# Adsorption Of Ternary Metal System Onto The Sawdust Of Locust Bean Tree (*Parkia biglobosa*): Equilibrium, Kinetics And Thermodynamics Studies.

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## ABSTRACT

The use of raw sawdust, RSD, of locust bean tree (*Parkia biglobosa*), a low-cost, locally available agroforestry waste as an adsorbent for removing a ternary mixture of heavy metals comprising of copper, lead and nickel (TMS) from aqueous solution was examined. Equilibrium data obtained from batch adsorption experiments were analysed with Langmuir, Freundlich and Temkin isotherm models, with Langmuir equation giving the best fit to the data. The effect of contact time, initial concentration and pH of the solution and dose of RSD on the efficiency of the sorption process was also evaluated. The kinetics of the sorption was studied using different models; it was observed to have followed pseudo–second order model with high $R^2$ values and close agreement between the theoretical and experimental values of $q_e$ for all initial TMS concentrations studied. The thermodynamic parameters of the adsorption showed that the process was feasible, exothermic and accompanied with increased randomness

Key words : Ternary metal system, adsorption, kinetics, isotherm, thermodynamics, *Parkia biglobosa.*

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## INTRODUCTION

Though heavy metals are natural components of the environment, their levels have undergone dramatic increase with increasing population and sophistication in human activities, especially since the beginning of industrial revolution (1). At least twenty metals have been classified as toxic, and 50% of these are being emitted into the environment in amounts that pose risks to human health (2). These toxic metals constitute a serious threat to the well-being of man, wildlife and even plants if present above certain threshold levels (3). Excessive release of the metals into the environment due to industrialization and urbanization has posed a great problem all over the world. They have been observed to be the cause of serious illnesses affecting vital organs and tissues of the human body (4, 5 and 6).

A major source of heavy metals in the environment is the discharge of untreated industrial effluents from industries such as paints, plating, fertilizers, mining, textile dyeing and processing, automobile manufacturing and metal processing (7, 8 and 9). Some heavy metals, being constituents of pesticides, paints and fertilizers, are introduced into the environment through the application of these products. Besides their toxicity, heavy metals are of utmost concern because, unlike organic pollutants which are mostly biodegradable, they do not degrade into non-toxic end products. They persist in the environment and even bioaccumulate in the food chain (10).

Cadmium, copper, zinc, iron, mercury and lead are metals of serious concern according to the world health organization. In fact, Lead together with mercury and cadmium have been referred to as " the big three" because of their significant negative impact on the environment (11).

Copper is an essential elements, it is important in the physiological functions of living tissues and regulate many biochemical processes when present in the trace concentrations (12). Health conditions like nephritic syndrome, copper intoxication and burn injuries have been associated with high concentrations of copper. The presence of high level of Cu(II) ions is of serious toxicological concern, as it is known to deposit in brain, skin, liver, pancreas and myocardium.

The increasing awareness about the hazardous nature of the metals has generated serious concern to government at various levels, pressure groups and individual activists (13). Nigeria is not left out of this serious concern, as the Federal Environmental Protection Agency (FEPA) was established in 1989. FEPA at the national level and SEPA (State environmental protection Agency) in some states of the federation later metamorphosed into full blown ministries of environment. The increased level of awareness in both the public and regulatory share led of awareness in both the public regulatory sphere need to the need to improve the treatment of industrial effluent, a major source of environmental pollution.

Several conventional methods such as coagulation/flocculation (14, 15), Oxidation process (16, 17) reverse osmosis, chemical precipitations, ion exchange and the use of activated charcoal (18) have being in use over the years for the removal of toxic heavy metals from wastewater . However, some of these technologies cannot effect complete removal of the pollutants, or are too expensive. There is therefore the need to develop more effective and economical technologies for the removal of heavy metals from effluents. This has led to the search for non-conventional low-cost materials for this purpose.

The current trend is to investigate the possibility of employing various agrowastes and biological materials that are available in commercial quantities for wastewater remediation by adsorption (19).This is a better alternative to the conventional techniques not only because it is cheap to process, but also because it is highly efficient and the materials are readily and abundantly available.

Various agroforestry by-products in their raw and modified forms have been studied; these include sugarcane bagasse, rice husk, soybean hulls, waste tea leaves, peanut shells and saw dust (20, 21). However, more work and investigations are still required to be carried out on some other locally available agricultural materials.

## MATERIALS AND METHODS

### Preparation of Adsorbent

A large quantity of *Parkia biglobosa* saw dust was collectedd from local saw mills in Ogbomoso South-west Nigeria. Debris and other relatively big foreign materials were hand-picked from the husk collected, after which it was extensively washed with tap water to remove soil and dust. It was then thoroughly rinsed with distilled water, drained and oven-dried at 105 $^0$C for 15 h. The dried material was then. ground, sieved and stored in air–tight containers as raw saw dust (RSD).

### Characterisation of the Adsorbent (RSD)

The adsorbent was characterized using FTIR spectroscopy and Scanning Electron Microscopy (SEM). The IR spectrum of RSD was recorded using Nicolet Avatar FT-IR within the ranre 4000 cm$^{-1}$ and 450 cm$^{-1}$. The morphology of the adsorbent prepared was examined on Hitachi 2300 Scanning electron microscope. Samples were coated with gold before being subjected to SEM analysis.

In this work, the adsorption property of chemically untreated saw dust of locust bean tree (*Parkia biglobosa*), as a low-cost and non-conventional adsorbent for the removal of a mixture of copper, lead and nickel from aqueous solution was studied. Though several works have been done on the adsorption of single heavy metals from aqueous solutions using agroforestry-based adsorbents, not much work has been reported on the adsorption of ternary heavy metal mixture, especially onto saw dust of *Parkia biglobosa*, hence the significance of this study. This work will also contribute to the search for low-cost adsorbents and the possibility of utilizing various agricultural and forestry by-products, which are in many cases also pollution sources.

### PREPARATION OF SORBATE

The adsorbate used in this study was a mixture of three heavy metals: copper, lead and nickel. Stock solutions (1000 mg/L) of the metals were prepared by dissolving an accurately weighed analytical grade Copper nitrate, Lead nitrate and Nickel nitrate in deionised water. Ternary metal system (TMS) working solutions of different concentrations, as required, were prepared by mixing equal volumes of the stock solutions and accurately diluting it with deionised water to give equal concentration (in g/L) of the metal ions in the mixture.

### BATCH ADSORPTION EXPERIMENTS

Batch adsorption experiments were carried out in which 20cm$^3$ of TMS of different concentrations was mixed with a definite mass (0.05-0.70g) of RSD in 150cm$^3$ plastics bottles and were agitated in a horizontal mechanical shaker (SM 101 by Surgafriend Medicals) at 120 rpm for pre-determined periods of time and temperature at natural pH. The mixture was filtered through whatman filter paper, and filtrate analyzed for it residual metal content using atomic absorption spectrophotometer. All experiments were carried out in duplicate and mean values determine were presented.

Mathematical quantitative evaluations were carried out by using the following equations:

$$q_e = \frac{(C_o - C_e)V}{M} \qquad (1)$$

$$q_t = \frac{(C_o - C_t)V}{M} \qquad (2)$$

$$R(\%) = \frac{C_o - C_t}{C_o} \; x \; 100 \qquad (3)$$

where $q_e$ and $q_t$ are the amount of dye adsorbed (mg/g) at equilibrium and at time *t* respectively; $C_o$ and $C_t$ are the initial concentration (at *t* = 0) and its concentration at time *t* = *t* (mg/L); M is the mass RSD (g); *V* is the volume of TMS (L) and *R* is percentage of metal removed.

Since adsorption is affected by physical and chemical variables, the influence of initial metal concentration, RSD dose, pH, temperature and contact time are investigated in this study.

## RESULTS AND DISCUSSION

### Characterization of RSD

The FTIR spectrum of RSD before adsorption (Fig. 1a) displays a number of absorption peaks, indicating the complex nature of the material. The spectrum revealed diagnostic bands at 3424 cm$^{-1}$ representing bonded – OH in the oxygen-containing functional groups. The positions of the C–H (2926 cm$^{-1}$), aromatic C = C (1604 cm$^{-1}$), C–O (1150 cm$^{-1}$) and carbonyl (1723 cm$^{-1}$) vibrations, contributed by those in the structure of cellulose, hemicellulose and lignin, which are common components of plant materials, are indicated by the spectrum of RSD (22). Thus, the FTIR spectrophotometric analysis indicates that the adsorbent has potential adsorption sites as represented by functional groups such as COOH, C = O, and C=C.

The FTIR spectrum of the adsorbent after heavy uptake in the ternary metal system is shown in Figure 1b. When compared with the FTIR spectrum of the adsorbent before any adsorption (Fig. 1a), there were remarkable differences in the position or occurrence of some diagnostic bands. There was a slight shift in the position of –OH or –NH band at 3424 cm$^{-1}$ in RSD before adsorption to 3430 cm$^{-1}$ after adsorption. A similar shift was also observed in the C=O stretch from 1723 cm$^{-1}$ to 1736 cm$^{-1}$. These observations showed that adsorption of the metal ions really occurred.

The Scanning Electron Microscope (SEM) was used to study the surface morphology of the adsorbent. The surface textural structure of RSD is presented as scanning electron micrographs observed at three different magnifications (x 100, x 500 and × 1000) (Fig. 2). The SEM images of RSD showed the irregular texture and porous nature of the surface of the adsorbent (Fig. 2). Its apparent rough surface is a pointer to high surface area (23), which enhances adsorption.

## Metal initial concentration and Contact time effects

The effect of contact time on the amount of $Cu^{2+}$, $Pb^{2+}$ and $Ni^{2+}$ adsorbed onto RSD was studied using three different initial concentrations ( 5, 20 and 50 mg/L) so as to optimize the adsorption time and to study the kinetics of the sorption process. A RSD dose of 0.25 g was added to 20 mL solution of the different concentrations of TMS at a temperature of 30 °C. Adsorption process was allowed to take place for a contact time of 3 h .

As contact time increases, the concentration of the three metals in the solution decreased rapidly at the beginning and later slows down until it remained constant at about 45 - 120 minutes, depending on the concentration of the metals. This indicates that the removal of the metals by RSD was very rapid at the beginning (Fig. 3). In fact, in all the initial concentrations used, and for all the metals, over 70% removal was achieved within the first 10 min (figure not shown). A contact time of 2 h was then taken as equilibrium time. The initial rapid phase may be due to the large number of vacant sites available at the initial period of the sorption (24). The amount of each metal adsorbed per unit mass of RSD also increased with increasing initial concentration of the metal ions. For example, the amount of $Cu^{2+}$ removed at 40 minutes contact jumped from 0.38 mg/g at the initial concentration of 5 mg/L to 1.48 mg/g and 3.17 mg/g, at the initial concentrations of 20 and 50 mg/L respectively. This may be because an increase in initial concentration enhances the interaction between the ions and the surface of the adsorbent (25). This however, leads to a corresponding reduction in the percentage removal of the metal ion (96.8, 88.9 and 76.6 % respectively). The same trend was also observed for the sorption of nickel.

Similar observation of a decrease in percentage removal with increasing initial concentration of sorbate, even though the amount adsorbed increased was reported in many works (26, 27). Removal efficiency ( R ) was higher for low concentration because of availability of unoccupied binding sites on the adsorbent. R decreased with increasing concentration because of nearly complete coverage of the binding sites at high metal concentrations.

However, lead was the most preferred for adsorption onto RSD of the three metals. For example, at the equilibrium time of 2 h, the adsorption capacities of the metals were 3.37, 3.91 and 1.34 mg/g for Cu, Pb and Ni respectively; indicating that Pb > Cu > Ni (Fig. 3).

## EFFECT OF RSD DOSE

Adsorbent dose is an important parameter in any adsorption process as it determines adsorption capacity at a given initial sorbate concentration. The effect of RSD dose on the adsorption of Cu (II), Pb (II) and Ni (II) ions was studied by varying the quantity of the adsorbent from 0.05 g to 0.70 g in 20 mL of 30 mg/L solution of TMS. while keeping other parameters (contact time, agitation speed, particle size, pH temperature) constant.

The results show that the adsorption capacity of RSD decreased with increasing adsorbent concentration. The adsorption capacity of RSD for copper ions in the mixture decreased from 3.75 to 0.49 mg/g with an increase in the adsorbent dose from 0.05 to 0.4 g (Fig. 4). Similar observations were also made in the adsorption of Pb (II) and Ni (II) ions. However, the removal efficiency, R, of the adsorbent generally improved with increasing dose. This can be attributed to the increase in the adsorbent pore surface areas and availability of more adsorption sites with increasing mass of adsorbent (26, 28).

The increase in removal efficiency with increasing adsorbent concentration was rapid at low dosage but gradually falls and describes a typical saturation curve. This is in line with Langmuir hypothesis of increasing competition among adsorbent particles per unit volume (28, 29, 30).

**Effect of pH**

The initial pH of a solution is a very important factor in an adsorption process (31). This is because a change in pH affects the nature and characteristics of both the adsorbent and the species of the adsorbate present, which eventually leads to a change in the adsorption (32, 33, 34).

In this work the effect of the initial pH of TMS on its adsorption by RSD was investigated over a range of pH values of 1.8 – 7.2 at the initial dye concentration of 30 mg/L. Change in the pH of the dye solution was effected using dilute NaOH and HCl solutions as appropriate. Figure 5 shows the effect of pH of TMS on the adsorption of the constituent metal ions. There was increase in the adsorption capacity of RSD for the three metal ions in TMS with increasing pH until a value of 3.7 for copper and nickel, and 2.7 for lead. There was only a slight variation in the adsorption of copper in the pH range 3.7 – 7.2, with the highest sorption observed at pH 5.6. For lead, 100% sorption (2.4 mg/g) was observed at a pH range of 3.7 – 7.2. There was, however, a drastic increase in adsorption capacity of RSD for lead from 0.64 to 2.35 mg/g (> 200% rise) with a change in pH from1.8 to 2.7. Similarly, a general increase in adsorption capacity was also observed in the adsorption of nickel from TMS. At acidic pH values the presence of $H^+$ ions in the system makes the surface of the adsorbent to acquire positive charge, which then repels the cations electrostatically (35). The increase in adsorption with rising pH in the acidic region can therefore be attributed to the decreasing competition between the heavy metal cations and $H^+$ ions for the active sites on RSD (36). Increase in pH leads to a decrease in the amount of $H^+$ ions on the surface of the adsorbent thereby reducing the repulsion between the positive surface charge and the cations of the heavy metals (37).

ADSORPTION ISOTHERMS

An adsorption isotherm model gives the equilibrium relationship between the sorbate in the fluid phase (solution) and the sorbate sorbed on the sorbent at constant temperature.(38, 39). They are very useful for obtaining the adsorption capacity so as to facilitate the evaluation of the feasibility of the adsorption process for a given application and for selection of the most appropriate sorbent at the optimum experimental conditions (38, 40). It is a factor which is important in optimizing the use of adsorbents (25, 32)

In this work, adsorption isotherms were carried out at initial concentrations of 5-60 mg/L. The Langmuir, Freundlich and Temkin isotherm models were employed to interprete the sorption process in order to understand the mechanism of adsorption of Pb (II) and Ni (II) ions by RSD.

The Freundlich isotherm is an empirical model which indicates the surface heterogeneity of the adsorbent. The equation is given as (41, 42):

$$q_e = K_f C_e^{1/n}$$ ------------------------------------------------------(4)

The linear form of the equation is:

$$\log q_e = \log K_f + \frac{1}{n}\log c_e$$ ---------------------------------------(5)

where $q_e$ is the amount of sorbate adsorbed at equilibrium (mg/g); $K_f$ (L/g) and $n$ are Freundlich constants which indicate the adsorption capacity of the adsorbent and adsorption intensity, respectively (43) , $c_e$ is the equilibrium concentration of sorbate in the solution (mg/dm$^3$)

A plot of *log* $q_e$ versus *log* $c_e$ gives a straight line of slope $1/n$ and intercept *log* $K_f$ from which $n$ and $K_f$ can be evaluated.

If $1/n < 1$, then the adsorption is favorable and the adsorption capacity increases with the occurrence of new adsorption sites. But if $1/n > 1$, the adsorption bond becomes weak and unfavorable adsorption takes place, leading to a decrease in adsorption capacity (42). The Langmuir isotherm equation is given as ( 44, 45):

$$qe = \frac{q_m k_a c_e}{1 + k_a c_e}$$ ---------------------------------------------------------(6)

where $q_e$ is the amount of dye adsorbed per unit mass at equilibrium(mg/g); $q_m$ is the maximum possible amount of dye that can be adsorbed per unit mass of adsorbent (mg/g); $c_e$ is concentration of sorbate in the solution at equilibrium (mg/dm$^3$); $k_a$ is the sorption equilibrium constant.

The linearised form of equation (6) is

$$\frac{c_e}{q_e} = \frac{1}{k_a q_m} + \frac{c_e}{q_m}$$ -----------------------(7)

A plot of $\frac{C_e}{q_e}$ versus $c_e$ gives a straight line, with a slope of $\frac{1}{q_m}$ and intercept $\frac{1}{k_a q_m}$.

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant $K_R$, the separation factor or equilibrium parameter, which is defined as:

$$K_R = \frac{1}{1 + K_a C_o}$$ ------------------------------------------------(8)

where $K_R$ is dimensionless separation factor; $K_a$ is Langmuir constant (dm$^3$ /mg); $C_o$ is the initial concentration of sorbate (mg/dm$^3$). The shape of the isotherm is linear if $K_R = 1$, it is irreversible if $K_R < 0$, unfavourable if $K_R > 1$ and favourable if $0 < K_R < 1$ (46, 47).

The Temkin isotherm model is given by the following equation (48, 49):

$$q = a + b \ln c_e \text{ -----------------------------------------------------(9)}$$

where $q$ is the amount of adsorbate adsorbed per unit weight of adsorbent; $C_e$ is the concentration of adsorbate in solution at equilibrium (mg/dm$^3$); $a$ is a constant related to adsorption capacity; $b$ is a constant related to adsorption intensity

A plot of $q$ versus ln $C_e$ gives a straight line from which the intercept ($a$) and the slope ($b$) can be evaluated. Temkin isotherm assumes that the more energetic adsorption sites are occupied first, and that the adsorption process is chemisorption i.e. the particles of the adsorbate get attached to the adsorbent through valent bond formation (42).

Parameters obtained from the linear plots of the three isotherm models as given by equations 5, 7 and 9 are presented in Table 1. From the correlation coefficient, $R^2$, values Langmuir seems to give the best fit. The maximum monolayer coverage, $q_m$ , is the appropriate parameter to consider when assessing the capacity of any adsorbent (40). The order of $q_m$ of RSD for the metals is: Pb (4.17 mg/g) > Cu (3.73 mg/g) > Ni (1.44 mg/g). This indicates that RSD has higher affinity for Pb (II) ions than for Cu (II) and Ni (II) ions present together in an aqueous system.

Plots of $K_R$ , a dimensionless separation factor, which is a characteristic of Langmuir isotherm model, against the initial concentration of metals in TMS is presented in Figure 6. $K_R$ values obtained for Cu (II) and Ni (II) ions fall between 0 and 1, indicating favourable adsorption (47).

The $K_f$ and n obtained from the linear plots of Freundlich isotherm are given on Table 1. The values of 1/n being less 1 may imply that there is an element of heterogeneity in the sorption process, especially for Cu (II) and Ni (II) ions. The values of Freundlich constant, $K_f$, obtained were 1.22, 3.41 and 0.69 for Cu, Pb and Ni respectively.. $K_f$ is an empirical constant which indicates the sorption capacity of the sorbent.

The Temkin parameters, $b_T$ and $K_T$ were evaluated and presented on Table 1.

## ADSORPTION KINETICS

To investigate the mechanism of the adsorption process, three rate equations and an intraparticle diffusion model by Webber-Morris were employed to test the experimental data. The kinetic models used were the Largergren pseudo-first order, the pseudo-second order and the Elovich models. The applicability of the models were ascertained by comparing the plots' goodness-of-fit tests using the regression coefficients, $R^2$ . The pseudo-first order model was described by Largergren as (50);

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \text{ ----------} \qquad (10)$$

where $q_e$ (mg g$^{-1}$) is the amount of dye adsorbed at equilibrium, $q_t$ (mg g$^{-1}$) is the amount of metal adsorbed at time $t$ and $k_1$ (min$^{-1}$) is the rate constant of pseudo-first order adsorption. The Largergren first order rate constant ($k_1$) and $q_e$ determined from the mode l for the metals, and their respective coefficients of correlation, $R^2$,are shown in Table 2. The experimental $q_e$ values did not agree at all with the values calculated from this model, $q_{e,mod}$ (Table 2). This, therefore, shows that the adsorption of TMS onto RSD does not follow a first order kinetics.

The pseudo-second order model gives the best description of the mechanism of TMS adsorption onto RSD. Apart from its having the highest $R^2$ for the three metals, the adsorption capacities calculated from this model was very close to the values obtained experimentally (Table 2). The pseudo-second order rate constant, $k_2$ obtained for the metals was of the order Pb (0.74 g/mg.min) > Cu (0.17 g/mg.min) > Ni (0.05 g/mg.min). The pseudo-second initial rate constant obtained from the model revealed a very low value for sorption of nickei in TMS.

The linear plots of Elovich equation for the three metal ions have relatively high correlation coefficients (Table 2). The Elovich model also can be said to be good for describing the sorption of TMS onto RSD. The Elovich initial adsorption rate constant, $\alpha$, for the adsorption of copper and lead are high, while the value was low for nickel (table 2).

The mechanism of the rate-limiting step in this sorption process is further investigated by fitting the experimental data in intraparticle diffusion plot. When the intraparticle mass transfer resistance is the rate-limiting step, the sorption process is said to be particle diffusion controlled (51). Several equations have been used to model the intraparticle diffusion.

According to Weber and Morris (52), a plot of sorption capacity at a given time, $q_t$ , versus $\sqrt{t}$ should be a straight line if intraparticle diffusion is involved; and if it is the only rate-determining factor, the line passes through the origin. This is from the equation:

$$q_t = K_d\, t^{0.5} \tag{11}$$

Where $K_d$ is the intraparticle diffusion rate constant.

However, if the plot has an intercept (i.e. does not pass through the origin), it shows that intra-particle diffusion may not be the only factor limiting the rate of the sorption process (53, 54). Poots et al., (53), however, proposed that during the early stages of sorption, some boundary layer resistance was involved. The equation was then modified as (55, 51) :

$$q_t = K_d\, t^{0.5} + X_1 \tag{12}$$

where $X_1$ depicts the boundary layer thickness (55).

$K_d$ and $X_1$ can be obtained from the slope and intercept respectively.

The correlation coefficients obtained from the plots were, 0.9107 – 0.9891 (0. Table 3). However, the straight lines do not pass through the origin i.e. the intercepts > 0 (Fig. 7). This deviation of the lines from the origin indicates that intra-particle diffusion may be a factor in the sorption process, but it is not the only controlling step (56). The intercept and the two-phase nature of the plot suggest that surface sorption is also an important factor in the sorption process, as indicated by the presence of boundary layer effect.

The first phase of the bilinear plot is attributable to boundary layer diffusion. Similar trend was reported in the literature (49, 57, 58). The second linear portion (phase II) indicates the micropore diffusion (59). The larger the intercept, the greater is the contribution of the surface sorption (boundary layer resistance) in the rate–limiting step (57). Both $K_{id}$ and $X_i$ have direct relationship with the initial concentration of the metal solution. So, the higher the initial concentration, the greater is the effect of boundary layer and its contribution on the rate determining step.

**Effect of temperature/ Thermodynamics**

Another way of elucidating sorption mechanism of adsorbate-adsorbent system is to study the effect of temperatue of the adsorbate system on the adsorption process so as to evaluate the thermodynamic parameters. This is with a view to ascertain the spontaneity of the sorption process. The thermodynamic parameters like Gibb's free energy change, $\Delta G^o$ (KJ/mol),the enthalpy change, $\Delta H^o$ (KJ/mol) and entropy change, $\Delta S^O$(J/mol/K) are then calculated (60, 61). The Gibbs free energy, $\Delta G^o$, is the fundamental criterion of spontaneity. A negative value of $\Delta G^o$ establishes the feasibility of an adsorption process (62).

In this work, these parameters were obtained from the following equations:

$$\Delta G = -RT\ln K \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. \ (26)$$

$$\Delta G = \Delta H - T\Delta S \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(27)$$

where

$\Delta S$ is the standard entropy change (J/mol/k)

$\Delta H$ is the standard entropy change (J/mol)

T is the absolute temperature(K)

K is the equilibrium constant

$\Delta H$ and $\Delta S$ were obtained from the intercept and slope of the plot of $\Delta G$ against T respectively.

Figure 8 shows the linear plots of $\Delta G$ versus T for the sorption of Cu (II), Pb (II) and Ni (II) ions in TMS. Table 4 shows the magnitudes of the thermodynamic parameters ($\Delta G$, $\Delta H$ and $\Delta S$) obtained at different temperatures (300-328 K). The negative values of $\Delta G$ confirmed the feasibility and spontaneity of the adsorption process at the temperatures studied. The $\Delta H$ values obtained from the plots for the three metals were negative, indicating that the adsorption processes were exothermic (Table 4). The $\Delta S$ values were, however, positive (Table 4). The positive values of $\Delta S$ is an indication that randomness increased at the RSD/TMS interface.

The sorption of Pb (II) ions was spontaneous as it has negative $\Delta G$ al all temperatures studied. However, the spontaneity of Cu (II) sorption become increasingly reduced with increasing temperature (Fig.8).

## CONCLUSION

The adsorptive removal of a mixture of copper, lead and nickel ions from aqueous solution by raw saw dust of locust bean tree was investigated under different experimental conditions, in this work. The results presented in the paper clearly show that the different operational parameters such as adsorbent dosage, initial dye concentration, temperature and contact time employed in this study, influenced the overall adsorption process. The Langmuir isotherm was found to have the best fit to the experimental data, with the highest regression coefficient. The sorption dynamics showed that the dye uptake rate was rapid at the beginning, attaining equilibrium in 2 h. The kinetics was best described by the pseudo-second order and Elovich models, with reasonably high linear regression coefficients. The thermodynamic parameters obtained indicated that the sorption process was feasible (negative $\Delta G$) and exothermic (negative $\Delta H$)**.** The low $\Delta G$ values points to the likelihood of physisorption. The sorption process was associated with a increase in the degree of randomness as $\Delta S$ was negative

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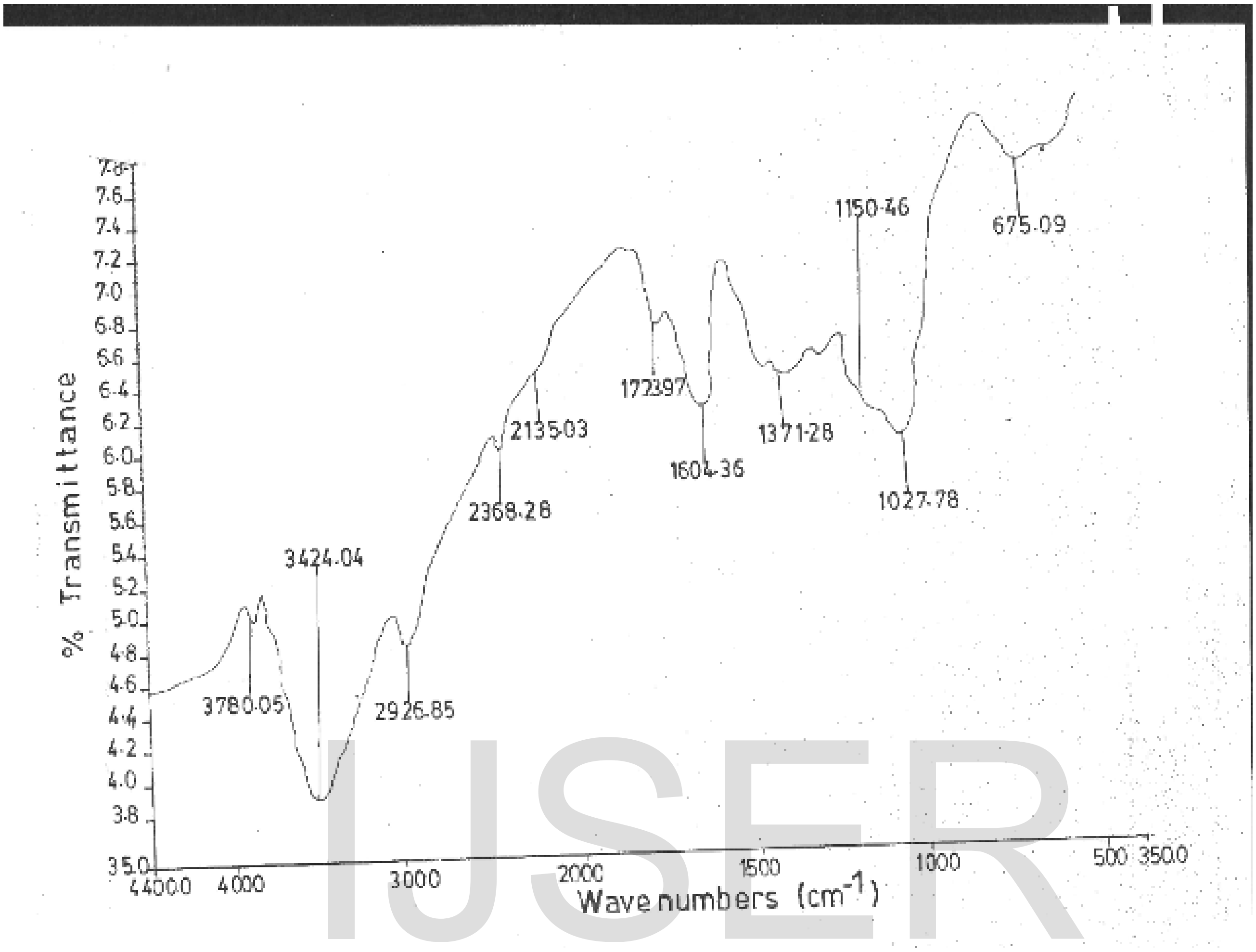


Fig.1as: FTIR spectrum of raw sawdust (RSD) before metal mixture adsorption

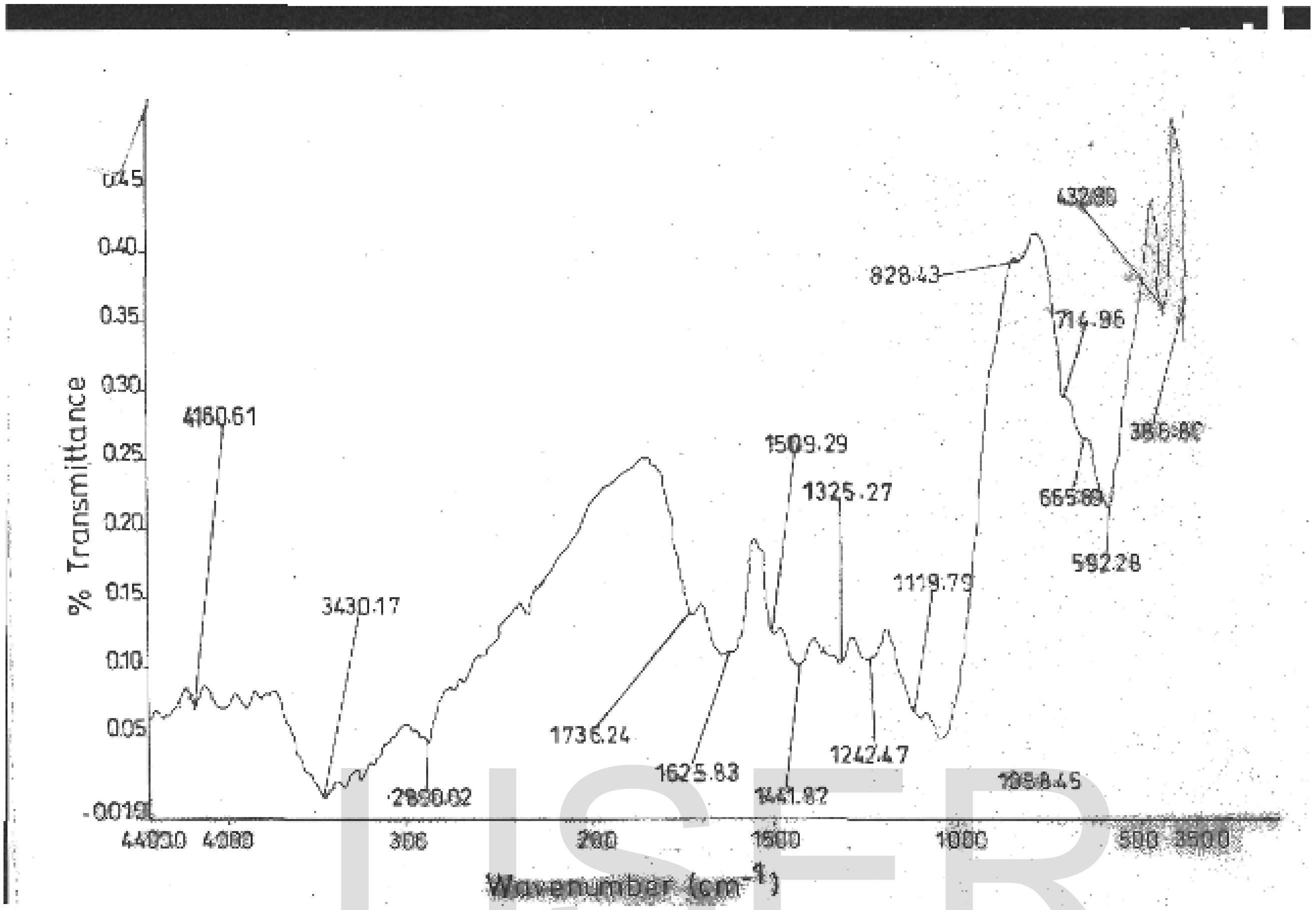
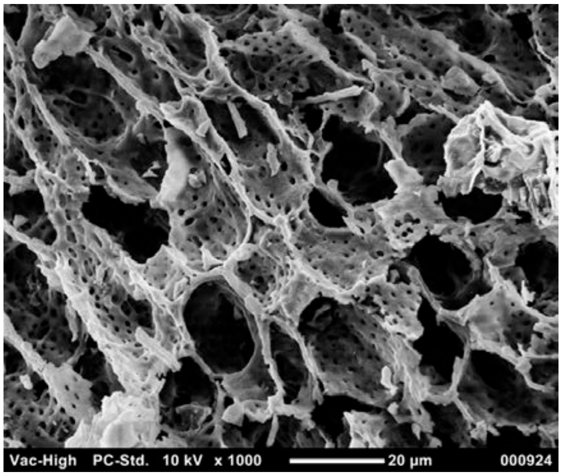
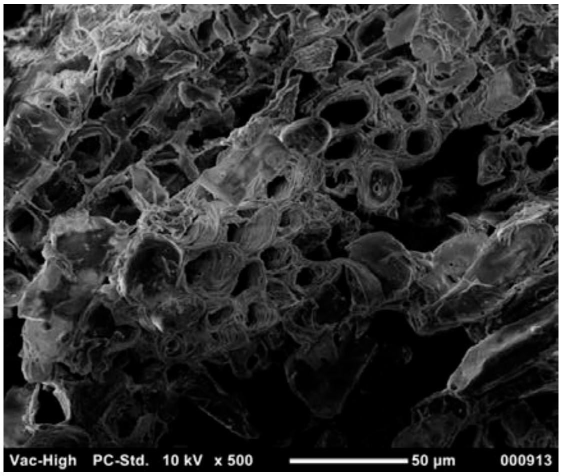


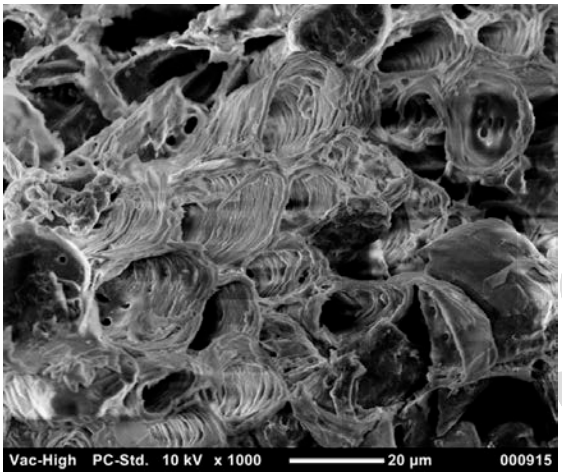
Fig.1b: FTIR spectrum of raw sawdust (RSD) after metal mixture adsorption



(a) X100 RSD



(b) X500 RSD



© X1000 RSD

Figure 2: SEM images RMH at different magnifications (a) x100, (b) x500, (c) x1000

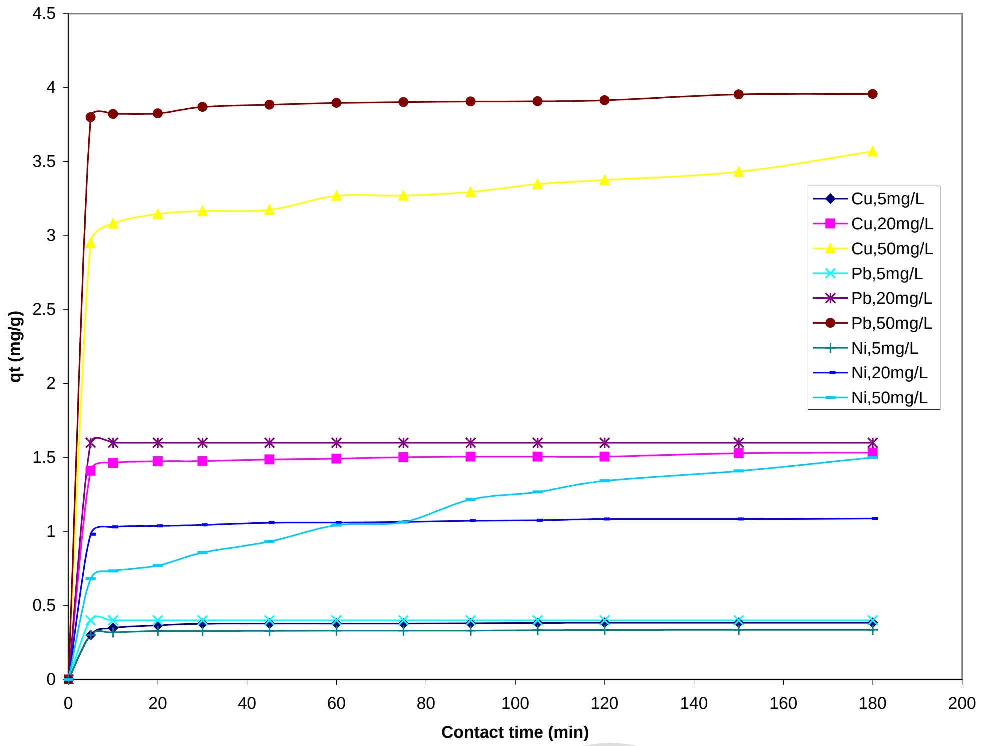


Figure 3: Effect of Contact time and initial metal concentration on the sorption of TMS by RSD.

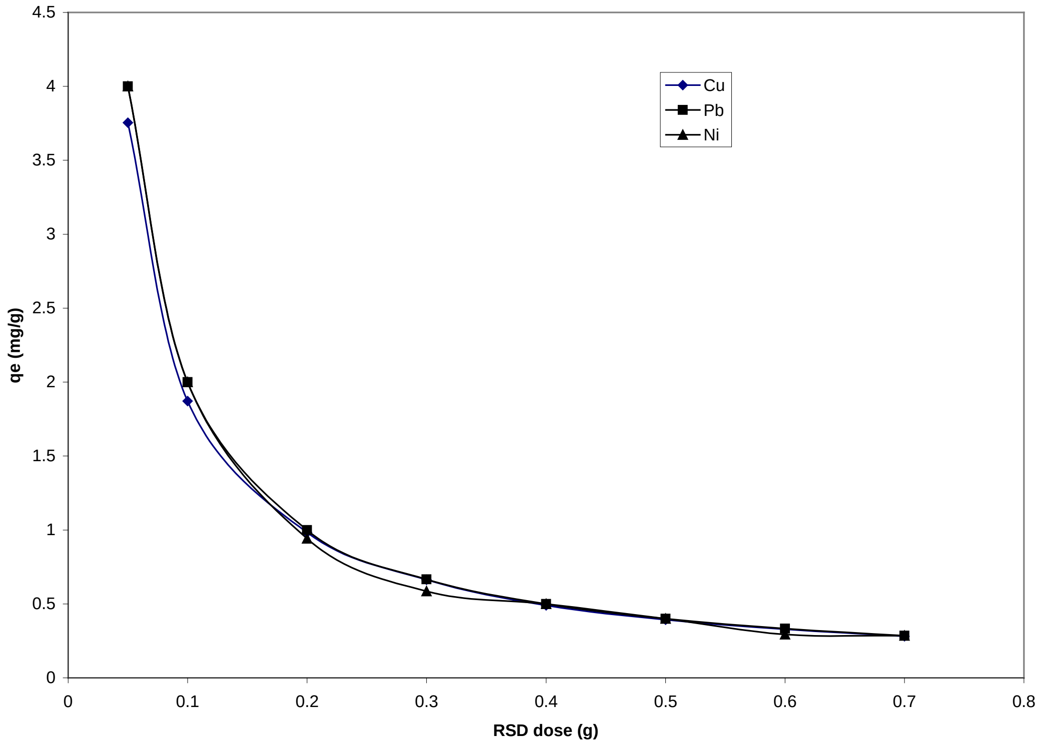


Figure 4 : Effect of RSD dose on the adsorption of Cu (II), Pb (II) and Ni (II) ions in TMS

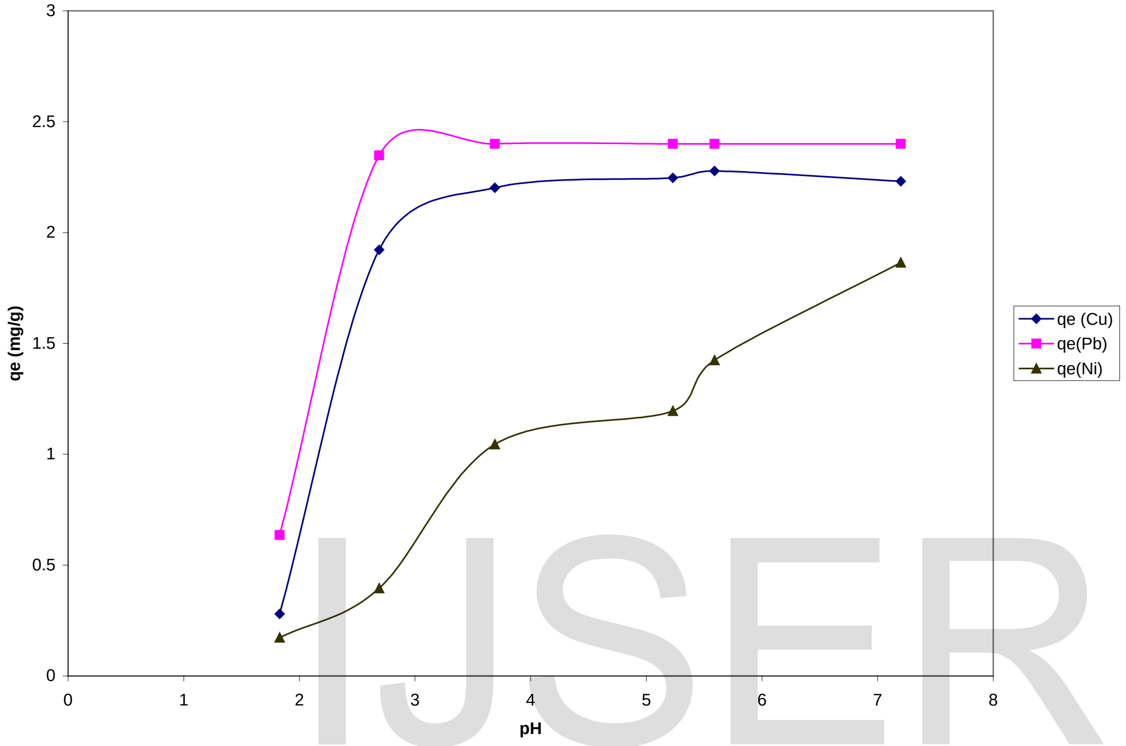


Figure 5 : Effect of the pH of TMS on the adsorption of Cu (II), Pb (II) and Ni (II) ions by RSD

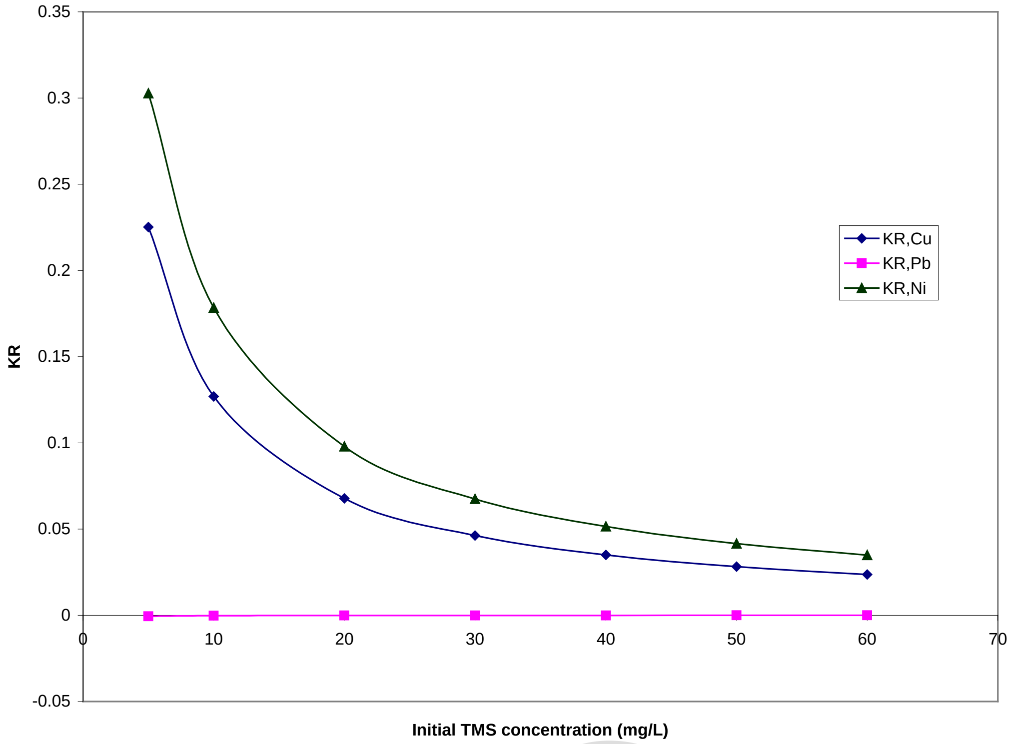


Figure 6 : Plots of $K_R$ versus initial concentrations of Cu, Pb and Ni in TMS

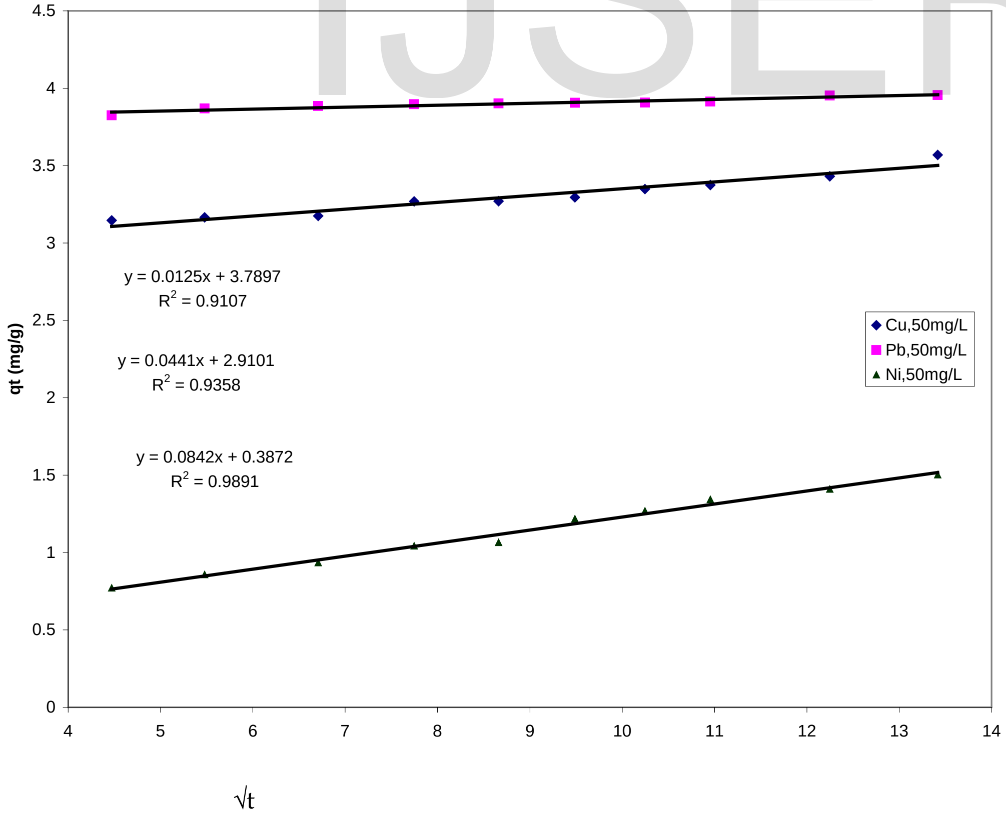


Figure 7 : Webber-Morris intra-particle diffusion plots for the sorption of Cu, Pb and Ni in TMS

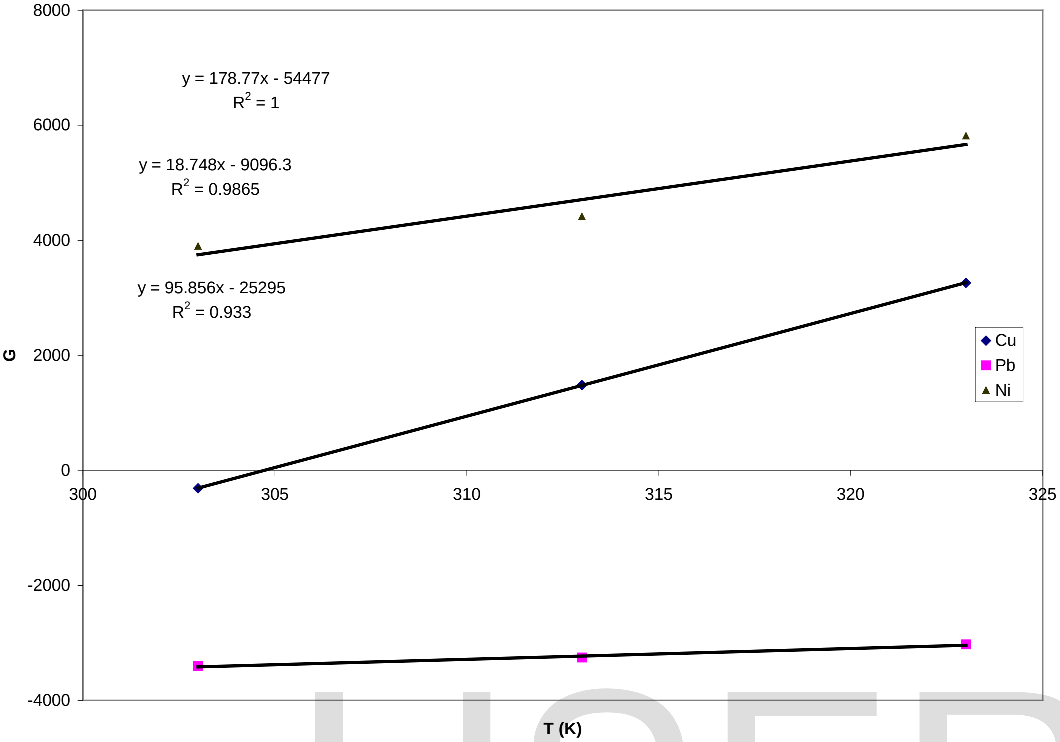


Figure 8 : Plots of Gibb's free energy change, ΔG, against absolute temperature

Table 1: Isotherm models parameters for TMS adsorption onto RSD

| **Metal** | **Langmuir** | | | **Freundlich** | | | **Temkin** | | |
|---|---|---|---|---|---|---|---|---|---|
| | **$R^2$** | **$q_m$** | **$K_a$** | **$R^2$** | **n** | **$K_f$** | **$R^2$** | **$b_T$** | **$K_T$** |
| **Cu** | 0.9934 | 3.73 | 0.69 | 0.9148 | 2.14 | 1.22 | 0.9358 | 0.695 | 10.48 |
| **Pb** | 0.9911 | 4.17 | - 342 | 1 | -1.47 | 3.41 | 1 | 1.24 | 0.85 |
| **Ni** | 0.9838 | 1.44 | 0.46 | 0.5732 | 5.46 | 0.69 | 0.7126 | 0.15 | 146.03 |

Table 2: Kinetics Model Parameters for the adsorption of TMS onto *Pakia biglobosa* saw dust

| | | **Pseudo- first order** | | | **Pseudo-second order** | | | | **Elovich** | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Metals in TMS** | $q_e$, exp | $q_{e,\ mod}$ | $K_1$ | $R_2$ | $q_{e,\ mod}$ | $K_2$ | H | $R_2$ | A | β | $R_2$ |
| **Cu** | 3.37 | 0.72 | 0.04 | 0.7451 | 0.39 | 0.17 | 1.98 | 0.9995 | $1.44\times10^{9}$ | 8.38 | 0.9572 |
| **Pb** | 3.91 | 0.30 | 0.04 | 0.706 | 3.92 | 0.74 | 11.31 | 1 | $3.74\times10^{40}$ | 25.91 | 0.9574 |
| **Ni** | 1.34 | 1.04 | 0.02 | 0.9111 | 1.42 | 0.05 | 0.09 | 0.9717 | 0.66 | 4.86 | 0.8736 |

$C_o$ = 50mg/L

Table 3: Weber-Morris Intra-particle diffusion model parameters for TMS adsorption onto RSD

| **Metals in TMS** | **$R^2$** | **$K_{id}$** | **$X_i$** |
|---|---|---|---|

| | | | |
|---|---|---|---|
| **Cu** | 0.9358 | 0.044 | 2.91 |
| **Pb** | 0.9107 | 0.013 | 3.79 |
| **Ni** | 0.9891 | 0.084 | 0.39 |

Table 4: Thermodynamics constants for the adsorption of TMS onto RSD

| **Metals in TMS** | **ΔH (KJ/mol)** | **ΔS (J/mol$K^{-1}$)** | **$R^2$** |
|---|---|---|---|
| **Cu** | -54.48 | 178.77 | 1 |
| **Pb** | -9.10 | 18.75 | 0.9868 |
| **Ni** | -25.30 | 95.86 | 0.933 |