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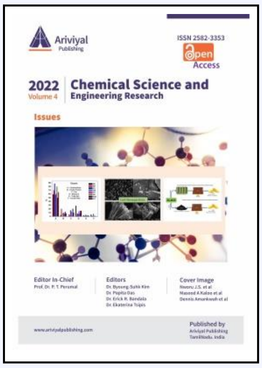

Kinetic, Equilibrium and Thermodynamics Study of the Adsorption of Pb(II), Ni(II) and Cu(II) Ions from Aqueous Solution using *Psidium Guajava* (Guava) Leaves

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Abstract: The kinetic, equilibrium and thermodynamic study of the adsorption of Pb^{2+}, Ni^{2+} and Cu^{2+} ions from aqueous solution by the leaf biomass of *Psidium Guajava* (Guava) leaves were investigated at different experiment condition. Optimum condition of pH, Contact time, biomass dosage, initial metal ion concentration and temperature were determined, the maximum adsorption capacity was found to be 9.88, 9.5 and 4.21 mg/g, for Pb^{2+}, Ni^{2+} and Cu^{2+}, respectively. The kinetic studies indicated that the adsorption process of the Pb^{2+}, Ni^{2+} and Cu^{2+} ions followed the pseudo-second-order model with R^2 value of 1.0, 1.0 and 0.674 respectively. Equilibrium studies showed that the adsorption of Pb^{2+}, Ni^{2+} and Cu^{2+} are well represented by both Freundlich and Langmuir isotherms with the Langmuir model given a better fit for Pb^{2+} with R^2 value of 0.990 and Langmuir constant K_L of 4.878, while Freundlich model was better fit for Ni^{2+} and Cu^{2+} ions with R^2 value of 0.892 and 0.471 respectively, Freundlich constant K_f value of 1.8923 and 0.0196 and (ΔG^0 -1705.02, -3745.18 and 401.18 $KJmol^{-1}$) showed that the adsorption of pb^{2+} and Ni^{2+} are spontaneous, While Cu^{2+} are non-spontaneous. These finding indicate that the leaves biomass of Psidium guajava could be used for the adsorption of Pb^{2+}, Ni^{2+} and Cu^{2+} ions from industrial effluents.

Keywords: *Psidium Guajava* (GUAVA) Leaves; Kinetic; Equilibrium; Thermodynamics Study; Adsorption of Metals

1. Introduction

Heavy metals are defined basically as metallic elements that have a relatively high density compared to water. With the assumption that heaviness and toxicity are inter-related, heavy metals also include metalloids, such as arsenic, that are able to include toxicity at low level of exposure in recent years, there has been an increasing ecological and global public health concern associated with environmental contamination by these metals.[1] Lead has been known since ancient time. It is naturally present in the earth's crust in small concentration. Lead is a well-known highly toxic metal and a cumulative poison; the common industries that deal with lead are the battery manufacturing. Motor vehicle repair cable making and metal grinding industries.[2] Nickel is silvery-white hard, malleable, and ductile metal. It is of the ion group and it takes on a high polish. It is a fairly good conductor of heat and electricity. In its familiar compounds, most nickel compounds are blue or green. Nickel dissolves slowly in dilute acids but, like iron, becomes passive when treated with nitric acid. Finely divided nickel adsorbs hydrogen.[3] Copper is a chemical element with the symbol Cu (from Latin: cuprum) and atomic number 29. It is a soft, malleable, and ductile metal with very high thermal and electrical conductivity. A freshly exposed surface of pure copper has a pinkish-orange color. Copper s used as a conductor of Heat and electricity, as building material, and as a constituent of various metal alloys, such as sterling silver used in jewellery, cupronickel used to make marine hardware and coins, and constantan used in stain gauges and thermocouples for temperature measurement. *Psidium guaiava*, the common guava, yellow guava, or lemon is an evergreen shrub or small tree native to the Caribbean, Central America and South America. It is easily pollinated by insects; when cultivated, it is pollinated mainly by the common honey bee, apis mellifera.[4] *Psidium guajava* (guava) is well known tropic tree which is abundantly grown for fruit. Many countries have a long history of using guava for medicinal purposes. This plant finds applications for the treatment of diarrhoea, dysentery, gastroenteritis, hypertension, diabetes, caries and pain relief and for improvement in locomotors coordination. Its leaf's extract is being used as a medicine in cough, diarrhoea, and oral ulcers and in some swollen gums wound. Its fruit is rich in vitamins A, C, iron, phosphorus and calcium and minerals. It contains high content of organic and inorganic compounds like secondary metabolites e.g. antioxidants, polyphenols, antiviral compounds, anti-inflammatory compounds.[4]

Aim: The research is aimed at exploring the potential of Psidium guajava for the removal of Pb^{2+}, Ni^{2+} and Cu^{2+} ions from aqueous solution for possible use as adsorbent for heavy metals removal from the environment.

Objective: The Specific objectives of the research are,

- To establish optimum condition such as (concentration of pH, temperature, time and adsorbent dose) for the adsorption of Pb^{2+}, Ni^{2+} and Cu^{2+} ions by *Psidium guajava*.
- To Study and understand the mechanism and kinetics of the adsorption process.
- To determine the thermodynamic of the adsorption process.
- To study the degree of interaction between the *Psidium guajava* leaves and the adsorbent and investigate the functional groups responsible for the adsorption by the leaves FTIR.

2. Material and Method

2.1. Material

The main material used in this research is *psidium guajava* (guava) leaves.

2.1.1. Apparatus/Instruments

The apparatus that were used for this work include:

PH meter (PH-98081, RoHS). Incubator shaker (S1500, start equipment). Lab oven (MC21438BPP, LG). Weighing balance (GF-2000-EC, A&D Instrument LTD). Micrometre sieve (140mm, Standard 425 MIC, SETHI). Crusher (Mortar & pestle). Filter paper (110mm, Whatman No1). Fourier transforms infrared spectroscopy FTIR. (PerkinElmer spectrum version, 10.03.09). Atomic Adsorption Spectroscopy (AAS Thermo Scientific).

2.1.2. Chemicals and Reagents

All chemicals and reagent was used in this study were of analytical grade (Merck Germany) $Pb(NO_3)$, $Ni(NO_3)_2$ $6H_2O$, $Cu(NO_3)_2$ $3H_2O$ and (The science company Assay: 97%) NaOH, HNO_3.

2.1.3. Preparation of Solutions

1000 g/l stock solution of $Pb(NO_3)_2$, $Ni(NO_3)_2$ and $Cu(NO_3)_2$ were prepared according to standard procedures by dissolving 1.9530 g and 3.7980 g each in 1L dionize water and serial dilution method from the stock solution to obtain different concentration by using the formula below

$$C_1V_1 = C_2V_2$$

Where C_1 is the concentration of stock solution V_1 is the volume of the stock solution, C_2 is the concentration of the dilute solution and V_2 is the volume of the dilute solution. Preparation of 1 m of HNO_3: 0.1 M of NaOH was prepared by dissolving 4.00 g of NaOH into 1000 ml volumetric flask and made up to mark with deionize water. Preparation of 1 m of HNO_3: 0.1 M of NO_3 was prepared by diluting 6.3 ml with 1000 ml deionize water in volumetric flask.

2.2. Sample Collection and Preparation

The *psidium guajava* (guava) leaves were used for this research work. The leaves were collected from Hammadu Kafi, Akko local government, Gombe State. The guava leaves was washed with tap water to remove dirtied and other particulate matter and then rinsed with distilled water. The sample leaves was oven dry about 100^{o}C for 24 hrs. The dried leaves were ground and then sieve to uniform size particles (140 µm). The prepared adsorbent was stored in a clean air-tight bottle until time of usage.

2.2.1. Sample Characterization

The adsorbent surface functional group loaded with adsorbent and unloaded was identified with Fourier Transform Infrared (FT-IR) spectroscopy; was used as background material.

2.3. The Batch Adsorption Experiment

Batch adsorption experiment was carried out to determine the effect of initial metal concentration, PH, adsorbent dose, temperature and contact time.

Effect of initial metal ion concentration: The effect of initial metal concentration adsorption of Pd^{2+}, Ni^{2+} and Cu^{2+} ion on *psidium guajava* was determined at different concentration of 40 ppm, 30 ppm, 25 ppm, 15 ppm and 10 ppm keeping the pH at 6, room temperature (25^{o}C). The pH was adjusted using 0.1 M HNO_3 and 0.1 M NaOH. 50 ml solution of Pd^{2+}, Ni^{2+} and Cu^{2+} ion were transferred into 100 ml conical flasks, 0.5 rpm. The solution was filtered using Whatman No 1 filter paper and filtrate was analysed with AAS.[5]

Effect of pH on the adsorption: The effect of PH ON the process of adsorption Pd^{2+}, Ni^{2+} and Cu^{2+} ion with *psidium guajava* was determined at different pH values of 3, 5, 6, 8 and 9 and optimum concentration of metal ions of 15 ppm Pb, and 25 ppm Ni and 40 ppm at temperature (30^{o}C). The PH was adjusted using 0.1 M HNO_3 and 0.1 M NaOH. 50 ml solution of Pd^{2+}, Ni^{2+} and Cu^{2+} ion were transferred into 100 ml conical flask, 0.6 g of *psidium guajava* sample were added and the solutions was shaken for 40 min at 150 rpm, the solutions were filtered Whatman No 1 filter paper and filtrate was analysed with AAS.[5]

Effect of adsorbent dose on the metal adsorption: Effect of adsorbent dose on Pd^{2+}, Ni^{2+} and Cu^{2+} ion by *psidium guajava* was determined at different amount of dosage of 0.2, 0.4, 0.6, 0.8 and 1.0 g, under optimum initial concentration of 15 ppm for Pb, and 25 ppm for Ni and Cu, pH of 3 for Pb and 9 for Ni and Cu was suspended in 50 ml of Pd^{2+}, Ni^{2+} and Cu^{2+} ion at room temperature (25^{o}C) the Pd^{2+}, Ni^{2+} and Cu^{2+} ions solutions were transferred into 100 ml contain flasks and left to shake for 40 min at 150 rpm the solution were filtered using Whatman No 1 filter paper and the filtrate was analysed with AAS.[5]

Effect of contact time on the adsorption: The effect of contact time on the adsorption process of Pd^{2+}, Ni^{2+} and Cu^{2+} ion by *Psidium guajava* was studied at the following time intervals 30, 50, 70, 90 and 110 min at optimum concentration of 15 ppm for Pb, and 25 ppm for Ni and Cu, pH of 3 for Pb 9 for Ni and Cu, adsorbent dose of 1g at room temperature (25^{o}C). 50 ml of solution of Pd^{2+}, Ni^{2+} and Cu^{2+} ion were transferred into 100 ml conical flasks. The solution was shaken for 40 min at 150 rpm at different time intervals. The solution was filtered Whatman No 1 filter paper and filtrate was analysed with AAS.[5]

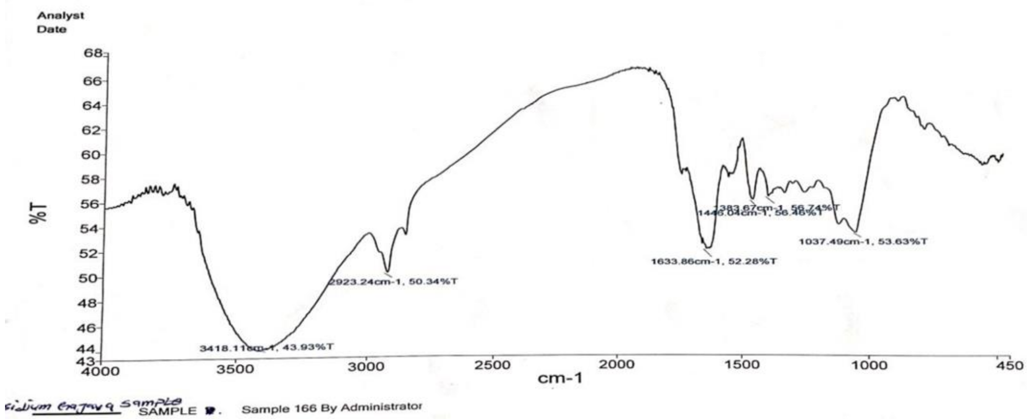

Fig. 1. IR spectra unloaded sample.

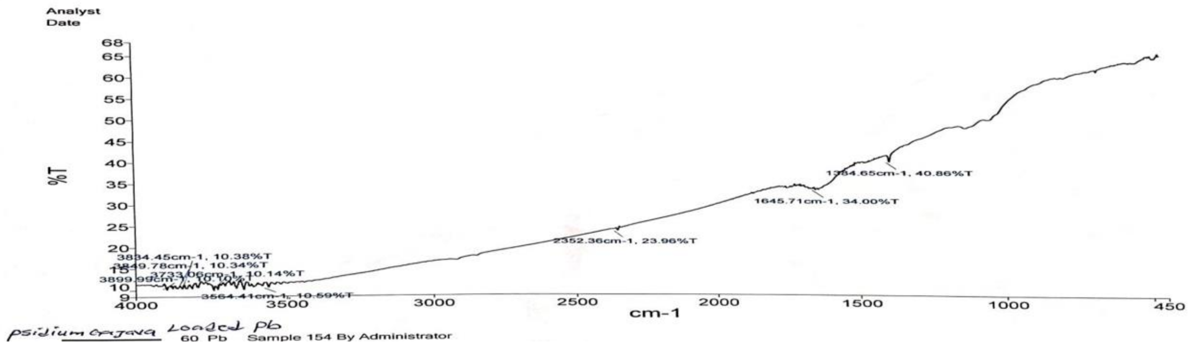

Fig. 2. FT-IR spectra loaded with Pb^{2+} ions.

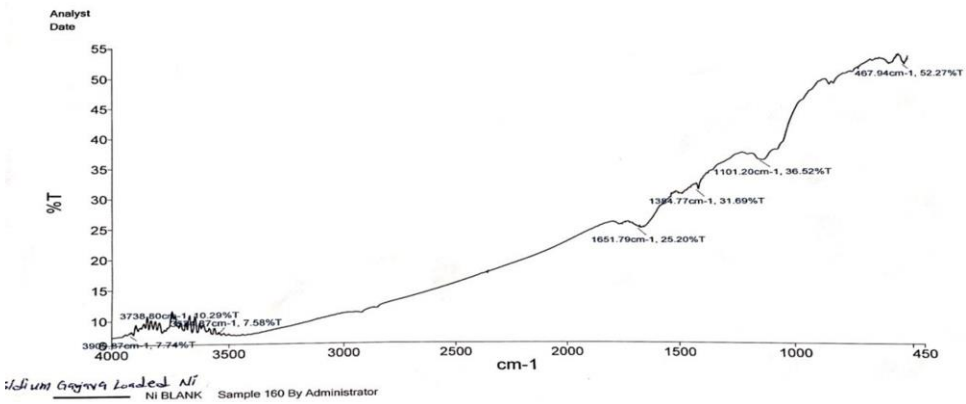

Fig. 3. FT-IR spectra loaded with Ni^{2+} ions.

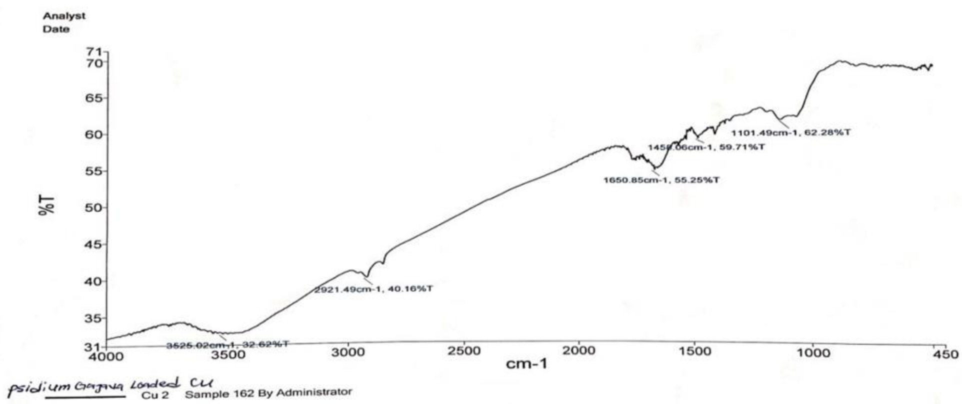

Fig. 4. FT-IRspecta loaded with Cu^{2+} ions.

Table 1. Result of the FT-IR analysis (Frequency (cm^{-1}))

Before adsorption	After adsorption Pb^{2+}	After adsorption Ni^{2+}	After adsorption Cu^{2+}	Functional group	Family of compounds
3443	3444	-	-	O-H stretching	Alcohols
2923	2924	2924.14	1650.76	C-H stretching	Alkanes
1633	1629	1634.01	1633.78	C=C stretching, C=N	Amides, Alkenes, Aromatics Imines.
1384	1384	1384.60	1384.45	O-H Bending	Aromatic, Imines
1033	-	1034.	1034.40	C-O stretching	Ethers, Esters, Alcohols,
1319	1320	-	-	NO_2 Stretching	Nitro.
1241	1251			C-O stretching	Ether, Esters, Alcohols

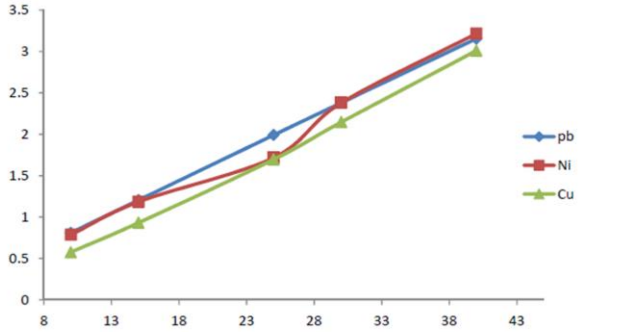

Fig. 5. Plots of quantity adsorbed against initial metal concentration on Pb^{2+}, Ni^{2+} and Cu^{2+} ions by *Psidium Guagjava* leaves at fixed (adsorbent dose of 0.6 g, PH =6.0, contact time = 40 min and Temp. of 25°C)

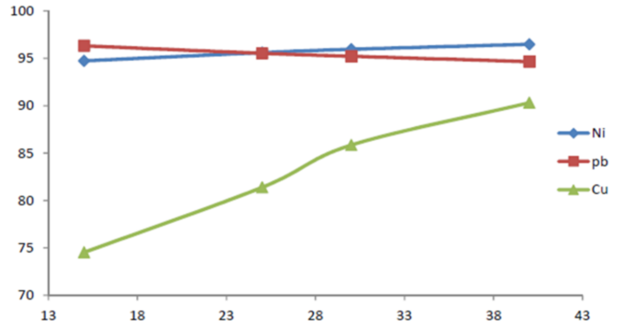

Fig. 6. Plots of percentage adsorption against initial metal concentration of Pb^{2+}, Ni^{2}+ and Cu^{2+} ions by *Psidium Guagjava* leaves at fixed (adsorbent dose 0.6 g, PH 6.0, contact time = 40 min and Temp. of 25°C)

Effect of temperature on the adsorption: The effect of temperature on the adsorption process of Pd^{2+}, Ni^{2+} and Cu^{2+} ion was studied at the following temperatures 30, 40, 50, 60 and 70°C at optimum pH of 3 for Pb and 9 for Ni and Cu. 50 ml of 15 ppm of Pd, 25 ppm for Ni and Cu were transferred into 100 ml conical flaks. 0.6 g of the adsorbents was added to Pd^{2+}, Ni^{2+} and Cu^{2+} ion the solution were shaken at 150 rpm for different temperatures, contact time of 110 min for Pb and 110 min for Ni and Cu. The solutions were filtered and the filtrated was analysed with AAS.[5]

2.4. Adsorption Isotherms of the Metals ions by the Leaves of Psidium Guajava

Data obtain from the adsorption study of were tested with freudlich adsorption isotherm and Langmuir adsorption isotherm to have a satisfactory description of the equilibrium state between the two phase in order to successfully represent the dynamic behavior of metals ions solution to solid (leaves) phase. Batch mode adsorption studies were carried out at 25 ± 1°C by varying the concentration metals ions.

3. Results and Discussions

3.1. FT-IR Analysis of Unloaded and Pb^{2+}, Ni^{2+} and Cu^{2+} ions-Loaded Leave of Psidium guajava

In order to ascertain the functional group that are the responsible for the adsorption of the metal ions in this study and possibly to explain the mechanism of the adsorption, FT-IR study was carried out on both the unloaded and the metal loaded adsorbent at the optimum pH (Table 1, Figs. 1 to 4). The FT-IR spectrum (Fig. 1) of the unloaded biomass shows a number of distinct absorption bands indicating the complex nature of the leaves.

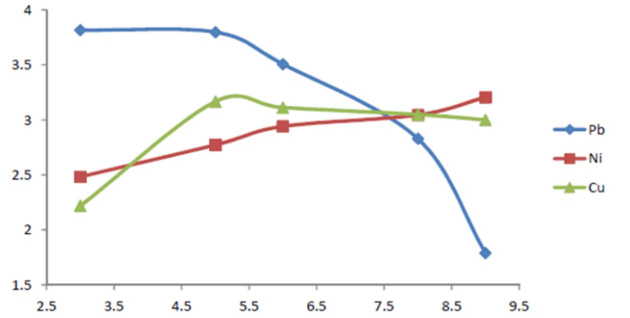

Fig. 7. Plots of quantity adsorbed against PH of Pb^{2+}, Ni^{2+} and Cu^{2+} ions by *Psidium Guagjava*.

3.2. Effect of Initial Metal Concentration

The amount of Pb^{2+}, Ni^{2+} and Cu^{2+} ions absorbed by Psidium Guajava leaves at equilibrium (Qe). The results indicate increased in adsorption capacity from 0.44 to 2.36 mg/g, 0.29 to 1.87 mg/g and 0.27 to 1.79 mg/g. Fig. 5 shows high relationship between the adsorption capacity and the metal ions concentration of the solution. The data indicate that adsorption capacity is increasing in initial concentration results in increase in number of available molecules per binding of molecules to the adsorbent.[2,6]

The initial concentration provides an important driving force to overcome all mass transfer resistances of the metal ions between the aqueous and solid phases. Hence, at higher initial concentration of metal ions it will enhance the adsorption process. Fig. 6 indicate the Pb^{2+} ions removal efficiency increased from 97.4% to 97.5% at the concentration of 50 ppm to 10 ppm after which the optimum was reached. This shows the optimum adsorption capacity is 2.36 mg/g at the concentration of 10 ppm for Pb^{2+}, the percentage removal of Ni^{2+} ions increased from 94% to 96.5% at the concentration of 10 ppm to 50 ppm which shows that the optimum adsorption capacity is 1.87 mg/g at concentration of 50 ppm for Ni^{2+}, and the percentage

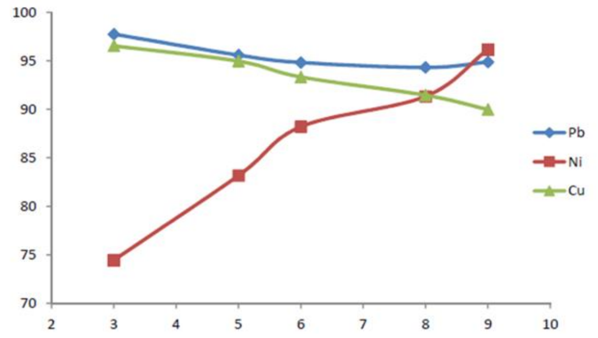

Fig. 8. Plots of percentage adsorption against PH of Pb^{2+}, Ni^{2+} and Pb^{2+} ions by *Psidium guajava*.

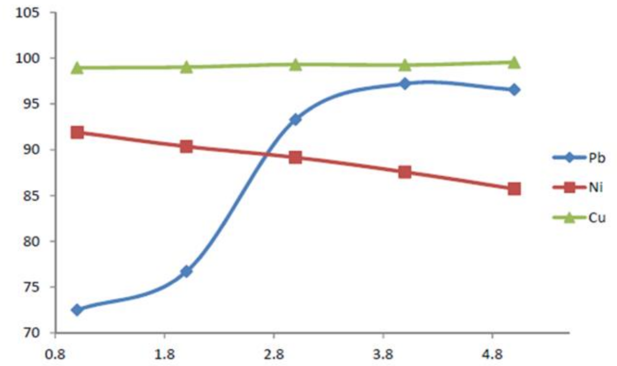

Fig. 10. Plots of percentage adsorption against adsorbent dose on adsorption of Pb^{2+}, Ni^{2+} and Cu^{2+} ions by *Psidium guajava.*

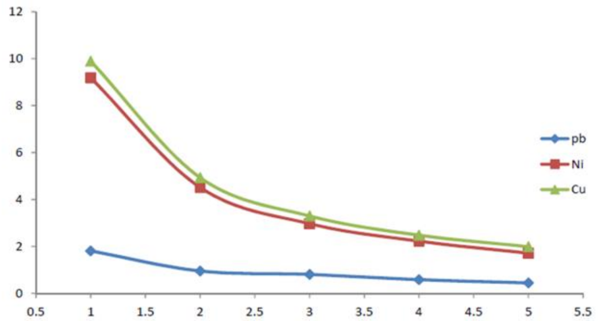

Fig. 9. Plots of quantity adsorbed against adsorbent dose on adsorption of Pb^{2+}, Ni^{2+} and Cu^{2+} ions by *Psidium guajava*.

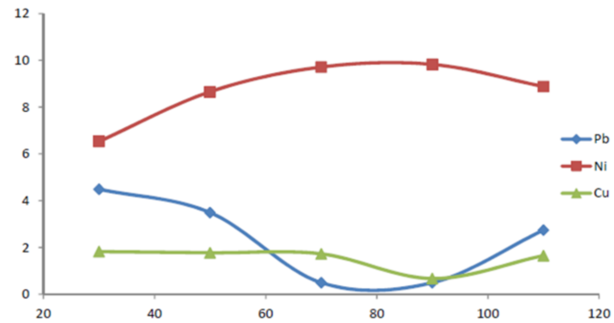

Fig. 11. Plots of quantity adsorbed against contact time on the adsorption of Pb^{2+}, Ni^{2+} and Cu^{2+} ions by *psidium guajava*.

removal of Cu^{2+} ions increased from 65% to 90.5% at the concentration of 10 to 45 ppm. That indicate the optimum adsorption capacity is 1.97 mg/g at 45 ppm for Cu^{2+}.

3.2.1. Effect of pH

The effect on adsorption of *psidium Guajava* leaves was investigate on Pb^{2+}, Ni^{2+} and Cu^{2+} ions at different PH value 3, 5, 6, 8 and 9, at optimum concentration of 40 ppm for lead(II), 10 ppm for Nickel(II) and 40 ppm for Cupper(II), fixed adsorbent dose of 6.0 g contact time of 40 min and Temp 25°C (Fig. 7).

Low percentage of adsorption was observed at PH 8 to 6 for Lead(II), and 3 to 4 for Nickel(II) and 6 to 9 for Copper(II), decrease in percentage of adsorption was observed at PH 8.0 for all metals, the optimum adsorption capacity was observed at PH 4 for Lead(II), with the percentage adsorption of 98.0%, while PH 9 for Nickel(II) with the percentage adsorption of 85% and PH 3 for Copper(II), with the percentage adsorption of 96.5% as shown in Fig. 8. the adsorption of metals ions is depend of PH, adsorption of heavy metals from aqueous solution depends on the properties of adsorbent and molecules of adsorbate transfer from the solution to the solid phase.[6] It has also been observed that adsorption capacities for heavy metals are PH depending. The result shows that high PH favours Lead (II), Nickel (II) and Copper (II) ions adsorption by *Psidium Guajava* leaves. At lower PH concentration of H^+ ions exceed that of metals ions H^+ therefore compete with metals ions for the surface area of the adsorbent, therefore preventing the metals ions from reaching the blinding site of the adsorbent.

3.2.2. Effect of Adsorbent dose on the Adsorption

The influence of adsorbent dose on adsorption capacity *Psidium Guajava* leaves was investigated on Pb^{2+}, Ni^{2+} and Cu^{2+} ions by varying the adsorbent dosage of 2.0, 4.0, 6.0, 8.0 and 1.0 g. Optimum conditions of metal concentration of 30 ppm of Pb^{2+} and 40 ppm for Ni^{2+} and Cu^{2+}, PH of 3 for Pb^{2+} and PH 9 for Ni^{2+} and Cu^{2+}, agitation time of 40 min and temperature of 25°C. The results that were obtained show the percentage removal increased with increase in amount of adsorbent dose. Percentage adsorption of pb^{2+}, Ni^{2+} and Cu^{2+} increased from 68 to 98%, 85 to 92% and 98.8 to 99.6% as shown in Fig. 9. It is also observed that the quantity adsorbed for all the metals ions from 0.2 g to 1.0 g as shown in Fig. 10. This can be explained by the fact that at low dosage concentration, there is limited surface area for adsorption, an increase in dosage results in more surface binding sites.

3.2.3. Effect of Contact Time on Adsorption

The effect of agitation time on adsorption capacity of *Psidium Guajava* leaves was investigated on Pb^{2+}, Ni^{2+} and Cu^{2+} ions solution at different contact time of 30, 50, 70, 90 and 110 min at optimum conditions of metal concentration of 30 ppm of Pb^{2+}, 40 for Ni^{2+} and Cu^{2+}, adsorbent dose of 1.0 g, at temperature of 25°C. The result that was observed in Fig. 11, shows that the percentage removal of Lead (II), increased with increase in contact time, until it reaches equilibrium contact time of 90 min, from 90 min to 110 min no increase in adsorption that was observed. The percentage adsorption (Fig. 12) increase from 78.0 to 93.5% in the early stage of adsorption more number of vacant sites are available for adsorption to precede.

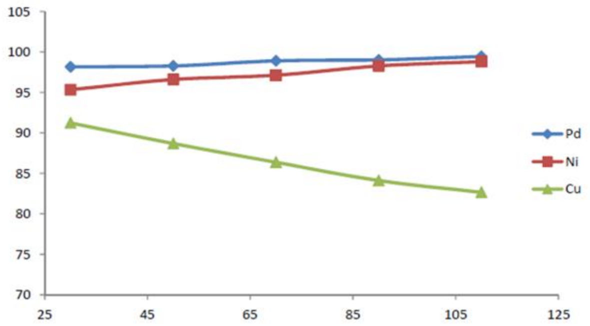

Fig. 12. Plots of percentage adsorption against time on the adsorption of Pb^{2+}, Ni^{2+} and Cu^{2+} ions by *Psidium guajava*.

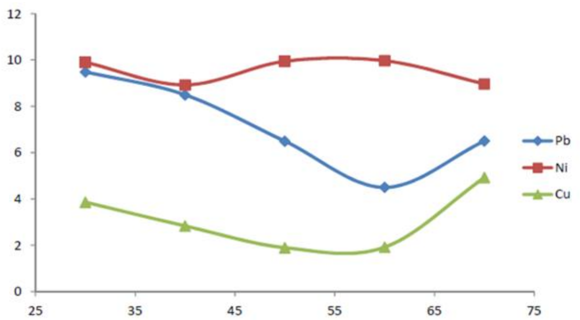

Fig. 13. Plots of quantity adsorbed against temperature on the adsorption of Pb^{2+}, Ni^{2+} and Cu^{2+} ions by *Psidium guajava* At optimum conditions.

As contact as contact time increases the adsorption capacity increase until it reaches optimum, the maximum number of sites that got adsorbed to the metal ions increase sites, thus rate of adsorption remain constant as agitation time increase.

3.2.4. Effect of Temperature on Adsorption

The equilibrium uptake of Pb^{2+}, Ni^{2+} and Cu^{2+} ions by *Psidium Guajava*, Was determined at different temperature of 30, 40, 50, 70 and 90°C, at optimum conditions of metal concentration of 10 ppm for Lead (II) 40 ppm for Nickel (II) and Copper (II). PH 6 and PH 8 for Ni and Cu, adsorbent dose of 1.0 g, agitation time of 110 for Pb and Ni and 60 for Cu the rate of adsorption was affected by temperature as shown in Fig. 13.

The percentage adsorption (Fig. 14) of lead(II) decrease with increase in temperature from 9.5% to 8.5% as the temperature 70°C. percentage adsorption of Ni increase from 4% to 5.6% at temperature of 25°C to 70°C, while the percentage adsorption of Cu was observed to be decrease from 25% to 73% between the temperature of 25°C to 730°C these shows that adsorption is endothermic up to the optimum temperature because the extend of adsorption decrease with increase in temperature (Adebayo et al., 2012).[6] The magnitude of increase declines as temperature increase from 40°C to 60°C. The slight decrease in adsorption with increase in temperature can be attributed to the attractive forces between adsorbent surface area and metal ions. The attractive forces at higher temperatures are likely to be weakened and the adsorption decreases as reported by [7] after studying the bio sorption of heavy metals from aqueous solutions by *saccharomyces Ceresidae*.

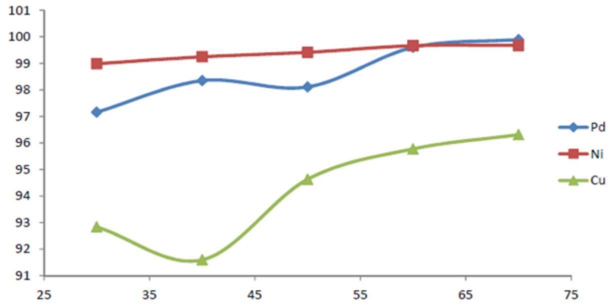

Fig. 14. Plots of percentage adsorption against Temperature on the adsorption of Pb^{2+}, Ni^{2+} and Cu^{2+} ions by *Psidium guajava*.

Table 2. Kinetics Parameters of Various Adsorbates

Absorbates	Pb(II) ions	Ni(II) ions	Cu(II)
Pseudo-first Order			
K_1	0.0392	0.0161	0.0057
qe	0.5046	0.0944	0.6714
R^2	0.940	0.942	0.911
Pseudo-second Order			
K_2	0	0	0.0265
qe	0.4990	0.010	0.4537
R^2	1	1	0.674

3.3. Adsorption Isotherms

Analysis of isotherm is very important for designing the adsorption process. The experimental data were analysed with Langmuir and Freundlich as the two most commonly use isotherm models. Langmuir adsorption isotherm models the monolayer coverage of the adsorption surfaces and assumes that sorption take places on a structurally homogeneous surface of the adsorbent the linearized equation is given in equation (10). Freundlich and Langmuir isotherm model was used to describe the equilibrium data. The Langmuir isotherm constant K_1 and Q_0 were calculated from the slope and intercept of the plot between 1/qe and 1/Ce. The Langmuir isotherm showed good fit to the experiment data with high correlation coefficient in case of Pb^{2+} ion with R^2 values = 0.970, 0.989 For Ni^{2+} and 0.47 for Cu^{2+} ions as shown in (Table 2). Q_0 and K_1 were calculated from the slope and intercept respectively. Freundlich isotherm best fit the experiment data of nickel(II) and copper(II) with a R^2 value of 0.990 for Lead, 0.989 for Nickel and 0.903 for Copper ions, Freundlich constants K_f and 1/n were calculated from the slope and intercept of the straight line of the plot of logqe versus logce. The magnitude of n gives a measured of favourable adsorption. Similar finding was reported by [8] when demining the adsorption of lead and copper ions from aqueous effluents on rice husk ash in dynamic system.

3.4. Adsorption Kinetics

Kinetics model were applied to test for the experimental data in order to check the mechanism of adsorption of the metals ions by *Psidium Gujava* leaves and the potential rate controlling steps mass transport and chemical reaction. Pseudo first order and pseudo second order kinetics model were tested.

Table 3. Thermodynamic parameters for the adsorption of Pb^{2+}, Ni^{2+} and Cu^{2+} ions on *Psidium Guajava* leaves

Adsorbates	ΔH (KJ/mol)	ΔS (KJ/mol/K)	ΔG	R^2
Pb(II)	1173.14	0.393	-1705.02	0.604
Ni(II)	1373.42	0.698	-3745.25	0.619
Cu(II)	-1512.81	-4.997	401.18	0.900

3.4.1. Pseudo First-Order Equation

The adsorption kinetics is being described by a pseudo first-order equation. The linearized form of the equation is given in equation (13). From the studied initial concentration, the rate constant (K_1) and theoretical equation of adsorption capacities (qe) was calculated from the slope and intercept of the linearized plots of (qe-q1) against t as shown in (Table 3). The correction coefficient (R^2) for the Lead (II), Nickel (II) and Copper (II) of the linear plots are 0.940, 0.989 and 0.911. Which indicate the data fit well to pseudo first order model? The calculated values of K_1 and qe for the Lead (II), Nickel (II) and Copper (II) are 0.5056, 0.0944, 0.6714 min^{-1} and 0.0392. 0.0161, 0.0057 mg g^{-1} in addition the theoretical and experimental qe values are not in good correlation with each other, therefore it could be suggested that the adsorption of all the metals ions did not fit pseudo first-order model when compare with the R^2 values of pseudo second-order model and calculated value of qe.

3.4.2. Pseudo Second-Order Equation

The experimental data was also applied to the pseudo-second order kinetic model gives in equation (16). The fit of this of this model was controlled by each plot of t/qe versus t. it can be seen from the results that R^2 values obtained for Pb^{2+}, Ni^{2+} and Cu^{2+} ions are higher than those obtained from pseudo second-order model best fit adsorption of Lead(II), Nickel(II) and Copper(II) respectively, the calculated K_2 and qe are 0.4990, 0.010, 0.4537 min^{-1} and 1, 1, 0.674 mg g^{-1}. Additionally, the theoretical and experimental qe values are in good correlation with each other. Therefore, followed pseudo second- order process, It was also adsorption using natural clay, pseudo second-order model is based on the adsorption capacity of solid phase and indicating that rate-limiting step is adsorption process.[6]

3.5. Thermodynamic Studies

Thermodynamic parameters of the adsorption process such as change in free energy ΔG (KJ/mole). Change in enthalpy ΔH (KJ/mole), and change entropy ΔS (KJ/mole/k), were determined at different temperature by using equation (19). The plot of logK Against 1/T the result show a good R^2 values for Pb^{2+}, Ni^{2+} and Cu^{2+} ions which are 0.604, 0.619 and 0.900. Gibbs free energy of the adsorption Pb^{2+}, Ni^{2+} and Cu^{2+} ions at different temperatures as presented in Table 4 has a negative value of ΔG which implies the process is feasible and spontaneous in nature.[2] The values of change in enthalpy ΔH, and change in entropy ΔS, of Pb^{2+}, Ni^{2+} and Cu^{2+} ions adsorbed by *Psidium Guajava* leaves biomass obtained are also present in table: 4, the positive values of ΔH, suggested the endothermic nature of the adsorption and a possible bond which occur between the metals ions and the adsorbent. The positive values of ΔS indicate increase ions on the *Psidium Guajava* leaves biomass. Similar finding was observed by researchers.[9,10,6]

4. Conclusions

The removal of Pb^{2+}, Ni^{2+} and Cu^{2+} from aqueous solution using leaves of Psidium Guajava as adsorbent; has been investigated. From the investigation, It was observed that the experimental parameters at optimum condition of PH, contact time, adsorbent dosage, initial metal ion concentration and temperature were determined for their potential effect on the efficiency of Pb^{2+}, Ni^{2+} and Cu^{2+} ions adsorption.

Based on the detailed experimental investigations it was determined to be 6 for Pb^{2+} and 3 for Ni^{2+} and Cu^{2+} ions, 110 mins for Pb^{2+} and Ni^{2+} and 30 mins for Cu^{2+} 0.4 g, 40 ppm of Pb^{2+} and Cu^{2+} and 30 ppm for Ni^{2+} ions and 70°C, 60°C And 30°C respectively. The maximum adsorption capacity was found to be 8.5, 5.6 and 6.8 mg/g. The kinetics studies indicated that adsorption process of the metal ion followed the pseudo second-order model with R^2 Value of 0.940, 0.942 and 0.911 respectively, Equilibrium studies showed that the adsorption of Pb^{2+}, Ni^{2+} and Cu^{2+} are well respectively by both Freundlich isotherm but the Langmuir model gave a better fit for Pb^{2+} with an R^2 value of 0.990 and Langmuir constant KL of 4.878. while Freundlich model give a better fit for Ni^{2+} and Cu^{2+} ions with R^2 value of 0.892 and 0.471, Freundlich constant K_f value of 1.8923 and 0.01958. The calculated thermodynamic parameter of Pb^{2+}, Ni^{2+} and Cu^{2+} ions are (ΔG -3745.25, 401.18 $KJmol^{-1}$, ΔH^0 1373.42, -1512.81 and 1173.14 $KJmol^{-1}$ and ΔS^0 0.698, -4.997 and 0.393 $KJK^{-1}mol^{-1}$). FTIR analysis suggested amino, hydroxyl and nitro combined intensively with Pb^{2+}, Ni and Cu^{2+} ions, the advantage of high metal adsorption capacity, the biomass leave of *Psidium Guajava* has the potential to be used as an efficient, effective methods and economic adsorbent material for the adsorption Pb^{2+}, Ni^{2+} and Cu^{2+} ions from polluted water.

Conflicts of Interest

The authors declare no conflict of interest.

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