

## Equilibrium Studies for the Removal of $Fe^{2+}$ , $Ni^{2+}$ , $Pb^{2+}$ , $Cu^{2+}$ and $Zn^{2+}$ in Wastewater on Formaldehyde Polymerized Peanut Test (ArachishypogaeaL.) Extract

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**Abstract:** Formaldehyde polymerized peanut testa extract (F-PTE) was used as an adsorbent to remove  $Fe^{2+}$ ,  $Ni^{2+}$ ,  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  in laboratory simulated wastewater (LSW) under various conditions. The results showed that the efficiency of the process depended significantly on the pH and temperature of the wastewater, initial adsorbate concentration as well as contact time, and partially on the amount of adsorbent used. The amount of  $Zn^{2+}$  removed by Formaldehyde polymerized and sulphonated peanut testa extract (FS-PTE) resin increased from 61.2% at room temperature (RT) to 72.1% at 50°C and 80.3% at 60°C. Amounts of the metal ions removed from the LSW equally increased from pH 2.0 to pH 8.0. The percentage of  $Fe^{2+}$  removed by F-PTE increased from 20.7% at 30 mins to 71.6% at 120 mins and thereafter, reduced to 68.4% at 150 minutes. Increase in initial concentration of the metal ions from 5.0 to 25.0 mg/L led to a corresponding decrease in the amount of metal ions removed. Metal ions recovered by both resins (F-PTE & FS-PTE) were unaffected when the agitation rate of LSW was altered. FS-PTE removed 72.1%  $Pb^{2+}$  in LSW when the water was stirred at 90rpm, 180rpm and 210rpm. Further results showed that equilibrium removal of the metal ions occurred at 120 minutes using 4.0g of adsorbent in a LSW containing 10ppm of individual metal ions at 60°C and pH 8.0. The adsorption mechanisms fitted well to Langmuir isotherm models with large  $R^2$  values indicating that adsorption of  $Fe^{2+}$ ,  $Ni^{2+}$ ,  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  on F-PTE is favourable while pseudo-first-order model explained the kinetic data. Thus, it supports the potential application of this technique in rehabilitating wastewater and mitigating the challenges of wastes disposal.

**Keywords:** Peanut testa extract, cation exchange resins, heavy metal ions, adsorption, Langmuir isotherm, pseudo-first-order

Date of Submission: 21-03-2018

Date of acceptance: 06-04-2018

### I. Introduction

The discovery of the ability of biological materials (Jorgetto *et al.*, 2014 and Onwu and Ogah, 2010) to accumulate metals and the successful application of the technique in the purification of water polluted by heavy metals such as: Fe, Ni, Pb, Cu and Zn motivated scientists to think of cheaper and eco- friendly agricultural wastes as substitutes to costly and harmful petrochemical products (Singh and Sharma, 2011) which hitherto were choice substrates for decontaminating water and aqueous mixtures laden with these substances (Osu and Odoemelam 2014). Abdelwahab (2007) stated that the study of the use of biodegradable agricultural remains for the purification of heavy metals polluted water is a progressive and an important research area of interest in environmental studies. Hubbe *et al.* (2011) and Argun and Dursun, (2006) found out that the ability of agricultural wastes such as: peanut shell and testa, orange peels, soybean hulls, banana leaves etc. to serve as metal ion adsorbents can be improved through chemical modification which exposes new binding sites (Chukwu *et al.* 2017; Nada *et al.* 2010; Nguyen and Nhung, 2009 and Marshall and Wartelle, 2004). In addition, Uchechukwu (2017); Igwegbe *et al.* (2016); Priya and Santhi (2015); Haftu *et al.* (2014); Abuh *et al.* (2013) and Yurtsever and Sengil (2009) carried out studies which show that in addition to physico-chemical properties, the efficiency of a modified agro waste in removing heavy metals pollutants in water depends on the chemical composition of the water as well as the environmental conditions under which the adsorption process occurs.

A notable consequence of the economic recession in Nigeria has led to increase in the popularity of cultivation and consumption of peanuts (*ArachishypogaeaL.*) in the country. In addition, the realization that eating peanuts helps to tame hunger for longer times has resulted in abundant generation of peanut testa waste. It is estimated that 35–45 gram of polyphenol rich peanut testa (Yu *et al.* 2005) is generated from every kilogram of peanut kernel and that the annual global production of this by-product of peanut processing industries

averages 0.74 million metric tonnes (Sobolev and Cole, 2003). In developed countries, peanut testa is currently under-utilized as a low value additive in some health promoting foods and animal feeds (Hathorn and Sanders, 2012; Holser, 2014 and Sobolev and Cole, 2003). Hence there is haphazard dumping of a large portion of this waste in the environment leading to pollution problems (Zhao *et al.*, 2012 and Sobolev and Cole, 2003).

Unfortunately, there is no facility in Nigeria or elsewhere in Africa where peanut testa is converted to any secondary product. It is therefore necessary to harness and identify new outlets by creating higher value products from this catechin rich (Holser, 2014) waste, by transforming them into cation exchange resins for removing contaminant metal ions in water. Apart from playing the dual role of wealth creation and environment clean-up, the use of peanut testa in water purification will satisfy the yearning of using waste materials to regenerate other wastes. It will lead to attitudinal change towards the waste, facilitate the development of a marketable technology for wastewater purification and expand the field of the use of agricultural wastes in water purification.

The present study examines the influence of temperature, pH, contact time, metal ion concentration, adsorbent dose and stirring speed on the efficiency of F-PTE and FS-PTE cation exchange resins in removing Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> in laboratory simulated single element wastewater by batch adsorption process.

## **II. Materials and Method**

The method for the syntheses, characterization and adsorption of Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> in LSW by F-PTE and FS-PTE are described in previous literature Chukwu *et al.* (2017) and Uchechukwu *et al.* (2016).

### **Adsorption of Metal Ions by F-PTE and FS-PTE at Various Conditions**

The efficiencies of F-PTE and FS-PTE resins in removing Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> in LSW were determined at various conditions by altering the condition of a parameter under investigation while keeping the rest of the conditions for the experiment constant. The conditions were: solution volume = 50mL, contact time = 60 minutes, metal ion concentration = 5ppm, pH = 6.0 ± 0.5, adsorbent dose = 1.0g, agitation speed = 150 rpm (revolutions per minute) and temperature = RT.

### **Effect of Variations in Temperature and pH**

Temperature studies were carried out at six different temperatures: RT, 40°C, 50°C, 60°C, 70°C and 80°C. While the influence of pH on the percentage adsorption of the metal ions, was varied from pH 2.0 to 10.0.

### **Effect of Variations in Adsorbate-adsorbent Contact Time**

The contact time experiment was carried out at 30mins, 60mins, 90mins, 120mins and 150mins. The effect of concentration of metal ions in LSW at six different concentrations (5ppm, 10ppm, 15ppm, 20ppm, 25ppm and 30ppm) was individually examined. The dependency of the amount of a modified PTE adsorbent added to LSW was studied using 0.5g, 1.0g, 2.0g, 4.0g, 6.0g, 8.0g and 10.0g portions of the adsorbent. While, the influence of agitation speed was investigated by mechanical shaking at 90rpm, 120rpm, 150rpm, 180rpm and 210rpm respectively.

## **III. Results and Discussion**

The results of the adsorption of Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> in individual element solutions by F-PTE and FS-PTE resins are presented in Uchechukwu *et al.* (2016) while the equilibrium and kinetic data for the processes are tabulated in Uchechukwu, (2017).

### **Effect of Variations in Temperature**

The graphical representations of the temperature dependency of the amounts of Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> in LSW removed by F-PTE and FS-PTE resins are shown in Figures I and II respectively. The results show that the percentage removal of the ions improved with rise in temperature of the water. The percentages removed which increased steadily from 30°C attained maximum values between 50°C and 60°C and shrank thereafter. Increase in the amounts removed at the initial stage is attributable to expansion of adsorbent pores while the thermal energy of LSW increased. It became easier for the metal ions to migrate to the adsorption sites of the resins as the temperature increased from 30°C to 60°C. The effect however, was counterbalanced when the temperature rose above 60°C at which point the amount of the ions removed diminished. Increasing the temperature of the wastewater above 60°C reduced the forces of attraction between the adsorbent molecules and the adsorbate ions which ultimately weakened the adsorbate-adsorbent bonds existing at the adsorption sites. Moreover, the thickness of the boundary layer on the adsorbent surface decreased when the temperature of the solution rose and increased the tendency of bound metal ions to break away from the adsorbent surface and enter the solution phase. The preponderance of this situation reduced the amount of ions removed when the temperature was increased further. Percentage removal of Pb<sup>2+</sup> was least in both F-PTE and FS-PTE in comparison to the other metal ions.

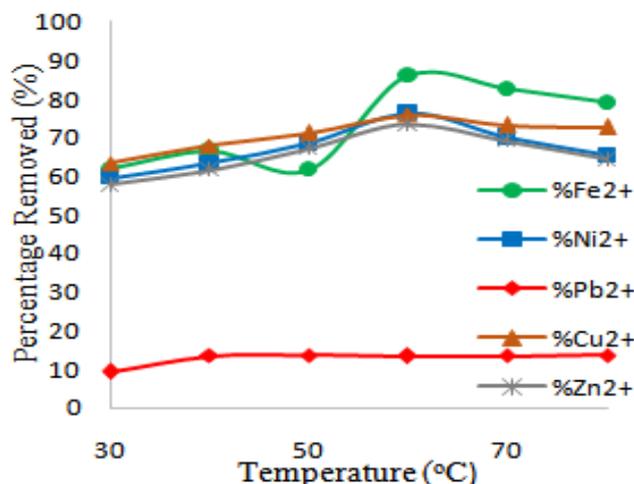


Fig. 1: Variations in Temperature on the Adsorption of Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> on F-PTE

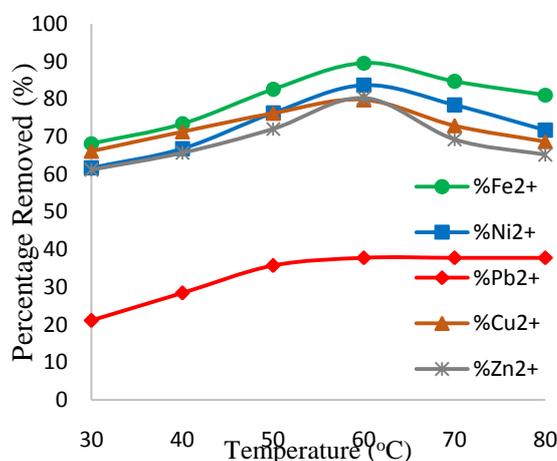
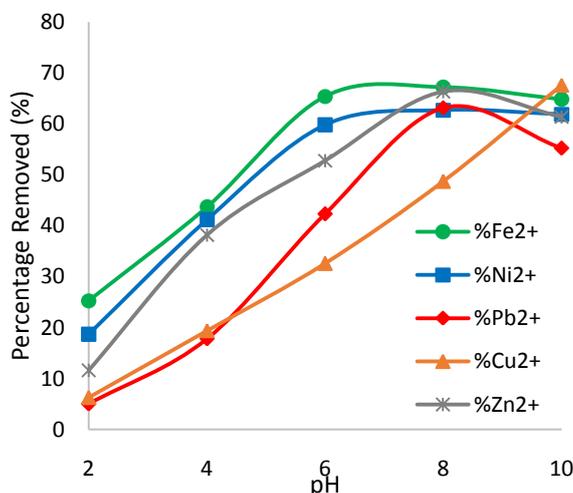


Fig. 11: Variations in Temperature on the Adsorption of Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> on FS-PTE  
Effect of Variations in pH

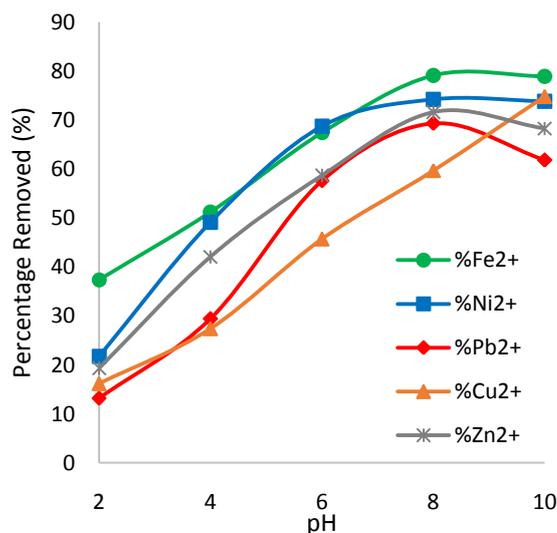
Apart from its effect on the solubility of metal ions and the ionization of the functional groups of the adsorbent, the pH of the adsorbate solution plays a significant role in the formation and sustenance of adsorbate-adsorbent complexes between the metal ions and molecules of the adsorbent. The results of the adsorption of Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> in LSW on F-PTE and FS-PTE resins at different pH values showed that when the pH of the solution was lower than 4.0, the percentages of the metal ions removed by the resins were little. The percentages which were observed to be minimal at pH 2.0 improved as the pH of LSW increased from 4.0 and attained maximum values between pH 6.0 and 8.0 (figures III and IV).

The observation is probably as a result of occupation of adsorbents' negatively charged sites by highly mobile and positively charged H<sup>+</sup> and H<sub>3</sub>O<sup>+</sup> when the pH of the solution was below 4.0. The H<sup>+</sup> and H<sub>3</sub>O<sup>+</sup> competed against the adsorbate ions for the adsorption sites of the adsorbents with the effect that the number of sites available for occupation by the metal ions reduced. Hence, only a little amount was bound and removed from the water. On the other hand, when the pH of the solution increased, the concentration of H<sup>+</sup> decreased and the adsorbents surfaces were occupied by increased number of negative charges. The condition created electrical repulsion between the resident negative charges on the adsorbents' surfaces and the -OH<sup>-</sup> groups produced as a result of the rising pH of the solution. It minimized the competition for adsorption sites between the metal ions and H<sup>+</sup> and H<sub>3</sub>O<sup>+</sup>, reduced the solubility of the metal ions and subsequently increased their adsorption and withdrawal from LSW. The percentages of the metal ions removed were observed to be highest when the pH of the water was 8.0 and diminished as the pH continued to increase beyond 8.0. It showed that adsorption of the metal ions by F-PTE and FS-PTE resins was not favourable in high alkaline solutions. The observed effect of high pH on metal ion adsorption is attributable to the tendency of the resin molecules to form different types of chelate compounds with the metal ions at different pH values. The stability of the produced resin-metal complexes affected the binding and removal of the metal ions in the water. Furthermore, the metal ions

precipitated as insoluble hydroxides and limited their adsorption and removal from the LSW. Abreu *et al.* (2012) found out that the formation of metal complexes by interactions with dissolved inorganic (CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, OH<sup>-</sup> and PO<sub>4</sub><sup>3-</sup>) ligands and CH<sub>3</sub>COO<sup>-</sup> groups in hydrocarbon produced water occurred at high pH and interfered with the ion exchange of the metal ions. The influence of the pH of the LSW on the removal of Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> by F-PTE and FS-PTE cation exchange resins are presented as plots in Figs. III and IV respectively.



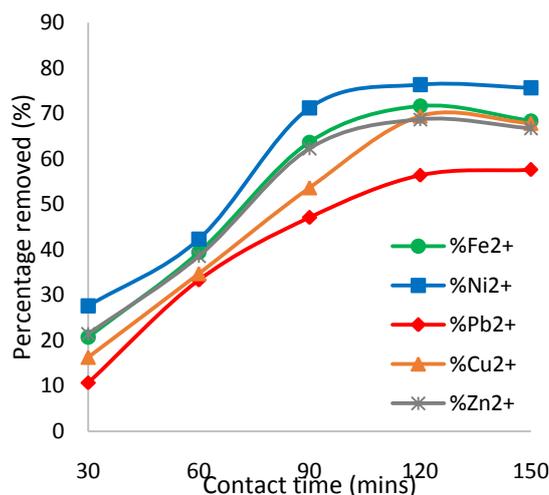
**Fig. III:** Variations in pH on the Adsorption of Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> on F-PTE



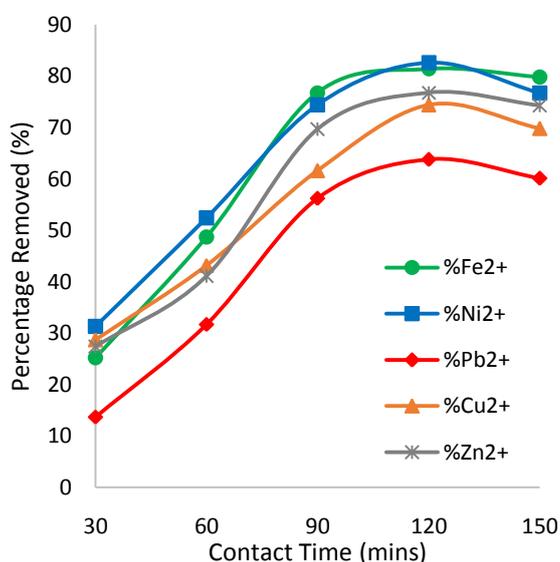
**Fig. IV:** Variations in pH on the Adsorption of Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> on FS-PTE  
Effect of Variations in Adsorbate-adsorbent Contact Time

Contact time is the length of time an adsorbent stays in and interacts with an adsorbate solution during an adsorption process. It is the shortest time required by an adsorbent to achieve equilibrium adsorption of an adsorbate after which there are no more changes in the amount of the adsorbate in the solution. The results for contact time experiment indicate that the adsorption of Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> increased with an increase in contact time prior to attainment of equilibrium. The graphical presentations of these are shown in figures V and VI for F-PTE and FS-PTE resins respectively.

The adsorption was observed to increase with progression in contact time between 30 mins and the 120 mins. The process which was fast initially, slowed down between 90 mins and 120 mins before declining gradually at 150 mins. The rapid adsorption of the metal ions at the initial stage was as a result of an avalanche of unoccupied adsorption sites on the resins' surfaces at this time. The process slowed down as the number of unoccupied sites reduced. Adsorption sites on F-PTE and FS-PTE resins became saturated between 120 mins and 150 mins and the amounts of metal ions removed spared because there were no more vacant sites on the adsorbents available for occupation.



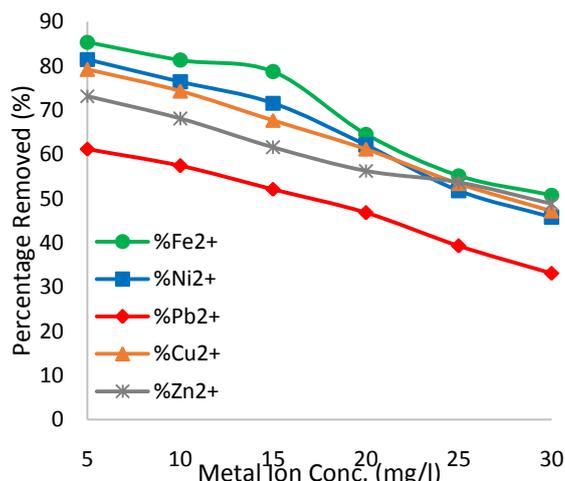
**Figs. V:** Variations in Adsorbate-adsorbent Contact Time on the Adsorption of Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> on F-PTE



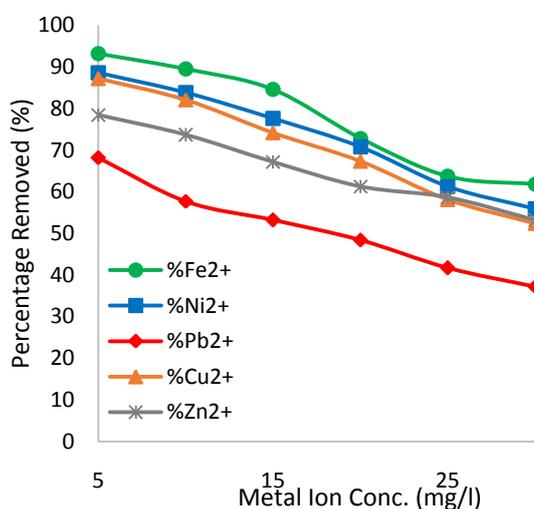
**Figs. VI:** Variations in Adsorbate-adsorbent Contact Time on the Adsorption of Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> on FS-PTE

#### Effect of Variations in Initial Metal Ion Concentration

The concentration of an adsorbate in an aqueous solution provides the driving force necessary to overcome the forces which oppose the migration of its ions from the solution to the surface of an adsorbent (Jorgettoet al., 2014). It can be seen from figures VII and VIII that the percentages of Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> removed by F-PTE and FS-PTE resins decreased appreciably as the concentration of the ions at the start of the experiment increased from 5 to 25 mg/L and tailed off subsequently. Decrease in the amounts removed is explainable by the fact that the ratio of the number of unoccupied sites of the adsorbents to the amount of adsorbate ions dropped. Unoccupied sites on the adsorbents became fewer in number for the amounts of the metal ions in the LSW. At saturation, the adsorbent could no longer add or reject adsorbate ions from the solutions. When the metal ion concentration was low, the available sites on the adsorbent were sufficient to occupy them. However, as their concentration began to rise, the metal ions became more numerous than the vacant sites. The ions competed with one another for the few vacant sites on the adsorbents, a little percentage was removed and the adsorption process became ineffective.



**Figs. VII:** Variations in Initial Metal Ion Concentration on the Adsorption of  $Fe^{2+}$ ,  $Ni^{2+}$ ,  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  on F-PTE



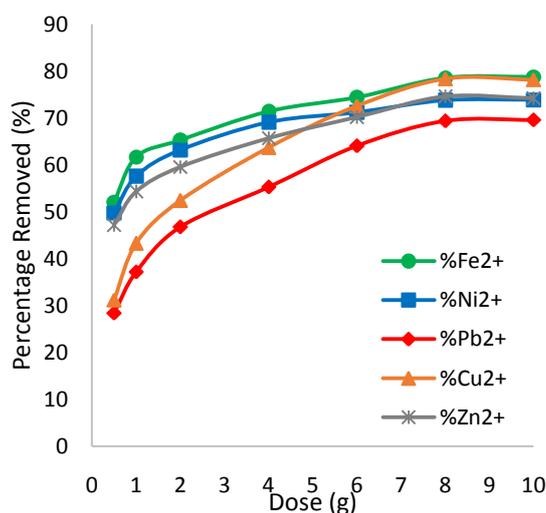
**Figs. VIII:** Variations in Initial Metal Ion Concentration on the Adsorption of  $Fe^{2+}$ ,  $Ni^{2+}$ ,  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  on FS-PTE

### Effect of Variation in Adsorbent Dose

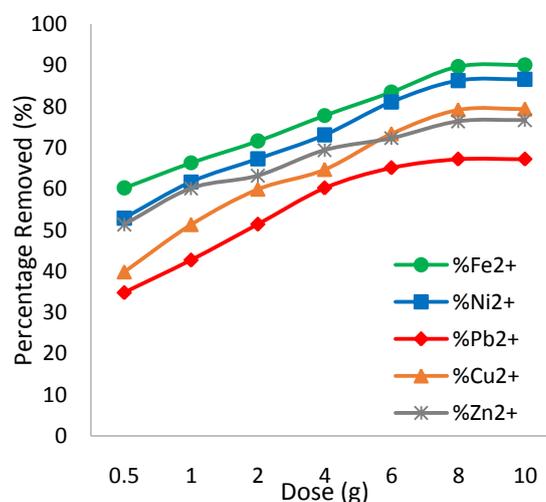
The amount of an adsorbent (adsorbent dose) added to the solution in an adsorption process determines the number of binding sites available for adsorption. It is useful to strike a balance between the adsorption capacity of the adsorbent under a defined set of operating conditions and the percentage of an adsorbate that results to equilibrium adsorption (Gupta and Babu, 2009).

From figures IX and X, the results of the effect of the amounts of adsorbents added on the percentages of  $Fe^{2+}$ ,  $Ni^{2+}$ ,  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  removed from the LSW show that the adsorption of the metal ions was partially influenced by the amount of F-PTE and FS-PTE cation exchange resins used. It showed that the percentages removed increased when the amounts of the adsorbents were increased up to a point beyond which there were hardly any noticeable changes in the amounts removed as more adsorbents were added. When the amounts of F-PTE and FS-PTE resin were individually increased from 2.0g to 4.0g, the percentage  $Fe^{2+}$  removed improved from 65.3% to 71.4% and 71.6% to 77.8% respectively but when it was raised from 8.0g to 10.0g, the percentage increase were: 78.6% to 78.8% and 89.7% to 90.1% for F-PTE and FS-PTE resin respectively. Although increasing the amount of adsorbent added in each case produced an increment in the amount of metal ion removed at the early stages, the magnitude of the increase did not show a valuable economic trend. The observed increase in adsorption at the early stages was because the concentration of metal ions at this stage was relatively higher than the amount of the adsorbent present in the solution. Moreover, as more adsorbent was introduced, the functional groups at the adsorption sites were not yet saturated hence unoccupied sites became too many for the fixed amount of metal ions. The large surface area of the resins and the numerous adsorption sites needed to be occupied leading to scrambling for the metal ions and resulting to higher metal ion removal

percentages at this stage. On the other hand, the tiny increments and the final drop in the amounts of the metal ions removed at the later stages of the experiments were the result of complete occupation of adsorption sites which led to the saturation of adsorbent surfaces by the metal ion adsorbates. At this point, equilibrium adsorption had been reached and neither the adsorbents nor the adsorbates respectively could receive or rebuff any more metal ions from/to the LSW. Gupta *et al.* (2011) discovered that addition of more adsorbents at this stage concealed the outer layer of the adsorbent cells, shielded the adsorption sites from the metal ions and led to reduced metal ion uptake by the adsorbent units. Together with Ackacha and Elsharif (2012), they explained that the phenomenon termed “solid concentration effect” was due to overcrowding of the adsorbate solution by particles of the adsorbents.



**Fig. XI:** Variations in Adsorbent Dose on the Adsorption of Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> on F-PTE

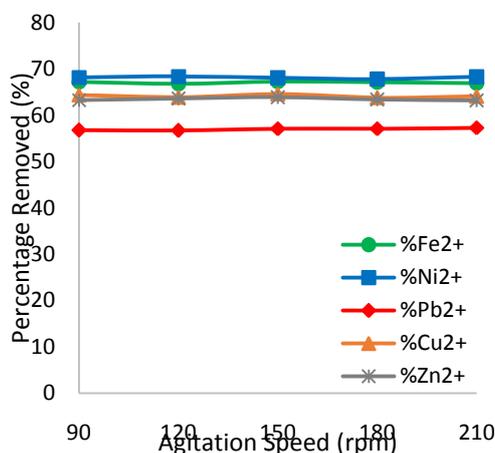


**Fig. X:** Variations in Adsorbent Dose on the Adsorption of Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> on FS-PTE

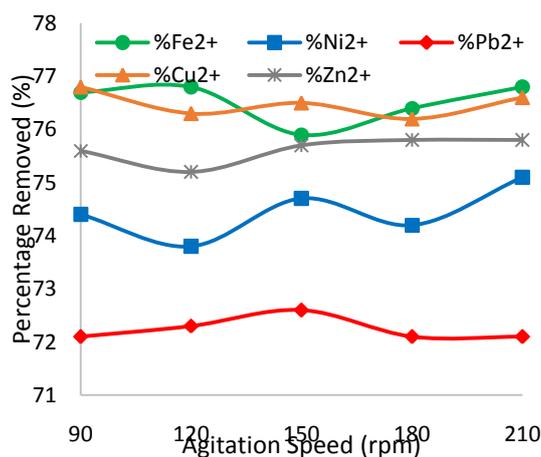
**Effect of Variations in Agitation Speed**

Agitation not only facilitates effective contact between the adsorbate and molecules of the adsorbent, it completes the movement of the adsorbate to the binding sites of the adsorbent. The results of the effect of stirring speed on the amounts of Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> in the LSW removed by F-PTE and FS-PTE resins are presented in Figures XI and XII. There was no significant effect observed between the efficiency of the adsorption of the ions and agitation rate of LSW within the range that was studied. It suggests that the magnitude of the stirring speed of the suspension played no significant role on the performance of F-PTE and FS-PTE resins as adsorbents. There were slight increments and reductions in the percentages of metal ions removed at the end of every session but the changes did not follow a clear pattern. When the LSW was stirred at 90rpm, 180rpm and 210rpm; 56.6%, 57.1% and 57.3% of Pb<sup>2+</sup> was removed by F-PTE respectively. While 72.1%, 72.1% and 72.1% of Pb<sup>2+</sup> was removed by FS-PTE for 90rpm, 180rpm and 210rpm respectively. Similarly, Oluyemiet *al.* (2012) could not establish equilibrium adsorption of Cd<sup>2+</sup> or Pb<sup>2+</sup> when the speed of stirring of the palm kernel

shell charcoal-wastewater suspension was increased. Yurtsever and Sengil (2009) found out that the adsorption capacity of Pb<sup>2+</sup> on modified QTR was unaffected by the stirring rate of the adsorbate-adsorbent mixture. The observations made by Sulaymonet *al.* (2014) and Singh and Sharma (2011) that the efficiency of GG in removing Cd<sup>2+</sup> improved with rise in the stirring speed of the contaminated water until it stabilized at equilibrium and that adsorption of Zn<sup>2+</sup>, Cd<sup>2+</sup>, Fe<sup>2+</sup>, Pb<sup>2+</sup> and Cu<sup>2+</sup> in the effluent of the Apex steel industry on GSA resin increased steadily when the effluent sample was stirred from 0 to 120 rpm respectively could not be verified.



**Figs. XI:** Variations in Agitation Speed on the Adsorption of Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> on F-PTE



**Figs. XII:** Variations in Agitation Speed on the Adsorption of Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> on FS-PTE

**Application of Adsorption Isotherm Models for the Adsorption of Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> on FS-PTE Resin**

Adsorption isotherm is the equilibrium relationship between the quantity of an adsorbed material and the concentration of that material in the liquid phase at constant temperature (Suman, 2013). It is a basic requirement for designing any adsorption system. The distribution of metal ions between the adsorbent and the liquid phase helps to determine the position of equilibrium or balance in an adsorption process and can be described by the equilibrium isotherm equation (Yurtsever and Sengil, 2009). The equation parameters and the underlying thermodynamic assumptions of the equilibrium modes provide insights into the mechanism of an adsorption process, the surface properties and affinities of an adsorbent for an adsorbate. The three most common isotherms for describing a solid-liquid adsorption system are the Langmuir, Freundlich and Redlich Peterson isotherms. In this study, isotherm parameters were determined using the Langmuir method due to its ability to model equilibrium while the adsorption data analyses were performed using the chi-square test.

In 1918, Langmuir developed a relationship between the amount of a gas adsorbed on the surface of an adsorbent and the pressure of that gas. The equations which are now referred to as Langmuir adsorption isotherms are theoretically based adsorption isotherms in an ideal case (Ho *et al.*, 2002, Allen and Koumanova, 2005 and Ho, 2004). Linear regression was used to determine the best fitting model. The coefficient of

determination, error due to the sum of squares (SSE), average relation error and the sum of absolute errors were used in the evaluation of the isotherm data and were found to be linear models

**The Langmuir Isotherm**

The theoretical Langmuir Isotherm (Langmuir, 1918) is often used to describe the adsorption of a solute from a liquid solution as:

$$q_e = \frac{qmKlCe}{1 + KlCe} \quad (1)$$

The constants qm and Kl are characteristics of the Langmuir equation and can be determined from a linearized form of equation 1 represented by equation 2:

$$\frac{Ce}{qe} = \frac{1}{qmKl} + \frac{Ce}{qm} \quad (2)$$

A plot of Ce / qe versus Ce is a straight line with slope; 1/qm and an intercept, 1/(klqm). Alternatively from equations 3 and 4,

$$\frac{1}{qe} = \frac{1}{qm} + \left(\frac{1}{Klqm}\right) \frac{1}{Ce} \quad (3)$$

and

$$qe = \left(\frac{Ci - Ce}{w}\right) V \quad (4)$$

Where:

w = weight of adsorbent

Ci = initial concentration

Kl = Langmuir constant

Ce = Equilibrium concentration.

V = volume of solution (ml)

qe = amount of metal ion (mg/g) adsorbed at equilibrium.

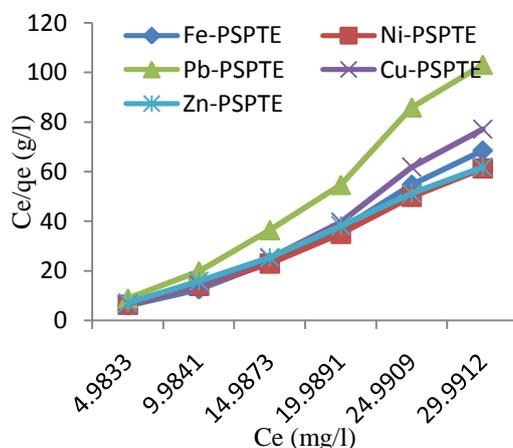
When Ce/qe was plotted against Ce, a straight line with slope; 1/qm and intercept of 1/qmKl was obtained.

The essential characteristics of the Langmuir equation can be represented by a dimensionless factor, Rl called the separation factor which is given in equation 5 below;

$$Rl = \frac{1}{1 + KlCo} \quad (5)$$

Co = the highest initial metal ion concentration (mg/L)

The linear plots of Langmuir isotherm for the effects of concentration, contact time and temperature on the adsorption of Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> on FS-PTE are shown in figures XIII to XV respectively. R<sup>2</sup> values for the corresponding isotherm data for the effect of contact time on the absorption of the same metal ions on FS-PTE were calculated to be: 0.96753, 0.97429, 0.95706, 0.93384 and 0.96755 for Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup>. The R<sup>2</sup> values for the corresponding isotherm data for the effect of concentration is 0.99724, 0.99957, 0.99934, 0.99969 and 0.99939 for Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> metal ions. While R<sup>2</sup> values for the corresponding isotherm data for the effect of temperature is 0.99748, 0.9986, 0.99521, 0.99451 and 0.99181 for Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> metal ions. It is evident from the R<sup>2</sup> values that the adsorption isotherms fitted well to the chosen Langmuir isotherm model because the coefficients of determination in most cases were far above 0.95.



**Fig. XIII:** Plot of CevsCe/qe for the Effect of Concentration on the Adsorption of Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> on FS-PTE

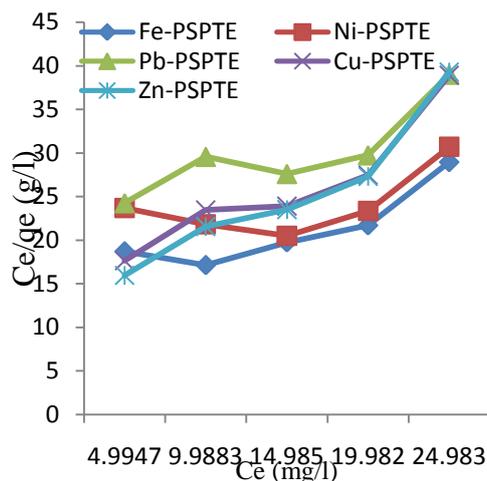


Fig. XIV: Plot of  $C_e/q_e$  vs  $C_e$  for the Effect of Contact Time on the Adsorption of  $Fe^{2+}$ ,  $Ni^{2+}$ ,  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  on FS-PTE

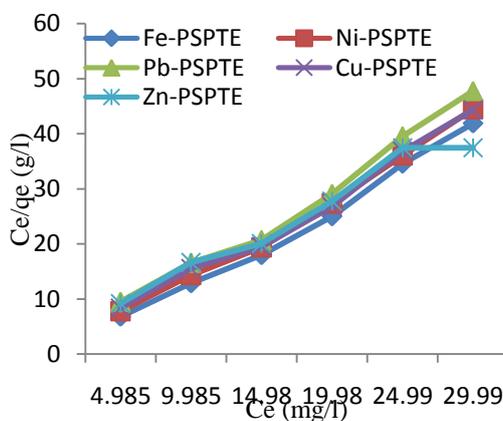


Fig. XV: Plot of  $C_e/q_e$  vs  $C_e$  for the Effect of Temperature on the Adsorption of  $Fe^{2+}$ ,  $Ni^{2+}$ ,  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  on FS-PTE

### Chemical Kinetics

Chemical kinetics explains how fast a chemical reaction occurs and the factors which affect the rate of that reaction. The most commonly used kinetic expressions to explain the solid/liquid adsorption processes are the pseudo-first-order kinetic and pseudo-second-order kinetic models (Kumar and Sivanesan, 2006). The pseudo-first-order and pseudo second-order kinetic models proposed by Huiet *et al.* (2005) have been found to explain the kinetics and provide best fits for the removal of heavy metal ions in most adsorption processes.

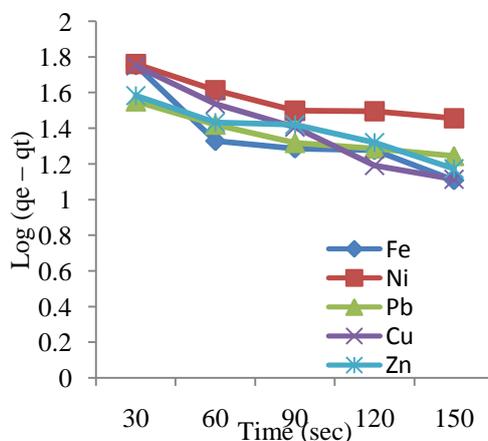


Fig. XVI: Plot of  $\log(q_e - q_t)$  vs Time Values for  $Fe^{2+}$ ,  $Ni^{2+}$ ,  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  on FS-PTE

The first order constant,  $K_1$  is obtained as  $-2.303 \times$  slope while the second order constant is obtained by dividing the square root of slope with the intercept. The calculation of chemical kinetics is very important to understand the rate of reaction (Wong *et al.*, 2003 and Ho and McKay, 1999). The pseudo-first-order equations based on equilibrium adsorption is expressed according to equation 6:

$$\log(q_e - qt) = \log q_e - \frac{K_1}{2.303} t \quad (6)$$

Where  $q_e$  and  $qt$  are the amounts of specie adsorbed in (mg/g) at equilibrium and at time  $t$ .  
 $K_1$  = the final order rate constant ( $\text{min}^{-1}$ ).

The plot of  $\log(q_e - qt)$  versus time (shown in figure XVI) gave  $K_1$  as slope and  $\log q_e$  as intercept. This plot shows that the rate of reaction depended mainly on one of the reactants hence it can be said to follow a pseudo-first-order kinetic model.

#### IV Conclusion

Formaldehyde polymerized peanut testa extract (F-PTE) and Formaldehyde polymerized and sulphonated peanut testa extract (FS-PTE) resins were used as adsorbents to remove  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  in laboratory simulated wastewater (LSW) under various conditions. Amounts of the metal ions removed from the LSW increased from pH 2.0 to pH 8.0. Increase in initial concentration of the metal ions from 5.0 to 25.0 mg/L led to a corresponding decrease in the amount of metal ions removed. Metal ions recovered by both resins (F-PTE & FS-PTE) were unaffected when the agitation rate of LSW was altered. Further results showed that equilibrium removal of the metal ions occurred at 120 minutes using 4.0g of adsorbent in a LSW containing 10ppm of individual metal ions at 60°C and pH 8.0. The adsorption mechanisms fitted well to Langmuir isotherm models with large  $R^2$  values indicating that adsorption of  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  on F-PTE is favourable while pseudo-first-order model explained the kinetic data. Thus, it supports the potential application of this technique in rehabilitating wastewater and mitigating the challenges of wastes disposal.

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IOSR Journal of Applied Chemistry (IOSR-JAC) is UGC approved Journal with Sl. No. 4031, Journal no. 44190.

Uchechukwu, T. O " Equilibrium Studies For The Removal Of Fe<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> And Zn<sup>2+</sup>In Wastewater On Formaldehyde Polymerized Peanut Test (*Arachis hypogaea* L.) Extract." *IOSR Journal of Applied Chemistry (IOSR-JAC)* 11.3 (2018): 63-74.