

Utilizing the Sorption Capacity of Local Nigerian Sawdust for Attenuation of Heavy Metals from Solution: Isotherm, Kinetic, and Thermodynamic Investigations.

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ABSTRACT

The feasibility of utilizing local sawdust (SD) material of Nigerian origin as low-cost adsorbent to remove Pb (II) and Cd (II) ions from a aqueous solution was investigated. Batch adsorption methodology was used to evaluate the effect of solution pH, initial metal ion concentration, adsorbent dose, agitation time and temperature. The adsorption was favored with maximum adsorption at pH 6.0. Equilibrium sorption time of 50 and 40 mins were obtained for Pb (II) and Cd (II) ions on the adsorbent. Fourier transform infrared (FTIR), X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) analysis were used to characterize the adsorbent.

The equilibrium isotherm data were analyzed using the Langmuir, Freundlich, Temkin, Dubinin–Radushkevich (D–R), Scatchard and Flory-Huggins isotherm models. Among the six isotherm models tested, Flory-Huggins, Langmuir and Temkin fitted well to the experimental data more than those of Freundlich, scatchard and Dubinin–Radushkevich and therefore gave a good description for the sorption of both ions onto SD.

The kinetic data were analyzed using the pseudo-first order, pseudo-second order equations, the Elovich equation and film diffusion rate equation. The pseudo-second order provided the best fit to the experimental data. Thermodynamic studies indicated an endothermic, spontaneous and a physicochemical process between both metal ions and SD. The results showed that the adsorption capacity of the local SD material can be utilized as a low-cost adsorbent for the removal of Pb (II) and Cd (II) ions from solution.

(Key terms: environmental pollution, heavy metals, adsorption, Nigerian sawdust, isotherm, kinetic, thermodynamics)

INTRODUCTION

Pollution of the environment with toxic substances, especially heavy metals has become one of the most serious environmental problems. The reason is because these heavy metals are known to be highly toxic at low concentration in water, non-biodegradable, and accumulate to certain level which causes different health problems in animals, humans and aquatic organisms. They are commonly found in aqueous effluents from paints, batteries, ceramic glazes, metal products, dye and pigment industries (Mohammad et al., 2010).

The heavy metals include Pb, Cd, Cu, Zn, Ni, and Cr (Argun and Dursun, 2008). Lead for instance is known to be highly toxic among heavy metals; it can interfere with enzyme activities and formation of red blood cells. Lead poisoning in humans causes severe damages to the kidney, nervous system, reproductive system, liver and brain (Naiya et al., 2009). Cadmium is one of the most toxic metals and is used in chemical industries in manufacturing of pesticides, herbicides and fungicides (Zahra et al., 2008). Cadmium is responsible for kidney tubular impairment, affects ion regulation, calcium metabolism and skeletal calcification. Cadmium poisoning also causes severe abdominal pain, vomiting, diarrhea and a choking sensation (Igwé and Abia, 2007).

Well known techniques for the treatment of wastewaters contaminated with lead, cadmium

and other heavy metals are solvent extraction, ion exchange, membrane filtration, reverse osmosis, precipitation evaporation, chemical oxidation or reduction, electrochemical treatment and activated carbon adsorption (Gode and Pehlivan, 2006). However, among these techniques, adsorption on activated carbon has been discovered to be the most effective and commercially applicable for the removal of lead, cadmium and other heavy metals from effluents. These techniques are expensive which limit their applications to developing nations. Due to the high cost involved in treating industrial wastewaters by the use of activated carbon, scientists are presently in search for cheaper alternatives (Abia and Asuquo, 2006).

Adsorption using low-cost materials as adsorbents have been researched extensively by scientists, which include the use of biomass materials, sawdust, clay, zeolite, kaolinite, illite, sepiolite, montmorillonite, and bentonite (Echeverria et al., 2005; Shukla and Roshan, 2005). However, most studies on adsorption of heavy metals using these materials usually involve chemical modification or other forms of treatments to help improve their adsorption capacity. As a result, the application of these treatments increases the cost of production which makes them expensive to developing nations.

In this study, local easily accessible and obtainable sawdust of Nigerian origin was utilized as a low cost adsorbent for the simultaneous adsorption of Pb (II) and Cd (II) ions from aqueous solution. The sawdust was utilized without chemical treatment or modification as a cheap alternative adsorbent because it is present in very large quantity in Emene, Enugu east local government area, Enugu State, Nigeria. Batch adsorption technique was applied and the influence of pH, concentration, temperature and agitating time were studied. Also, equilibrium, kinetics and thermodynamic parameters were determined.

EXPERIMENTAL

Adsorbent Preparation and Characterization

The sawdust was obtained from a saw mill in Enugu State, Nigeria. It was then washed with de-ionized water to get rid of unwanted materials and possibly some heavy metals attached to the surface. The saw dust was sundried for several

days, after which it was ground or pulverized to powdery form. The sample was then passed through 100 μm mesh sieve to obtain the sawdust (SD) adsorbent. The SD was characterized with the Fourier transform infrared spectrophotometer (Shimadzu FT-IR 8400s), X-ray diffractometer (MD Randicon model) and scanning electron microscope (SEM) (Hitachi S4800 model).

Adsorbate Preparation

The entire chemicals for the study was of analytical grade obtained from Sigma-Aldrich and were used without further purification. A laboratory solution of lead (II) and cadmium (II) ions were prepared by dissolving appropriate amounts of $\text{Pb}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2$, respectively in 50ml of de-ionized water in a beaker and stirred properly with a glass rod to ensure proper dissolution. Thereafter the 50mL solution was then placed in 1 liter volumetric flask and made up to the meniscus mark with de-ionized water to obtain a stock solution of concentration 1000 mg/L of the metal ions. Several lower concentrations of the metal ions which include 200, 400, 600, and 800mg/L were then prepared from the stock solution by serial dilution. The pH of each of the solution was adjusted to the required value by the addition of 0.1M NaOH or 0.1M HCl before the adsorbent was added.

Adsorption Study

Batch adsorption procedure was applied to determine the effect of pH, initial metal ion concentration, adsorbent dose, temperature and agitation time. Batch adsorption experiment was performed by adding 0.1 g of the adsorbent to 20 ml of a given solution in a pretreated glass bottle at room temperature of 300 K. The influence of pH (2.0–8.0), initial metal concentration (200, 400, 600, 800, and 1000 mg/L), adsorbent dose (0.1, 0.2, 0.3, 0.4, and 0.5 g), contact time (10, 20, 30, 40, 50, 60, 90, and 120 min) and temperature (300, 313, 323 K) were evaluated.

The bottles were placed in a thermo-stated water bath for temperature regulation when the effect of temperature was studied. In order to evaluate the effect of a particular parameter, that parameter was varied while others were kept constant at the optimum conditions of pH 6.0, contact time 120 min, metal concentration 200 mg/L. At the end of

a given agitation time of sorption the solutions were centrifuged for 15 min at 5000 rpm. Atomic Absorption Spectrophotometer (AAS) (Buck scientific model 210VGP) was used to determine the concentration of metal ions remaining in solution.

The following equations were utilized in the calculation of percentage removal of metal ions and the adsorption capacity of the adsorbent for metal ions respectively:

$$\text{Removal (\%)} = \frac{100 [C_0 - C_e]}{C_0} \quad (1)$$

$$q_e \text{ (mg/g)} = \frac{v[C_0 - C_e]}{m} \quad (2)$$

where q_e (mg/g) is the adsorption capacity, C_0 (mg/L) is the initial metal ion concentration in solution, C_e (mg/L) is the metal ion concentration remaining in solution at equilibrium, v (litres) represents the volume of solution used for the adsorption and m (g) is the mass of the adsorbent used.

RESULTS AND DISCUSSION

Adsorbent Characterization

The adsorbents were characterized to determine the surface nature and functional groups, the mineral identification and the morphology of the adsorbents using the Fourier Transform Infrared (FTIR) spectroscopy, X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) respectively. The FT-IR analysis allows spectrophotometric observation of adsorbent surface in the range 400 – 4000 cm^{-1} and serves as a direct means for the identification of the functional groups on the surface.

The FTIR spectrum of SD is shown in Figure 1. A broad OH band was observed at 3403.1 cm^{-1} , which indicated an outer surface –OH stretching vibration. Absorption bands at 2810.4 - 2922.2 cm^{-1} is attributed to the CH_3 stretching vibration of aliphatics organic compounds while bands the band at 1640 cm^{-1} corresponds to the C=O group (Nwadiogbu *et al.*, 2013). The C=C group was observed by bands at 1304 - 1461 cm^{-1} . Absorption band at 1129.4 cm^{-1} corresponds to the C-O group (Das and Mondal, 2011). In general, the spectra of the adsorbent showed the presence of surface functional groups responsible

for the adsorption of Pb (II) and Cd (II) from the contaminated solution.

The X-ray Diffraction technique is a powerful tool to analyze the crystalline or amorphous nature of materials. The X-ray diffraction spectrum of the adsorbent is shown in Figure 2. The XRD spectra showed several peaks of low and high intensity which indicated an irregular structure of the adsorbent.

Scanning electron microscopy (SEM) of the adsorbent is shown in Figure 3. The SEM is used to examine the surface morphology and the porous nature of the material responsible for adsorption of metal ions. From the SEM images, it is observed that the adsorbent revealed a porous nature, considerable number of heterogeneous pores, an irregular surface and particle aggregation of various shapes and sizes (Meitei and Prasad, 2013). The presence of pores helps in the diffusion of metal ions into the adsorbents during the sorption of metal ions from solution (Dawodu and Akpomie, 2014). In general, the porous nature of the adsorbents revealed their suitability for adsorption of Pb (II) and Cd (II) from aqueous solution.

Effect of Initial Solution pH

The initial pH of solution is one of the most important factors in the adsorption of metal ions onto adsorbents as it affects the surface charge of the adsorbent and the degree of ionization and specification of the adsorbate (Meitei and Prasad, 2013). The effect of pH on the simultaneous adsorption of Pb (II) and Cd (II) ions onto SD is shown in Figure 4 and Figure 5.

From Figure 4, It was observed that the percentage removal of both metal ions on the adsorbent showed an increase with increase in initial pH of solution. With an increase in initial pH of solution from 2.0 to 8.0, the percentage removal of Pb (II) increased from 63.45 to 99.15%, while in Figure 5 the adsorption capacity increased from 25.38 to 39.66 mg/g. Similarly, with an increase in the initial pH of solution from 2.0 to 8.0, the percentage removal of Cd (II) showed an increase from 57.85 to 97.1%, while the adsorption capacity also increased from 23.14 to 38.84 mg/g. The low adsorption recorded at lower pH values is simply due to excess H^+ ions in solution which competes with

the metal ions for the active sites of the adsorbent, resulting in a low removal.

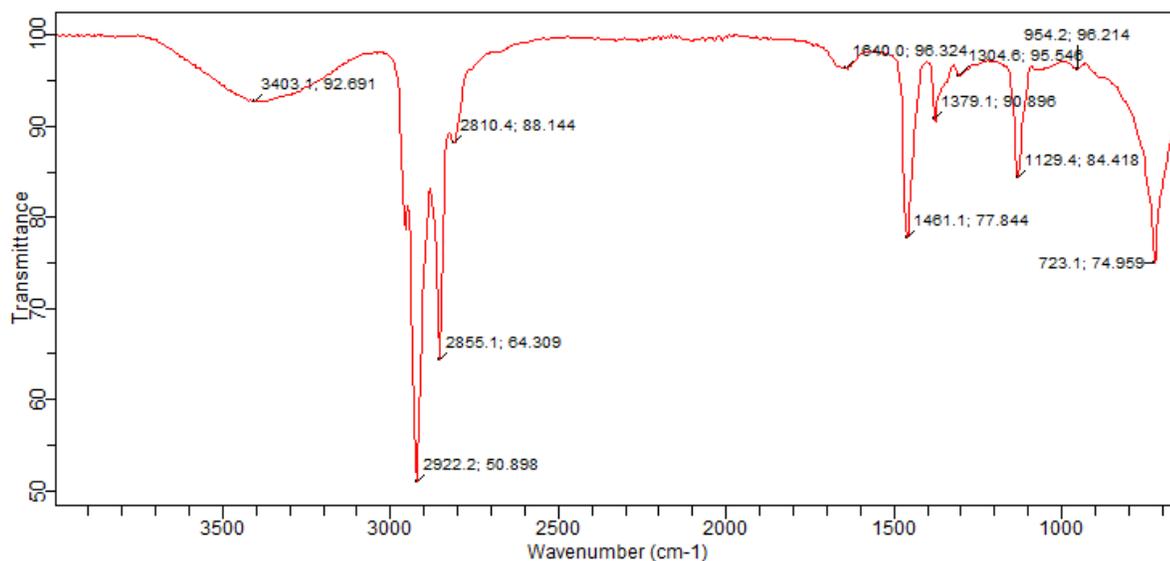


Figure 1: Fourier Transform Infrared Spectrum of Sawdust.

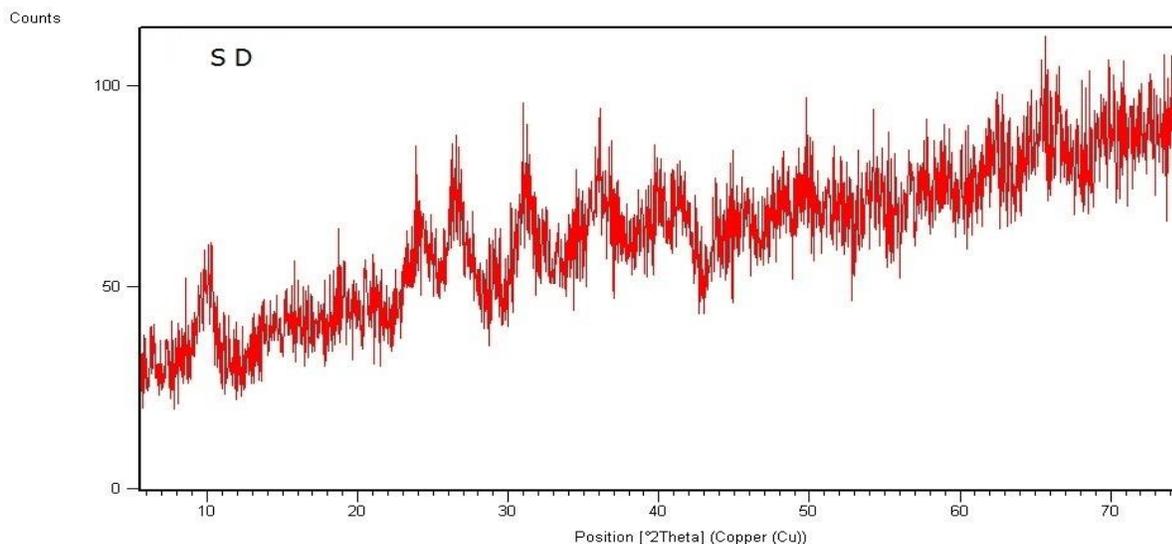


Figure 2: X-ray Diffraction Spectrum of Sawdust.

As pH of the solution increases, the concentration of H^+ ions in solution decreases, this reduces the competition between the metal ions and H^+ ions for the active sites of the adsorbents leading to an increase in percentage removal of metal ions. Furthermore, at higher pH values greater than 6.0, there is the precipitation of metal ions from solution in the form of hydroxides and this usually

accounts for the higher removal recorded at pH 7.0 and 8.0.

Also, comparing the adsorption of the two metal ions at all pH values on all the adsorbents, the following trend was observed $Pb(II) > Cd(II)$. The difference in this adsorption trend of $Pb(II)$ and $Cd(II)$ may be attributed to differences in

behavior of these metals or their ions in solution (Barka et al., 2013).

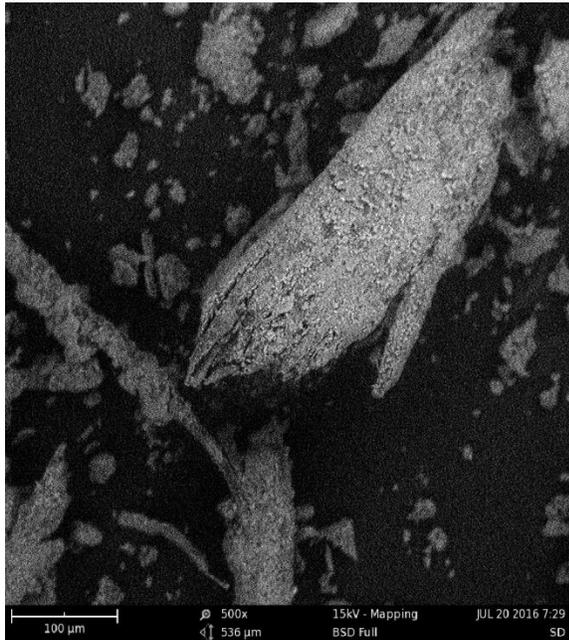


Figure 3: Scanning Electron Microscopy of Sawdust.

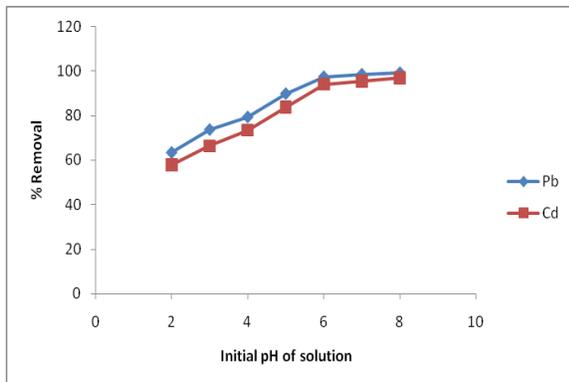


Figure 4: Effect of Initial pH of Solution on the Percentage Removal of Heavy Metals.

Effect of Initial Metal Ion Concentration

The amount of metal ions adsorbed by an adsorbent is a function of the initial concentration of the adsorbate (metal ion), which makes it an important factor to be considered for efficient adsorption. The effect of initial metal ion concentration on the percentage removal of Pb (II) and Cd (II) onto the adsorbent is shown in Figure 6.

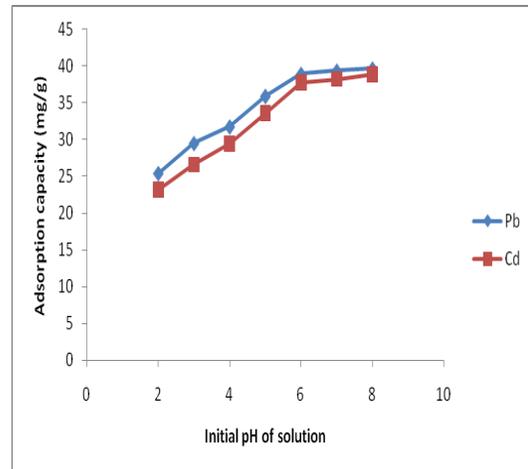


Figure 5: Effect of Initial pH of Solution on the Adsorption Capacity of the Adsorbent for Heavy Metals.

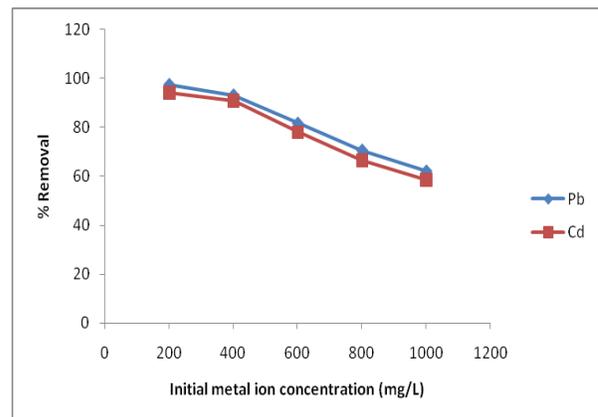


Figure 6: Effect of Initial Metal Ion Concentration on the Percentage Removal of Heavy Metals.

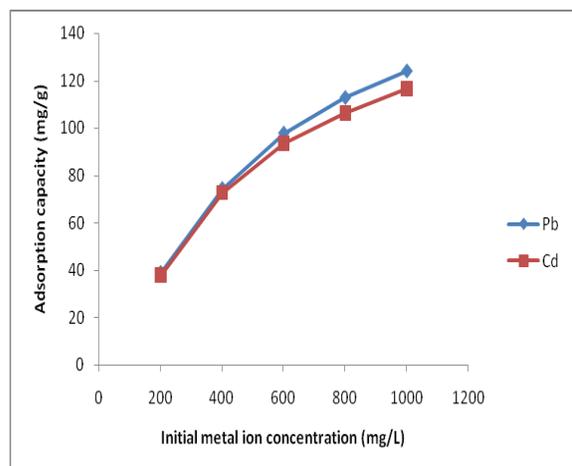


Figure 7: Effect of Initial Metal Ion Concentration on the Adsorption Capacity of the Adsorbents for Heavy Metals.

A decrease in percentage adsorption of both metal ions on the adsorbents with increase in initial metal ion concentration was observed. This decrease in percentage adsorption with increase in metal ion concentration is due to the fact that at lower concentrations, more of the metal ions would be removed by the abundant active sites on the adsorbent. At higher concentrations, more metal ions would be left un-adsorbed due to saturation of the active sites of the adsorbents (Chen et al., 2008). The effect of initial metal ion concentration on the adsorption capacity of the adsorbents for Pb (II) and Cd (II) was also determined as illustrated in Figure 7.

Unlike the decrease observed in percentage adsorption, an increase in adsorption capacity for both metal ions on the adsorbent with increase in initial metal ion concentration was recorded. The increase in adsorption capacity with initial metal ion concentration observed is attributed to the increasing concentration gradient which acts as a driving force to overcome the resistances to mass transfer of metal ions between the aqueous and solid phase. In fact, higher concentration in solution implies higher metal ions fixed at the surface of the adsorbent and maximum utilization of the active sites (Barka et al., 2013). The metal ions adsorption by the adsorbents followed the trend Pb > Cd and metal concentration of 200 mg/L was utilized in this study due to the high percentage removal recorded.

Adsorption Isotherm

Adsorption isotherm expresses the relationship between the amounts of adsorbate removed from the liquid phase by unit mass of adsorbent at a constant temperature. Adsorption isotherms are basic requirements for the design of adsorption systems. A precise mathematical description of equilibrium adsorption capacity is very important for reliable prediction of adsorption parameters and quantitative comparison of adsorption behavior for different adsorbent systems.

The parameters of equilibrium isotherms often give useful information on sorption mechanism, surface properties and affinity of the adsorbent. It is therefore important to determine the most suitable correlation of equilibrium curves in order to optimize the conditions for designing adsorption systems (Vagheti et al., 2008). In this study, the Langmuir, Freundlich, Temkin, Dubinin–Radushkevich (D–R), Scatchard and Flory–

Huggins isotherms were tested to analyze the equilibrium data, and the results are shown in Table 1.

Table1: A Comparison of the Langmuir, Freundlich, Tempkin, Dubinin–Radushkevich (D–R), Scatchard and Flory-Huggins Isotherm Constants for the Adsorption of Pb(II) and Cd(II) Ions unto Sawdust.

Isotherm Models	Pb(II)	Cd(II)
Langmuir		
q_L (mg/g)	142.86	125
K_L (L/mg)	4.0×10^{-2}	3.1×10^{-2}
R^2	0.995	0.996
Freundlich		
K_F	27.23	20.80
$1/n$	0.264	0.297
N	3.79	3.37
R^2	0.968	0.929
Tempkin		
A (L/g)	1.449	0.629
B (mg/g)	19.53	21.08
R^2	0.998	0.983
Dubinin-Radushkevich		
q_m (mg/g)	101.900	99.186
β (mol ² /J ²)	5×10^{-6}	2×10^{-5}
R^2	0.855	0.905
Scatchard		
q_s (mg/g)	118.277	118.600
b (L/mg)	0.083	0.040
R^2	0.919	0.975
Flory-Huggins		
K_{FH}	3.443×10^{-4}	2.722×10^{-4}
n_{FH}	-0.733	-0.966
R^2	0.986	0.975

The Langmuir isotherm is used to describe adsorption phenomena and is based on the assumption that uptake occurs on a homogenous surface by monolayer sorption without interaction between adsorbed molecules. The linear form of the Langmuir isotherm equation can be expressed as (Langmuir, 1918):

$$C_e/q_e = 1/q_L K_L + C_e/q_L \quad (3)$$

where q_e is the monolayer adsorption capacity of the adsorbent (mg/g), K_L is the Langmuir adsorption constant (L/mg) related to the energy of adsorption, which quantitatively reflects the affinity between the adsorbent and adsorbate, and q_L is the maximum monolayer adsorption capacity of adsorbent (mg/g). The constants q_L and K_L can be determined from the slope and the intercept of the linear plot of C_e/q_e against C_e .

From Table 1, the correlation coefficient (R^2) of Pb (II) and Cd (II) were very high, 0.995 and 0.996 indicating a good fit of the Langmuir isotherm model in the description of the sorption process by SD. This indicated that the surface of the adsorbent is homogenous in nature and involves a monolayer sorption of Pb (II) and Cd (II) ions. The maximum monolayer adsorption capacity for Pb (II) and Cd (II) by SD are 142.86 mg/g and 125.00 mg/g, respectively. The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor (R_L) defined by the relationship:

$$R_L = 1/[1 + K_L Co] \quad (4)$$

where Co is the initial metal ion concentration in (mg/L) and K_L is the Langmuir equilibrium constant (L/mg). The value of the separation factor provides important information about the nature of the adsorption process. The adsorption is said to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). For the initial metal concentration from 200 to 1000 mg/L for both metal ions used in this study, the values of R_L ranged from 0.02 to 0.14; indicating a favorable adsorption of Pb (II) and Cd (II) ions onto SD.

The Freundlich isotherm model is applied to non-ideal sorption on heterogeneous surfaces and the linear form of the equation is given as (Freundlich, 1906):

$$\log q_e = \log K_F + [1/n] \log C_e \quad (5)$$

where K_F (mg/g) (mg/L)^{1/n} and n are Freundlich adsorption constants related to the adsorption capacity and intensity of the adsorbent respectively. The constants were determined by the linear plot of $\log q_e$ versus $\log C_e$.

As seen from Table 1, the values of the correlation coefficient (R^2) (0.968 and 0.929) for Pb (II) and Cd (II) ions for Freundlich model were lower than those of the Langmuir isotherm model. Furthermore, if the value of n lies between 1 and 10, it indicates a favorable adsorption (Dawodu and Akpomie, 2014). The value of n obtained is 3.79 and 3.37 for Pb (II) and Cd (II) ions respectively, indicating a favorable adsorption process.

The Temkin isotherm model unlike the Langmuir and Freundlich isotherms takes into account the interactions between adsorbents and metal ions to

be adsorbed and is based on the assumption that the free energy of sorption is a function of the surface coverage (Chen et al., 2008). The linear form of the Temkin isotherm model is expressed (Temkin and Pyzhev, 1940):

$$q_e = B \ln A + B \ln C_e \quad (6)$$

where $B = RT/b_T$, T is the temperature (K), R is the ideal gas constant (8.314 J/mol K) and A and b_T are constants. The constant B is related to the heat of adsorption and A is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy. The plot of q_e versus $\ln C_e$ enables the determination of A and B . The values of the regression coefficient (R^2) of 0.998 for Pb (II) and 0.983 for Cd(II) obtained from Temkin model are very high as those of Langmuir model and therefore better than those of the Freundlich model of low R^2 values.

The Dubinin–Radushkevich (D–R) isotherm model which does not assume a homogenous surface or a constant adsorption potential as the Langmuir model was also applied in the analysis of the experimental data. The linear form of the D–R isotherm model is written as (Dubinin et al., 1947):

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (7)$$

Where q_e (mg/g) is the adsorption capacity, q_m (mg/g) is the theoretical saturation capacity, β (mol²/J²) is a constant related to the mean free energy of adsorption per mole of the adsorbate and ε is the Polanyi potential expressed as (Anirudan and Schithra, 2010):

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (8)$$

where R (J/mol K) is the gas constant and T (K) is the absolute temperature. The D–R constants qm and β were calculated from the linear plot of $\ln q_e$ versus ε^2 and are shown in Table 1. From linear regression values, R^2 of 0.855 and 0.905 for Pb(II) and Cd(II) ions, are much lower than the Langmuir and Temkin values. Therefore among the four isotherms tested so far the Langmuir and Temkin isotherms fitted well to the experimental data.

The Scatchard isotherm was applied to verify the homogenous or heterogenous nature of the adsorbent in comparison with the data obtained from the Langmuir and Freundlich isotherm. The linear form of the Scatchard isotherm also called

independent site oriented model is expressed as (Anirudan and Schithra, 2010) follows:

$$q_e/C_s = q_s b - q_e b \quad (9)$$

where q_s (mg/g) and b (L/mg) represent the Scatchard isotherm sorption parameters. If a straight line is obtained from the Scatchard plot of q_e/C_e against q_e , then the adsorbent presents only one type of binding site (Homogenous surface), but if a deviation from linearity is obtained, then the adsorbent has more than one type of binding site (Heterogenous surface) (Anirudan and Schithra, 2010). From Table 1, the R^2 values of 0.919 and 0.975 obtained for Pb(II) and Cd(II) ions, showed slight linearity which indicates a homogeneous surface of SD and this accounts for the good fit to the experimental data obtained by the Langmuir model.

The Flory-Huggins isotherm was used to evaluate the degree of surface coverage characteristics of adsorbate on the adsorbent and is expressed in its linear form by the following equation (Horsfall and Spiff, 2003):

$$\log(\Theta/C_i) = \log K_{FH} + n_{FH} \log(1 - \Theta) \quad (10)$$

where $\Theta = (1 - C_e/C_i)$ is the degree of surface coverage, K_{FH} (L/g) and n_{FH} represent the Flory-Huggins equilibrium isotherm constant and model exponent, respectively. A linear plot of $\log(\Theta/C_i)$ versus $\log(1 - \Theta)$ indicates the application of this isotherm to the sorption process. The R^2 of 0.986 and 0.975 presented by the Flory-Huggins model obtained for Pb(II) and Cd(II) ions, are higher than those of Freundlich, Scatchard and Dubinin-Radushkevich, but lower than the Langmuir isotherm, therefore this model was not suitable in the description of metal sorption on SD.

Effect of Adsorbent Dose

Adsorbent dosage is also a very important parameter which can affect significantly the adsorption of heavy metals on adsorbents (Li *et al.*, 2013). The effect of adsorbent dosage on the percentage removal of Pb (II) and Cd (II) ions onto the adsorbent is shown in Figure 8. An increase in the percentage removal of both metal ions with increase in adsorbent dose was obtained. The increase in percentage removal of metal ions with increase in adsorbent dosage was due to increased surface negative charge and decrease in the electrostatic potential near the solid surface

that favors sorbent-solute interaction (Unuabonah, 2007). It may also be attributed to an increase in the number of available active sites with increasing adsorbent dose (Unuabonah, 2007). Similar results have been reported (Barka *et al.*, 2013).

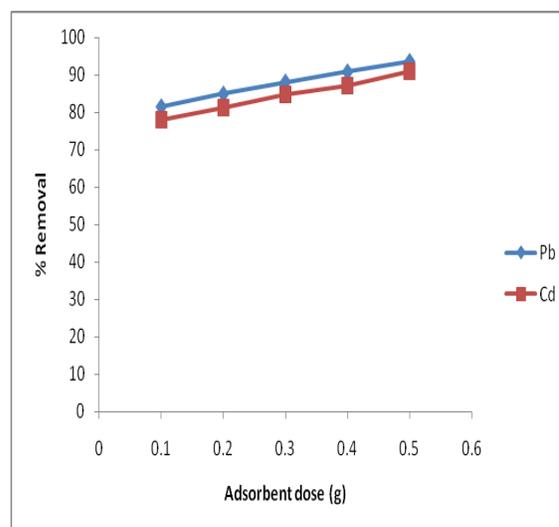


Figure 8: Effect of Adsorbent Dose on the Percentage Removal of Heavy Metals. (10)

Furthermore, a decrease in the adsorption capacity of metal ions with increase in adsorbent dosage was obtained as shown in Figure 9. This decrease in equilibrium adsorption capacity per unit mass of adsorbent may be due to the higher adsorbent dose providing more active adsorption sites, which results in the adsorption sites remaining unsaturated during the adsorption reaction (Li *et al.*, 2013). This decrease can also be attributed to a decrease in the total adsorption surface area and increase in diffusion path length resulting from overlapping or aggregation of adsorption sites (Ahluwalia and Goyal, 2007). The adsorption trend for metal ions was Pb>Cd and adsorbent dose of 0.1 g was chosen in this study due to its high adsorption capacity for metal ions recorded.

Effect of Agitation Time

The effect of agitation time on the adsorption of metal ion on any adsorbent is important in order to envisage when equilibrium adsorption is achieved. In this regard, the effect of agitation time on the adsorption of Pb (II) and Cd (II) ions onto the adsorbent was determined as shown in Figure 10 and 11.

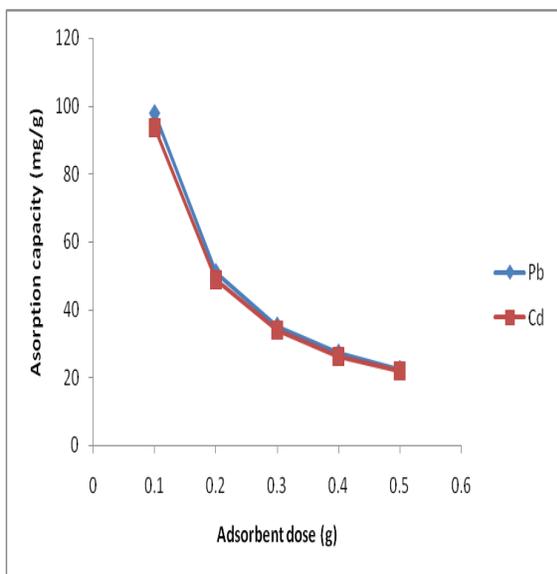


Figure 9: Effect of Adsorbent Dose on the Adsorption Capacity of the Adsorbents for Heavy Metals.

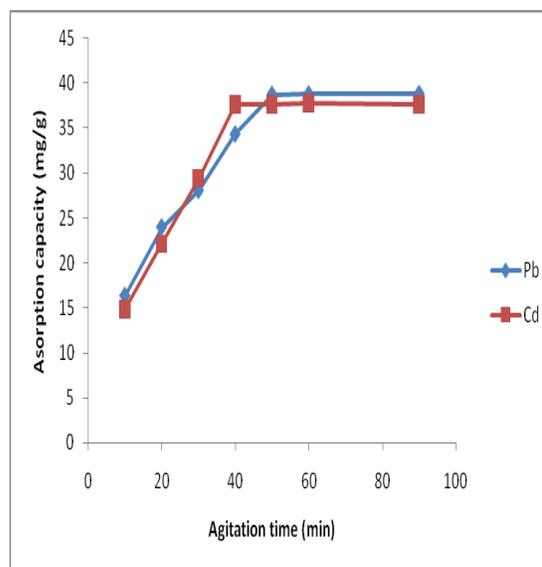


Figure 11: Effect of Adsorbent Agitation Time on the Adsorption Capacity of the Adsorbents for Heavy Metals.

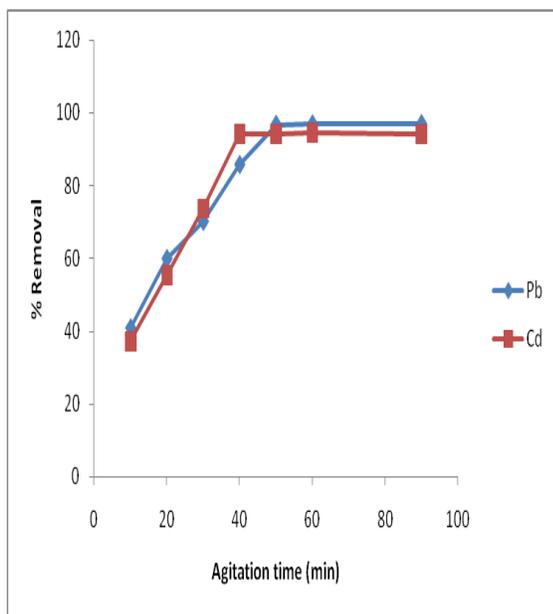


Figure 10: Effect of Agitation Time on the Percentage Removal of Heavy Metals.

It was observed that both the percentage removal and adsorption capacity of the metal ions from solution were initially rapid and then diminished gradually until an equilibrium time beyond which there was no significant increase in the removal rate and adsorption capacity.

The fast adsorption at the initial stages is due to the presence of vacant and abundant active sites on the adsorbents which becomes used up with time and becomes saturated thereby attaining equilibrium (Gupta et al., 2003). It was observed that different equilibrium times were attained for the two metal ions on all the adsorbents. Equilibrium sorption time of 50 and 40 min were obtained for Pb (II) and Cd (II) ions on the adsorbent. An agitation time of 120 min was utilized in this study to ensure equilibrium sorption of both metal ions on the adsorbent was attained. The faster rate of adsorption of Cd (II) when compared to Pb (II) is due to the smaller ionic radii of Cd (II) (0.097 nm) than Pb (II) (0.12 nm) which makes it to diffuse faster to the surface of adsorbents due to its smaller size than the bulkier Pb (II) ion (Akpomie and Dawodu, 2015).

Kinetic Studies

Adsorption kinetic models were applied to the experimental data in order to analyze the rate of adsorption and possible adsorption mechanism of Pb(II) and Cd(II) ions onto SD. The kinetic models applied in this study are the pseudo-first order, pseudo-second order, Elovich Equation and the film diffusion equation.

The pseudo-first order kinetic model also known as the Lagergren equation is expressed as (Lagergren, 1898):

$$\log(q_e - q_t) = \log q_e - (K_1 t / 2.303) \quad (11)$$

where qt and q_e are the amounts of metal ions adsorbed at time t and at equilibrium in (mg/g), respectively. K_1 is the pseudo-first order adsorption rate constant (min^{-1}). The slope and intercept of the plots of $\log(q_e - qt)$ versus t were used to determine the rate constant (K_1) and q_e , and the values are recorded in Table 2.

From Table 2, it is seen that the pseudo-first order equation provided a poor fit to the experimental data of both metal ions. This is indicated by the low values of their linear regression (R^2) not close to 1. However, the values of $q_{e,cal}$ were higher than the experimental values obtained.

Table 2: Comparison of the Kinetic Model Equation Constants for the Adsorption of Pb(II) and Cd(II) Ions unto Sawdust.

Kinetic models	Pb(II)	Cd(II)
$q_{e,exp}$ (mg/g)	38.94	37.76
Pseudo-first-order		
$q_{e,cal}$ (mg/g)	53.21	182.39
K_1 (min^{-1})	0.078	0.143
R^2	0.816	0.886
Pseudo-second-order		
h (mg/g min)	3.06	3.18
K_2 (g/mg min)	1.48×10^{-3}	1.54×10^{-3}
$q_{e,cal}$ (mg/g)	45.45	45.45
R^2	0.987	0.979
Elovich equation		
α (mg/g min)	6.097	5.872
β (g/min)	0.0996	0.0997
R^2	0.890	0.824
Film diffusion		
K_{fd}	0.078	0.143
D	0.313	1.576
R^2	0.816	0.856

The pseudo-second order kinetic model is based on the assumption that chemisorptions is the rate determining step and is given as (Li et al, 2013):

$$t/q_t = 1/K_2 q_e^2 + t/q_e \quad (12)$$

where K_2 is the equilibrium rate constant of pseudo-second order adsorption (g/mg min). The values of q_e and K_2 were calculated from the slope and intercept of the linear plot of t/qt against

t and the values are recorded in Table 2. The initial sorption rate, h (mg/g min), was also calculated from the equation:

$$h = K_2 q_e^2 \quad (13)$$

The pseudo-second order model provided a good fit to the experimental data as can be seen from the high regression regression (R^2) values of 0.987 and 0.979 for Pb(II) and Cd(II) ions, respectively. The pseudo-second order model having been found to provide the best fit among the four kinetic models tested in this study is in line with most adsorption studies (Das and Mondal, 2011; Badmus et al., 2007). However, the best fit presented by the pseudo-second order models indicated chemisorptions as the major process for the adsorption of metal ions on the adsorbent. This model was found applicable in the description of the sorption of Pb(II) and Cd(II) ions unto SD.

The adsorption data was also analyzed using the Elovich equation. The Elovich equation was first developed to describe the kinetics of chemisorptions of gas unto solids (Akpomie and Dawodu, 2015). The linear form of the Elovich equation is presented:

$$q_t = [1/\beta] \ln(\alpha\beta) + [1/\beta] \text{Int} \quad (14)$$

where α is the initial sorption rate constant (mg/g min) and the parameter β is related to the extent of surface coverage and the activation energy for chemisorptions (g/mg).

The constants α and β were obtained from the slope and intercept of the linear plot of qt versus $\ln t$ and the values are presented in Table 2. From Table 2, the correlation coefficient of both Pb(II) and Cd(II) ions are also low, not close to 1 as in pseudo-first order kinetic model and therefore provided poor fit to the experimental data.

When the transport of the adsorbate from the liquid phase up to the solid phase boundary plays the most significant role in adsorption, the process would likely conform to the film diffusion model. The liquid film diffusion mechanism can be expressed as:

$$\ln(1 - F) = -K_{fd} t + D \quad (15)$$

Where F is the fractional attainment of equilibrium, ($F = q_t/q_e$) and K_{fd} (mg/gmin) is the

adsorption rate constant of film diffusion model. A linear plot of $\ln(1 - F)$ versus t with zero intercept would suggest that the kinetics of adsorption is controlled solely by diffusion through the liquid film surrounding the solid adsorbent. Also, the occurrence of the intercept may indicate that film diffusion is not the only rate controlling mechanism. As observed from table 2, the R^2 values obtained for Pb(II) and Cd(II) ions were lower than those of the pseudo-second order model. This implies that film diffusion (surface phenomenon) played less roles in the adsorption process of the metal ions than the pseudo-second order model.

Adsorption Thermodynamics

The result on the effect of temperature on the simultaneous adsorption of Pb(II) and Cd(II) ions onto SD is presented in Figure 12 and 13. From the graphs, an increase in the percentage removal and adsorption capacity of both metal ions with increase in solution temperature from 300 to 323 K was obtained. This shows that the process is endothermic in nature. The increase may be due to a greater kinetic energy acquired by the metal ions with temperature increase resulting in an easier diffusion from the bulk solution unto the surface of SD.

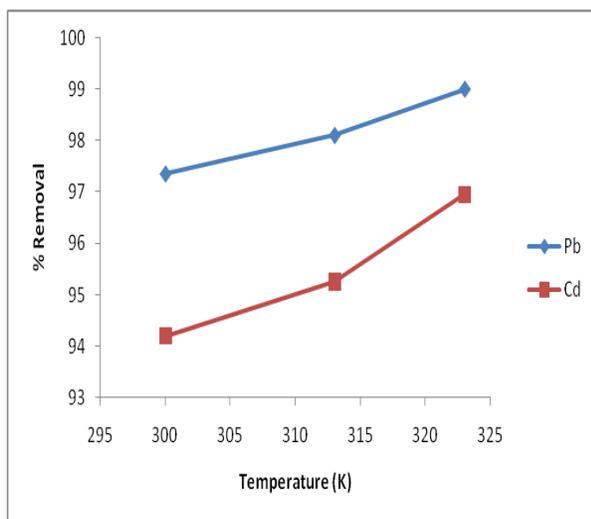


Figure 12: Effect of Solution Temperature on the Percentage Removal of Heavy Metals.

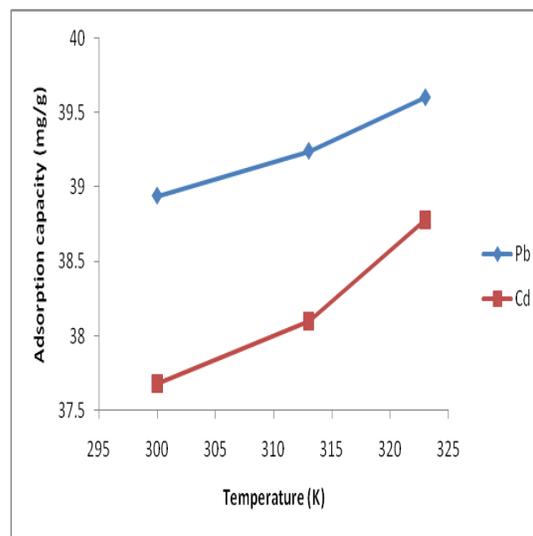


Figure 13: Effect of Solution Temperature on the Adsorption Capacity of Heavy Metals.

The standard free energy (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) of thermodynamic parameters were determined to evaluate the feasibility of the adsorption process (Liu and Liu, 2008). The standard free energy of the adsorption is related to the thermodynamic equilibrium constant (K_c) by the following equation:

$$\Delta G^0 = -RT \ln K_c \quad (16)$$

where T is the temperature (K), R is the ideal gas constant (8.314 Jand Kc/mol K) is defined by the equation:

$$K_c = C_a/C_e \quad (17)$$

where $C_a = C_o - C_e$ is the metal ion concentration adsorbed from solution at equilibrium (mg/L) and C_e is the equilibrium metal ion concentration in solution (mg/L). Also, the Gibb's free energy is related to the enthalpy change (ΔH^0) and entropy change (ΔS^0) at a constant temperature by the Van't Hoff (Liang et al., 2010) equation:

$$\ln K_c = - (\Delta H^0 / RT) + (\Delta S^0 / R) \quad (18)$$

The values of ΔH^0 and ΔS^0 were calculated from the slope and intercept of the plot ($\ln K_c$ versus $1/T$) and the calculated thermodynamic parameter values are presented in Table 3.

The values of ΔH° obtained for both metal ions are positive, indicating the endothermic nature of the adsorption process, which explains the fact that adsorption efficiency increased with increase in temperature. Positive values of ΔS° also indicated an increase in randomness at the solid/liquid interface during the sorption process while low values of ΔS° indicated that no remarkable change on entropy occurred.

It is clear that the reaction is spontaneous in nature as negative values of ΔG° were obtained at all temperatures studied. It was also observed that ΔG° increased with increase in temperature which indicates an increase in the spontaneity of the process with temperature. The magnitude of the enthalpy change (ΔH°) provides information about the type of sorption. The heat evolved during physisorption generally lies in the range of 2.1–20.9 kJ/mol, while the heat of chemisorptions generally falls in the range of 80–200 kJ/mol (Liu and Liu, 2008).

From Table 3, the values of ΔH° for Pb(II) and Cd(II) ions are 33.87 and 22.86 kJ/mol respectively, which are higher than 20 but less than 80 kJ/mol indicating a physicochemical sorption of metal ions on SD rather than solely physical or chemical adsorption. Such physicochemical adsorption has been reported (Liang et al., 2010).

CONCLUSIONS

Nigerian sawdust (SD), as a low-cost adsorbent, was successfully utilized for the simultaneous removal of Pb(II) and Cd(II) ions from aqueous solution by batch adsorption method. The adsorption process was found to be dependent on many factors such as the solution pH, initial concentration of metal ions, agitation time, adsorbent dose, and temperature.

The adsorption of Pb(II) ions by SD was found to be higher than that obtained for Cd(II) ions. Optimum removal of both metal ions was obtained at a pH of 6.0, agitation time of 120 min and an adsorbent particle size of 100 μm . Among the six isotherm models tested, Flory-Huggins, Langmuir and Temkin fitted well to the experimental data more than those of Freundlich, scatchard and Dubinin–Radushkevich and therefore gave a good description for the sorption of both ions onto SD.

Kinetic parameters were also analyzed using the Lagergren pseudo-first order, pseudo-second order, Elovich equation and film diffusion rate equation. The pseudo-second order provided the best fit to the experimental data and this is in line with most adsorption studies. This indicates that chemisorption is the major process for the adsorption of the metal ions on the adsorbent.

Thermodynamic analysis showed that the process was spontaneous and endothermic in nature. The values of the enthalpy change (ΔH°) indicated a physicochemical mechanism for both metal ions onto the adsorbent.

Table 3: Thermodynamic Parameters for the Adsorption of Pb(II) and Cd(II) Ions from Solution unto Sawdust.

Metal ion	T(K)	Kc	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/molK)	R ²
Pb(II)	300	36.74	-8.99	33.87	0.14	0.927
	313	51.63	-10.26			
	323	99.00	-12.34			
Cd(II)	300	16.24	-6.95	22.86	0.10	0.909
	313	20.05	-7.80			
	313	31.78	-9.29			

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