

on the adsorption capacity of metal ions of Pb(II) and Cu(II). A 20 mL of each metal ion solution [Pb(II) and Cu(II)] was agitated for 60 min with adsorbent (PPS, ATPPS and BTPPS) in a 50 mL centrifuge bottle according to variables and parameters (Table-1). All the adsorption studies were done in duplicates to ensure repeatability and accuracy of the experimental data.

The adsorption capacity was determined using eqn. 1:

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

where  $q_e$  is the adsorption capacity (mg/g),  $C_o$  and  $C_e$  are initial and equilibrium concentrations (mg/L), respectively.  $V$  is the volume of the metal ion solution (mL) and  $m$  is the mass of adsorbent (g).

The obtained experimental data were further treated by nonlinear equations to determine kinetic models; pseudo-first order (PFO) (eqn. 2), intra-particle diffusion (eqn. 3) and pseudo-second order (PSO) (eqn. 4).

$$q_e = q_t (1 - e^{-k_1 t}) \quad (2)$$

$$q_t = k_i (t^{1/2}) + C \quad (3)$$

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

where  $q_e$  is the amount adsorbed (mg/g) and  $q_t$  is the amount adsorbed at equilibrium (mg/g) and  $t$  is time;  $k_1$  is rate constant of PFO ( $\text{min}^{-1}$ ) and  $k_2$  is rate constant of PSO ( $\text{g mg}^{-1} \text{min}^{-1}$ ). The  $k_i$  is the rate parameter ( $\text{g g}^{-1} \text{min}^{1/2}$ ) and  $C$  is the concentration of cations on the adsorbent surface.

The adsorption isotherm models were determined by Langmuir, Freundlich and Temkin using eqns. 5, 6 and 7, respectively.

$$q_e = \frac{Q_o b C_e}{1 + b C_e} \quad (5)$$

$$q_e = k_f C_e^{1/n} \quad (6)$$

$$q_e = \frac{RT}{b_T} \ln(k_T C_e) \quad (7)$$

$Q_o$  is (adsorption capacity) $_{\text{max}}$  per milligram of adsorbent in (mg/g),  $b$  is a solute surface interaction energy,  $k_f$  is Freundlich capacity factor and  $1/n$  is the isotherm linearity parameter.  $R$  is the gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ),  $T$  is temperature (K),  $b_T$  and  $k_T$  are rate constants for Temkin model

**Reusability:** The reusability of PPS, ATPPS and BTPPS was examined using 0.1 g of Pb(II)/Cu(II)-loaded adsorbent. The adsorbed Pb(II)/Cu(II) ion was desorbed by agitating twice in 20 mL of 0.5 M HCl at 200 rpm for 30 min and then rinsed

several times with ultra-pure water at 200 rpm for 60 min before reuse.

## RESULTS AND DISCUSSION

**SEM analysis:** The surface morphology analysis of PPS, ATPPS and BTPPS was examined from the SEM. The images of untreated paw-paw seeds (PPS), acid treated paw-paw seeds (ATPPS) and base treated paw-paw seeds (BTPPS) are shown in Fig. 2a-f. The images of PPS in (Fig. 2a-b) show none porous irregular morphology. The images of ATPPS in Fig. 2c-d and BTPPS in Fig. 2e-f exhibited porous surface morphology. The cavities on ATPPS and BTPPS surfaces may have formed because of the refinement of some lignocellulosic materials on paw-paw seeds outer surface during reflux by acid and base treatment exposing the inner porous surface. Mitic-Stojanovic [24], also reported that acid and base treatment of biomass may result in a more orderly arrayed morphology as compared to that in a

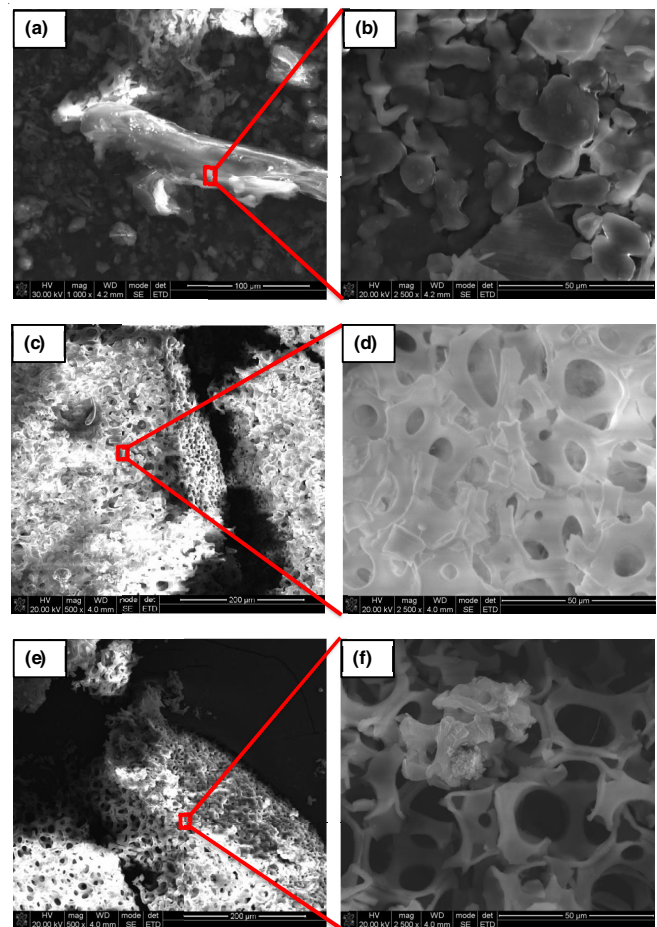


Fig. 2. SEM images (a-b) PPS adsorbent, (c-d) acid treated ATPPS and base treated (e-f) BTPPS

TABLE-1  
SUMMARY OF ADSORPTION EXPERIMENTS VARIABLES AND PARAMETERS;  
ADSORBENTS: PPS, ATPPS AND BTPPS; METAL IONS: Pb(II) AND Cu(II)

Variables	Variable levels					Volume of metal ion solution (mL)	Mass of adsorbent (g)	Concentration of metal ion solution (mg/L)	Duration of adsorption (min)
	0.1	0.2	0.3	0.4	0.5				
Adsorbent dosage (g)	0.1	0.2	0.3	0.4	0.5	20	–	100	60
Time dependent (min)	5	10	15	30	60	20	0.1	100	–
Concentration (mg/L)	20	40	60	80	100	20	0.1	–	60
Temperature (°C)	25	30	40	50	60	20	0.1	100	60

untreated state. Both ATPPS and BTPPS surface cavities seems they could easily be penetrated by metal ions and further adsorbed at interior active sites.

**FTIR analysis:** IR spectra of untreated (PPS), acid treated (ATPPS) and base treated (BTPPS) adsorbents are shown in Fig. 3 in the range of 4000-450  $\text{cm}^{-1}$ . Medium bands exhibited in PPS, ATPPS and BTPPS in the range of 3549-3426  $\text{cm}^{-1}$  is attributed to (-OH) stretch. The sharp band in all adsorbents at 2925  $\text{cm}^{-1}$  alike is the stretching of (-CH). The bands at 1720, 1718 and 1710  $\text{cm}^{-1}$  for PPS, ATPPS and BTPPS, respectively are associated to (-C=O). The spectra of all adsorbents look similar for the most wavenumbers. However the observed changes were slight shifts in band heights and the major change was two distinct bands that appeared at 883 and 817  $\text{cm}^{-1}$  for the acid treated (PPS) not exhibited PPS and BTPPS. This suggests the possibility of some functional groups cleavage upon acid pre-treatment. The major change in BTPPS spectrum was appearance of three distinct bands at 1150, 883 and 707  $\text{cm}^{-1}$  not exhibited PPS and ATPPS. This also suggests the possibility of some functional groups cleavage upon base pre-treatment.

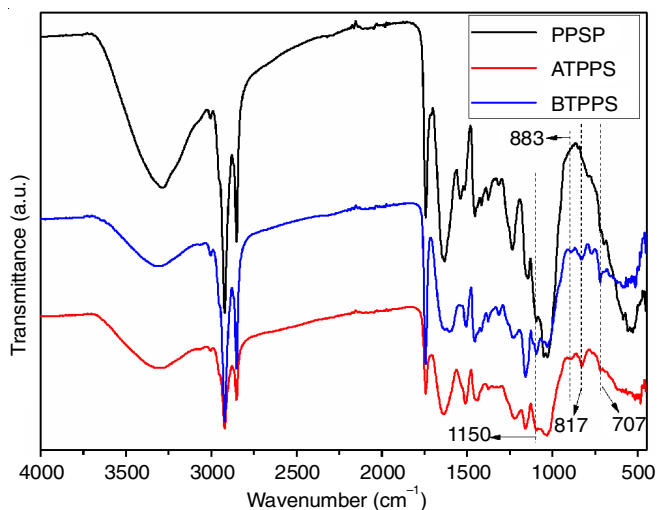


Fig. 3. FTIR spectra of PPS, ATPPS and BTPPS

**TGA analysis:** Thermal stability of PPS, ATPPS and BTPPS were studied by TGA profiles in the range of 30-900  $^{\circ}\text{C}$  as shown in Fig. 4. It was noticed that the weight loss profiles of PPS and ATPPS followed the same pattern. Their first weight loss was at 45-102  $^{\circ}\text{C}$  this is due to the loss of moisture. Second weight loss was observed at 255-510  $^{\circ}\text{C}$  this is the breakdown of lignocellulosic materials. BTPPS followed a distinct TGA profile;

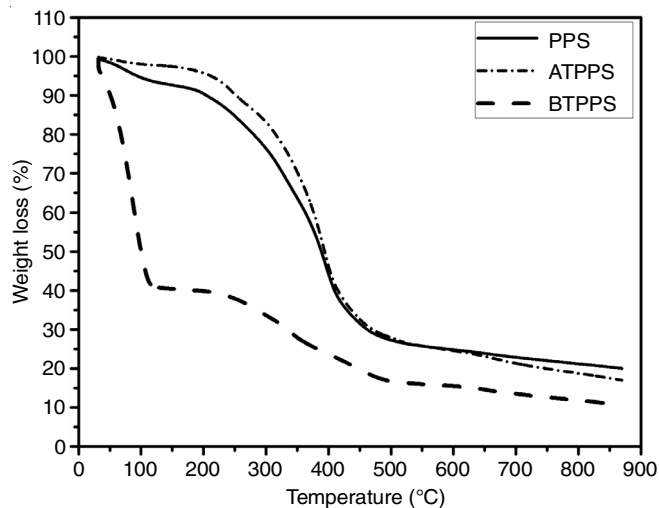


Fig. 4. TGA profiles of PPS, ATPPS and BTPPS

its first weight loss was at 32-100  $^{\circ}\text{C}$  due to the loss of moisture. Second weight loss was observed at 220-523  $^{\circ}\text{C}$ , due to the breakdown of lignocellulosic materials *i.e.* cellulose, hemicellulose and lignin.

### Adsorption studies

**Concentration effect and isotherm models:** The concentration effect studies were carried out by varying adsorbate Pb(II) and/or Cu(II) solutions concentrations (20, 40, 60, 80 and 100 mg/L) at constant temperature of 25  $^{\circ}\text{C}$  (298 K) onto PPS, ATPPS and BTPPS as shown in Fig. 5a-c. The observed trends expressed high removal at elevated concentrations for Pb(II) and Cu(II) ions. The adsorption trends also indicated that ATPPS and BTPPS adsorbents had better performance than PPS. The adsorption of Pb(II) ions exhibited higher removal than Cu(II) onto all adsorbents. Better performance shown by ATPPS and BTPPS may be linked to superior surface area exhibited after acid and/or base treatment and additional active sites. However moderate adsorption on PPS may be linked to less surface area exposed and high quantity of lignocellulosic materials that hinder the adsorption.

The concentration effect data at 25  $^{\circ}\text{C}$  (298 K) were further fitted to Langmuir, Freundlich and Temkin isotherm models as shown in Table-2. It was observed that both Cu(II) and Pb(II) removal onto PPS, ATPPS and BTPPS fitted Langmuir isotherm model better with ( $r^2$ ) values ranging between (0.8459-0.9305) and  $Q_0$  values were closer to obtained experimental values. Langmuir isotherm model is suggestive of monolayer adsorption

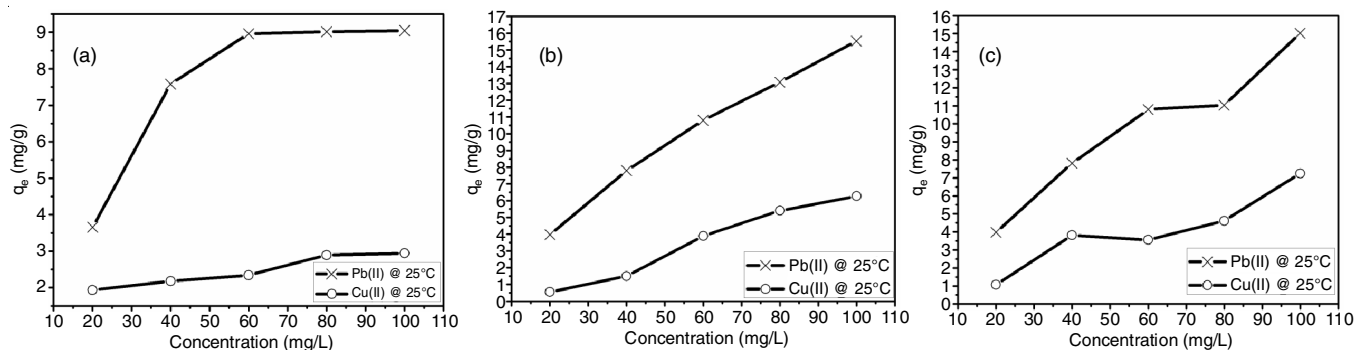


Fig. 5. Concentration effect of Pb(II) and Cu(II) onto (a) PPS, (b) ATPPS and (c) BTPPS

TABLE-2  
ISOTHERM MODELS PARAMETERS

Isotherm model	Parameter	PPS		ATPPS		BTPPS	
		Cu(II)	Pb(II)	Cu(II)	Pb(II)	Cu(II)	Pb(II)
Langmuir	$Q_e$ (mg/g)	2.997	9.478	13.03	14.02	16.82	12.59
	B	0.1413	0.7599	$6.8 \times 10^{-5}$	1.422	0.00316	2.414
	$r^2$	0.8508	0.8459	0.9241	0.9308	0.8513	0.8990
Freundlich	1/n	1.085	5.316	3.521	7.162	0.1801	7.330
	$k_f$	4.531	6.736	2.290	4.172	1.176	5.418
	$r^2$	0.9364	0.7781	0.2506	0.9037	0.8056	0.8278
Temkin	$k_T$	0.9556	1.590	0.8768	1.246	0.9071	1.515
	$b_T$	-4.886	-1.580	-5.101	-6.115	-4.834	-1.17
	$r^2$	0.1978	0.6906	0.6018	0.5346	0.0469	0.0881
Experimental	$Q_e$ (mg/g)	2.943	9.044	6.266	15.53	7.245	15.03

without interaction between adsorbed molecules. Freundlich and Temkin isotherm models could not be used to describe the adsorption.

**Time dependent and kinetic models:** The adsorption rate trends for Pb(II) and Cu(II) ions onto PPS, ATPPS and BTPPS adsorbents are shown in Fig. 6a-c. It was observed that the removal rate for both adsorbates was rapid within the initial 30 min of adsorption process, thereafter the rates slowed down. The initial rapid rate (within 30 min) is linked to vast empty adsorption sites on adsorbents. Once most adsorption sites were saturated, ease accessibility to adsorbents surface was restricted. This resulted in interstitial spaces and slowed the rate after 30 min.

In this study three models; pseudo-first order (PFO), pseudo-second order (PSO) and intra-particle diffusion (IPD) were used

to determine the kinetics of removal of Pb(II) and Cu(II) ions onto PPS, ATPPS and BTPPS. This helps in predicting the followed adsorption mechanisms for Pb(II) and Cu(II) onto adsorbents. Various applied models and corresponding parameters are shown in Table-3. A best fit is determined by correlation coefficient ( $r^2$ ) value closer to one and the calculated adsorption capacity ( $q_e$ ) value closer to the experimental value for either PFO or PSO. It was observed that PFO was the best fit than PSO in all regards. The ( $r^2$ ) values for PFO were closer to 1 ranged between (0.8513-0.9918) and the determined ( $q_e$ ) values were closer to the experimental values. PSO ( $r_2$ ) values lacked unity therefore, it could not be used to describe neither Pb(II) or Cu(II) adsorption. A best fit to PFO model indicates that the followed mechanism for Pb(II) and Cu(II) removal was more inclined towards physisorption.

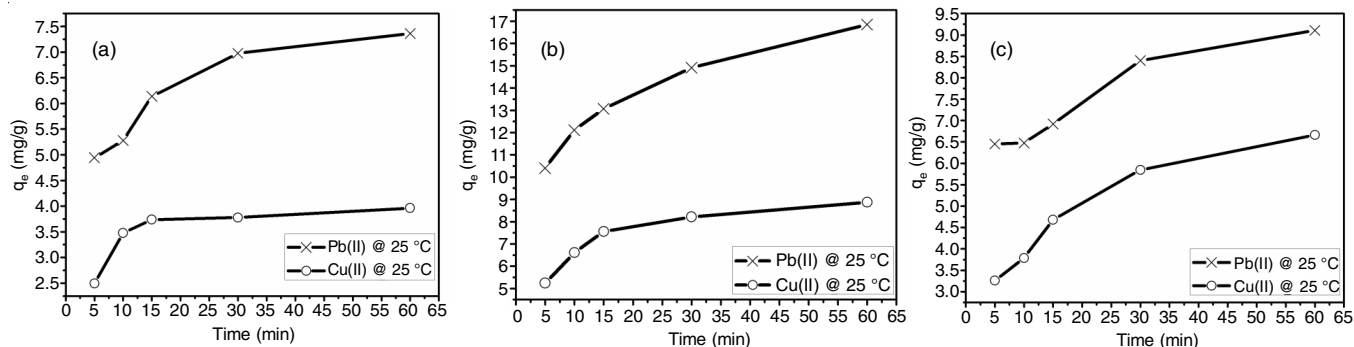


Fig. 6. Time dependent studies on adsorption of Pb(II) and Cu(II) onto (a) PPS, (b) ATPPS and (c) BTPPS

TABLE-3  
KINETIC MODELS PARAMETERS

Kinetic model	Parameter	PPS		ATPPS		BTPPS	
		Cu(II)	Pb(II)	Cu(II)	Pb(II)	Cu(II)	Pb(II)
PFO	$q_e$ (mg/g)	3.890	6.920	8.454	15.38	6.361	8.164
	$K_1$ ( $\text{min}^{-1}$ )	0.2108	0.1931	0.1701	0.1807	0.1015	0.2322
	$r^2$	0.9918	0.8513	0.9674	0.8686	0.9463	0.9434
PSO	$q_e$ (mg/g)	18.41	7.825	20.36	10.83	49.31	27.56
	$K_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	0.2865	0.1629	0.1369	0.0742	0.2063	0.1338
	$r^2$	0.0402	0.0782	0.0513	0.0950	0.0667	0.0440
IPD	C (mg/g)	2.5487	4.0703	4.5693	8.354	1.9812	5.0294
	$K_i$ ( $\text{g g}^{-1} \text{min}^{1/2}$ )	0.6868	1.223	1.463	2.703	1.0084	1.485
	$r^2$	0.7700	0.4354	0.7985	0.1054	0.7567	0.5592
EPA	%	37.2	44.7	48.5	59.4	70.2	44.8
ESA	%	62.8	55.3	51.5	49.6	29.8	55.2
Experimental	mg/g	3.961	7.361	8.873	16.84	6.660	9.1048

\*EPA = Estimated pore adsorption of IPD; \*ESA = Estimated surface adsorption of IPD.

Intraparticle diffusion (IPD) kinetic model parameter,  $C$  (mg/g), was used to determine the nature of the adsorption (surface or pore adsorption). The values for  $C$  suggest the amount of the adsorbate on the adsorbents surface. Weber and Morris [25] stated that if the value equals the experimental  $q_e$  value, then surface adsorption accounted for the bulk of the cations removal from solution. It is observed in Table-3 that ESA (estimated surface adsorption) dominated most adsorption processes, while EPA (estimated pore adsorption) occurred in Pb(II) onto ATPPS and Cu(II) onto BTPPS.

**Dosage effect:** Fig. 7a-c show the removal capacity increased as the adsorbent dosage increased from 0.1 to 0.5 g. The increase in removal capacity could be linked to abundant active sites that participated at higher adsorbent dose; this also decreased the competitiveness between metal ions for binding sites therefore this led to increased removal.

**Temperature effect and thermodynamic parameters:** Temperature effect on the removal of Pb(II) and Cu(II) was evaluated at varied temperatures (25, 30, 40, 50 and 60 °C). There was no significant increase in Pb(II) removal as temperature increased from 25 to 30 °C in all adsorbents (Fig. 8a-c). However, from 40 to 60 °C an immense increase was observed, Olu-Owolabi *et al.* [26] stated that increased removal at elevated temperature was linked to the fact that the repulsive forces which act as barriers to the adsorption process are restricted as temperature increased leading to easier adsorption. The removal of Co(II) increased with increasing temperature from 25 to 60 °C.

Thermodynamic parameters *i.e.* Gibbs free energy ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were determined as shown in Table-4. The obtained positive values for  $\Delta S^\circ$  according to Mohubedu *et al.* [27] indicated an increase in degree randomness of adsorbate ions, while negative value

Adsorbent	$\Delta H^\circ$ (KJ mol <sup>-1</sup> )		$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	
	Cu(II)	Pb(II)	Cu(II)	Pb(II)
PPS	-84.16	88.20	32.62	-32.38
ATPPS	-197.8	-197.4	66.04	-62.92
BTPPS	-216.1	-224.1	70.88	71.74

Temp. (°C)	$\Delta G^\circ$ (KJ mol <sup>-1</sup> )					
	PPS		ATPPS		BTPPS	
	Cu(II)	Pb(II)	Cu(II)	Pb(II)	Cu(II)	Pb(II)
25	-7.955	-6.187	-6.747	-4.114	-6.527	-4.184
30	-7.435	-6.223	-6.596	-3.871	-5.378	-4.139
40	-5.270	-3.985	-4.009	-0.2920	-3.296	-2.049
50	-5.107	-3.472	-1.954	-1.767	-0.9364	-0.2950
60	-5.229	-3.571	0.2468	-1.963	-0.9865	-3.783

suggests that adsorption involved associative mechanism. The calculated negative  $\Delta G^\circ$  values indicated that the processes were spontaneous and feasible.

**Reusability test:** Economic benefits of PPS, ATPPS and BTPPS were estimated by investigating the reusability of the biosorbents. The data of five cycles of PPS, ATPPS and BTPPS towards Pb(II) and Cu(II) ions adsorption/desorption are shown in Fig. 9a-c. The Pb(II) and Cu(II) sorption capabilities in Fig. 9a-c exhibit a slow downward trend with increasing cycle numbers to five. It is also observed that Pb(II) decreased from 94.2 to 88.2 % and Cu(II) decreased from 78.9 to 69.5 % for PPS, while in case of ATPPS Pb(II) decreased from 98.2 to 88.4 % and Cu(II) decreased from 85.3 to 75.3 %. And Pb(II) decreased from 99.2 to 92.0 % and Cu(II) decreased from 90.3 to 78.2 % for BTPPS. At the end of 5th cycle, PPS, ATPPS and BTPPS adsorbents retained more than 88% of their initial

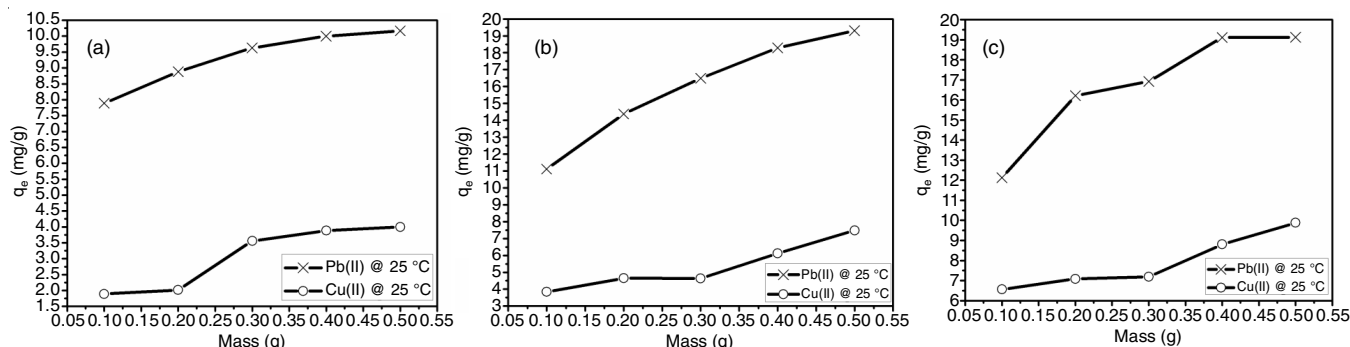


Fig. 7. Adsorbent dosage effect on sorption of Pb(II) and Cu(II) onto (a) PPS, (b) ATPPS and (c) BTPPS

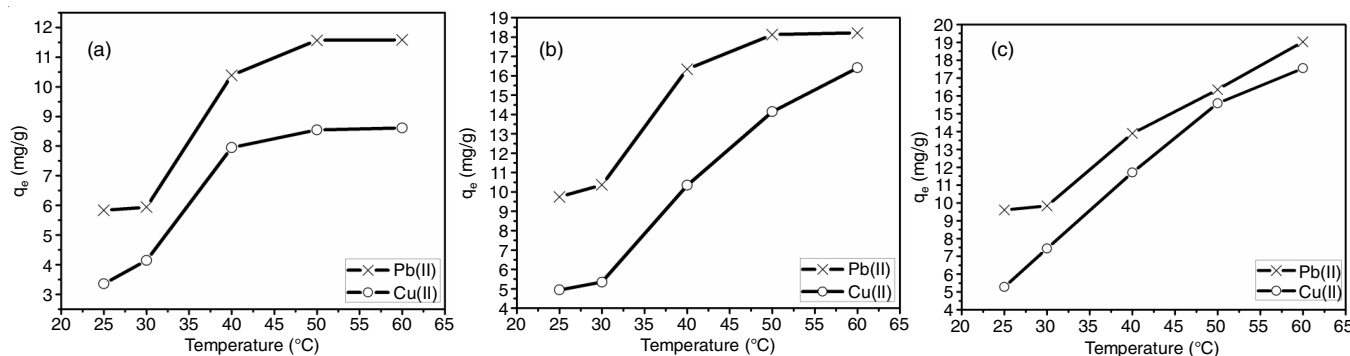


Fig. 8. Temperature effect studies on adsorption of Pb(II) and Cu(II) ions on (a) PPS, (b) ATPPS and (c) BTPPS

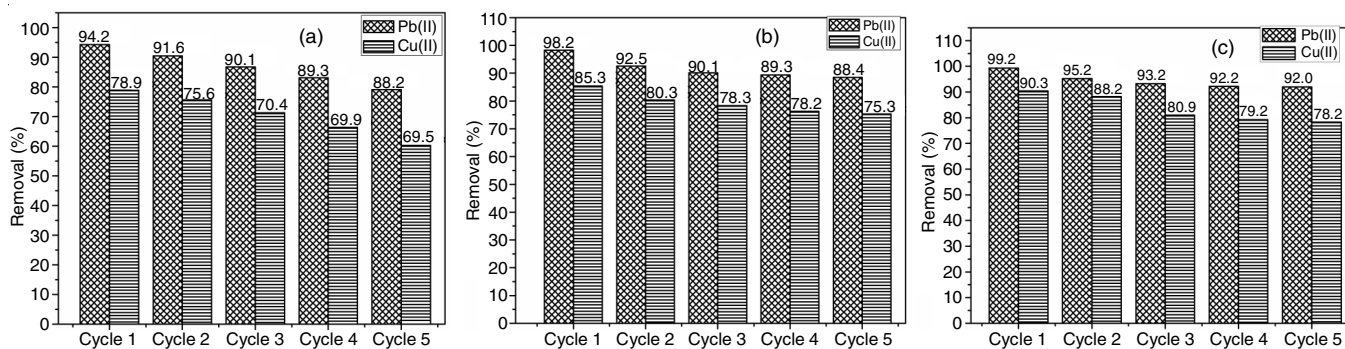


Fig. 9. Reusability data of (a) PPS, (b) ATPPS and (c) ATPPS adsorbents

TABLE-5  
BIOSORPTION STUDY OF THE PPS, ATPPS AND BTTPS WITH THOSE OF SIMILAR BIOMASS ADSORBENTS

Adsorbent	Pollutant	$q_c$ (mg/g)	Ref.
Mango stone	Pb(II)	16.0	[7]
Kaolinite- <i>Carica papaya</i> composite	Cd(II)	1.9	[28]
Bentonite- <i>Carica papaya</i> composite	Cd(II)	10.9	[29]
<i>Carica papaya</i> leaves	Pb(II)	11.13	[30]
<i>Anacardium occidentale</i> leave	Pb(II)	11.53	[30]
<i>Borrassus aethiopicum</i> (African fan palm)	Pb(II)	12.19	[31]
Feldspar- <i>Carica papaya</i> composite	Cd(II)	12.6	[32]
PPS	Cu(II)	2.943	This study
ATPPS	Cu(II)	6.266	This study
BTTPS	Cu(II)	7.245	This study
PPS	Pb(II)	9.044	This study
BTTPS	Pb(II)	15.03	This study
ATPPS	Pb(II)	15.53	This study

Pb(II) and Cu(II) sorption capacities. The reusability results suggest that the PPS, ATPPS and BTTPS adsorbents may be reusable in wastewater treatment.

**Comparative study:** In order to estimate the effectiveness of PPS, ATPPS and BTTPS as adsorbents for water treatment, their biosorption capacities for Cu(II) and Pb(II) ions were compared with other biomaterials previously reported for this purpose. The maximum capacities of biomaterials reported in this work and other literature are given in Table-5. ATPPS and BTTPS biosorption were better than other biosorbents reported in literature, the best biosorbent in this study was ATPPS towards Pb(II) ions (15.53 mg/g) followed by BTTPS (15.03 mg/g). This comparative study showed that ATPPS and BTTPS biosorbents were better than similar biosorbents.

## Conclusion

The acid treated paw-paw seeds (ATPPS) and base treated paw-paw seeds (BTTPS) were prepared by reflux of paw-paw seeds (PPS) with 1M acid HCl:HNO<sub>3</sub> (1:1) and 1 M base NaOH, respectively. Both ATPPS and BTTPS adsorbents exhibited higher biosorption capability and porous surface than the raw material. The removal of both metal ions by ATPPS and BTTPS was more inclined towards physisorption. Adsorption rate rapidly increased within the starting 30 min then afterwards slowed down. Experimental maximum capacities ( $Q_c$ ) in pre-treated materials was higher 15.53 and 15.03 mg/g towards Pb(II) ions for ATPPS and BTTPS respectively, this implied ATPPS is a better adsorbent towards Pb(II) ions. For Cu(II) ions removal, it was 6.266 and 7.245 for ATPPS and BTTPS respectively, implying BTTPS was a better adsorbent towards

Cu(II) ions. Thermodynamic parameter ( $\Delta G^\circ$ ) gave negative values indicating that the biosorption processes were spontaneous and feasible. Higher and more rapid biosorption rates were observed for Pb(II) ions than Cu(II) on all adsorbents. ATPPS and BTTPS biosorption capacities for Pb(II) and Cu(II) removal were better than other adsorbents reported in literature.

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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