Adsorption Potentials of *Carica Papaya* in Remediating Pb^{4+} and Cr^{3+} From Metal-Galvanizing Industrial Wastewater

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Abstract - Industrial wastewater pollutants in form of toxic heavy metals have been a major cause of concern for environmental engineers in the 21st century. There is increasing research interest in using alternative low-cost adsorbents for industrial wastewater remediation. This paper focused on studying the adsorption capacity of Carica papaya stem in remediating Pb^{4+} and Cr^{3+} from metal-galvanizing industrial wastewater. Samples of wastewater for study were collected from Sprintex Metal-Galvanizing Industries Nigeria Limited, Ikorodu, Lagos State of Nigeria. Carica papaya stem was obtained locally from the premises of Ogun-Osun River Basin Development Authority (OORBDA), Abeokuta, Ogun State, Nigeria. A freshly cut stem was peeled off , the peel was thoroughly washed with de-ionized water, oven-dried at 105^0C for 24hrs, then grinded in a mill and later sieved to obtain a well-graded adsorbent. This was then dosed into the wastewater up to 1.0g at intervals of 0.2g, for adsorption study and the optimum dosage determined. One-Factor-At a-Time (OFAT) batch experiments were conducted on effects of contact time, dosage, rate of agitation and pH. Langmuir and Freundlich Isotherm models, pseudo 1st and 2nd Order kinetics models were employed as baseline parameters for the adsorption study of the metals. Findings revealed that Carica papaya stem as an adsorbent is very efficient in remediating Cr^{3+} and efficient in that of Pb^{4+} from metal-galvanizing wastewater, with adsorption capacity of 0.114 and 0.247mg/g respectively for Pb^{4+} and Cr^{3+}. The material is a good sorbent for the removal of Cr^{3+} from aqueous solution of wastewater range from 0 to 2 mg/L with optimum adsorbent dose of 0.2 g/L at $9 < pH < 12$ under the minimum equilibrium time of 2 hours. There is a sharp decrease in adsorption above $pH < 9$. Maximum observed adsorption is about 70% removal of Cr^{3+}. Conversely, the adsorbent is a fairly good sorbent for the removal of Pb^{4+} from aqueous solution of wastewater range from 0 to 1.5 mg/L with optimum adsorbent dose of 0.2 g/L at $3 < pH < 6$ under the minimum equilibrium time of 2 hours. There is a sharp decrease in adsorption above $pH > 6$. Maximum observed adsorption is about 50% removal of Pb^{4+}. The adsorption patterns of Pb^{4+} and Cr^{3+} with Carica papaya were both optimum with Freundlich isotherm model. The one of Pb^{4+} largely follows the Pseudo 2nd Order kinetics models, whereas the same model was perfectly observed by the Cr^{3+}adsorption. Considering the cost, ease of preparation and minimal slugde after treatment, the application of Carica papaya in remediating from metal-galvanizing industrial wastewater is hereby strongly recommended.

Keywords: Carica papaya, adsorption, adsorbent, wastewater, heavy metals.

1. INTRODUCTION

Several definitions have been assigned to heavy metals. They have been defined as subset of elements that exhibit metallic properties, having a specific density between 5 and 6 g/cm^3 (Suciu *et al.*, 2008), found in all kinds of soils, rocks and water in terrestrial and freshwater ecosystem (Adelekan and Abegunde, 2011). They comprise of the transition metals, some metalloids, lanthanides, and actinides. Also heavy metals can be said to be any metallic element that has a relatively high density and is toxic or poisonous even at low concentrations (Lenntech, 2010; Obodai *et al.*, 2011; Yahaya *et al.*, 2012). They are intrinsic, natural constituents of our environments (Aderinola *et al.*, 2009). These heavy metals are detectable either in their elemental state or bound in various salt complexes.

Heavy metals concentrations in industrial wastewater have been a major set-back in re-application of water by mankind. Heavy metals concentration in industrial effluent is hazardous and its increase is a potential contributing factor to poor health status of residents within the environment where it is being generated. Excess exposure in children to lead (Pb) causes impaired development, reduced intelligence, short-term memory loss, disabilities in learning and coordination problems, and risks of cardiovascular disease. Lead is also employed in the manufacture of lead storage batteries, solders, bearings, cable covers, ammunition, plumbing, pigments and caulking, its ingestion by human negatively affects the internal organs (Wuana and Okieimen, 2011). Chromium is used in metal alloys and pigments for paints, cement, paper, rubber, etc and is detrimental to human health (Lenntech, 2010).

Galvanizing is a process of applying a protective zinc coating to steel or iron, to prevent rusting. The methods generally employed for the galvanization of iron or steel are Hot-dip Galvanizing (HDG) and Mechanical Galvanizing (MG). Galvanization protects in two ways: formation of coating corrosion-resistant zinc which prevents corrosive substances from reaching the more delicate part of the metal. The zinc serves as a sacrificial anode so that even if the coating is scratched, the exposed steel will still be protected by the remaining zinc. The zinc protects its base metal by corroding before iron, for better results application of chromates over zinc is also seen as an industrial trend.

In galvanizing industries heavy metals are being discharged in higher percentage, this makes the industries generating heavy metals such as Cd, Cr, Cu, Ni, As, Pb, and Zn, some of the most hazardous among the chemical-intensive ones. Because of their high solubility in the aquatic environments, heavy metals can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body. If the metals are ingested beyond the permitted concentration, they can cause serious health disorders (Babel and Kurniawan, 2004). Considering the highly toxic nature of these metals in various industrial effluents, it is therefore of great necessity to search for possible means of reducing their concentrations in the industrial effluents. It is however noted that most of the heavy metals are soluble in water and form aqueous solutions, and consequently cannot be removed by ordinary physical means of separation.

There are many methods that are currently being used for treatment of the wastewater generated from the galvanizing industries. Electrolytic deposition method is mainly used for treating cyanide-containing wastewater where cyanide wastes are subjected to electrolysis at high temperatures (95°C) for several days (Upadhyay and Kanjan, 2006). Evaporation of foundry wastewater has been studied to recover the foundry metals. Single stage and multiple stage evaporation have been employed. Because of high cost of equipment this method is not commonly used (Upadhyay and Kanjan, 2006). Adsorption using activated carbon is one of the most attractive methods for heavy metal removal from wastewater because of its high efficiency in removing metals. This method is not that popular in developing countries because of high initial and operating costs (Monser and Adhoum, 2002). Flocculation is one of the widely used methods for removing suspended particles from wastewater. It is a process in which the metal to be removed is separated out from the solution as floes or flakes which can then be easily removed. Flocculation is often preceded by coagulation where, by the addition of a coagulant, substances are aggregated into microscopic particles which then flocculate into larger floes (Semerjian and Ayoub, 2003). Chemical Precipitation is one of the cost effective ways of removing heavy metals from wastewater. In this method a chemical additive is selected in such a way that it will make the metal that is to be removed from the wastewater insoluble (Upadhyay and Kanjan, 2006). Ion exchange is a process in which the metal ions are removed from the aqueous phase by the exchange of cations or anions between the exchange medium and the wastewater (Upadhyay and Kanjan, 2006).

Biosorption is a biological sorption method used for heavy metal removal from wastewater. Live or dead microorganisms or their derivatives are used in biosorption. In this method the metal ions are complexed by the functional groups present on their outer surfaces through the action of ligands. It is an effective and a cheaper method compared to the other removal techniques.

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (*adsorbent*), forming a molecular or atomic film (*the adsorbate*). Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. Similar to surface tension, adsorption is a consequence of surface energy. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physi-sorption, chemi-sorption, ion exchange and specific adsorption. There are lots of adsorbents that are effective for heavy metal removal from industrial wastewater. The adsorbents may be of mineral, organic or biological origin, zeolites, industrial byproducts, agricultural wastes, biomass, and polymeric materials (Kurniawan *et al.*, 2005).

The effectiveness of low cost adsorbents for heavy metals removal is being studied widely with the aim of finding cheap natural adsorbents that are easily available and which are effective in removing the toxic heavy metals in the metal-galvanizing wastewaters. Studies has been done on natural wastes where materials such as cotton, walnut waste, peanut skin, sugarcane waste and onion hull, coffee grounds, tea leaves, apple wastes, wool fiber, bark and other cellulosic materials, cottonseed hulls, rice straw, soybean hulls and linseed flax have been studied. Some of these reports from literature described how abundant biological materials could be used to remove at very low cost, even small amounts of toxic heavy metals from industrial effluents **(**Liu *et al.*, 2004; Moon *et al.*, 2006). In general, they present good adsorption capacity. These unconventional natural adsorbents have advantages other than being abundant in nature. Most of them need less prior processing and are waste by-products from some other industry. So, they are an alternative to costlier adsorbents like activated carbon, or synthetic polymers.

Accumulation of heavy metals has been observed to be drastically harmful to wastewater generated from the galvanizing industries. This has been observed to occur as a result of the presence of some elements of higher concentrations in the wastewaters. Generation of effluents from metal-galvanizing industries has been a major source of pollution to nearby streams in the environment. It was observed that there is lack of adequate treatment of this generated wastewater and this result in nutrient depletion, the accumulation of toxic compounds in biomass and sediments, loss of dissolved oxygen in water and other nuisances. This calls for an urgent need to devise a means of reducing the concentrations of these heavy metals. Reduction or removal of heavy metals through agricultural means is one of the most efficient methods of heavy metals removal from industrial wastewaters.

This study involves the use of agricultural product (*Carica papaya* stem) which acts as the absorbent that attaches the heavy metals to itself during the adsorption process. This method is widely used since it removes or reduces the higher concentrations of wastewaters to the bearable maximum level and makes it to be less toxic for the human being. *Carica papaya* Linn belongs to family Caricaceae, it is native to tropical America and was introduced to India in 16th century. The plant is recognized by its weak and usually un-branched soft stem yielding copious white latex and crowded by a terminal cluster of large and long stalked leaves, is rapidly growing and can grow up to 20m tall (Parle *et al*., 2011). The stem, leaf and fruit of papaya contain plenty of latex. The latex from unripe papaya fruit contains enzymes papain and chymopapain; other components include a mixture of cysteine endopeptidases, chitinases and an inhibitor of serine protease.

The aim of this project is to remediate Pb^{4+} and Cr^{3+} from metal-galvanizing effluent using adsorbent produced from *Carica papaya*_stem through a cost-effective and an environmentally friendly process. The specific objectives are: to identify the specific heavy metals present in the galvanized industrial wastewater; to determine the concentrations of these heavy metals; to determine the effectiveness of *Carica papaya* stem in the remediation of galvanized industrial wastewater; and to carry out the adsorption study of the remediation process with the isotherm and kinetic models.

2. METHODOLOGY

(a) Collection of wastewater: Samples of wastewater for study were collected from Sprintex Metal-Galvanizing Industries Nigeria Limited, Ikorodu, Lagos State of Nigeria. These were corked in sterilized 10-litre, air-tight plastic keg and immediately transferred to the Environmental Laboratory, Department of Civil Engineering, Ladoke Akintola University of Technology, Ogbomoso, Nigeria for analysis.

(b) Adsorbent material and preparation: The *Carica papaya* stem for this study was obtained locally from the premises of Ogun-Osun River Basin Development Authority (OORBDA), Abeokuta, Ogun State, Nigeria. A freshly cut stem was peeled off to obtain its outer skin. The peel was thoroughly washed with de-ionized water to remove all possible impurities and contaminants. This was later oven-dried at 105^0C for 24hrs (Gueu *et al*., 2007) and then grinded in a mill. The adsorbent so prepared was graded in Seive No. 200 and the fines passing through the sieve stored in a corked sterilized 2-litre plastic containers.

(c) Adsorption study: This was carried out with 50ml of wastewater sample poured into 100ml conical flask and 0.2g of prepared adsorbent was added, placed on J.P Selecta orbital shaker (Model No: 3000974 at 150 revolutions per minute (rpm) at room temperature for 2hrs. The suspension was filtered with Dr. Watts filter paper 12.5cm (100 circles) and the filtrate subjected to AAS analysis.

(d) Effect of adsorbent dosage: This was studied with varying dosages of 0.2, 0.4, 0.8, and 1.0g into 50ml of samples respectively and agitated at 150 rpm for 60mins at the suspension was filtered with Dr. Watt's filter paper and the filtrate analyzed by AAS.

(v) Contact time study: This was performed as 0.2g of adsorbent was added to different conical flask containing 50 mL of wastewater, the flask was closed and placed in a rotary shaker and agitated at 150rpm for each of the different contact times chosen as 20, 40, 60, 80, 100 and 120 mins. The content of each flask was filtered and analyzed by AAS after each agitation time.

(vi) pH effect on treatment: The 50ml portion in 3 conical flasks had their pH adjusted to 2, 4 and 6 respectively. 0.2g of adsorbent dosage, being the optimum established from the pilot study, was used and subjected to 150rpm rotary incubation for 1hr at 32^0C.

(vii) Rotating speed experiment: 0.2g of the adsorbent was measured into 50ml of the sample and subjected to various agitation rpm starting from 150 to 350 at 50rpm intervals. The filtrate from each batch was then subjected to AAS analysis.

(viii) Digestion of wastewater samples: This was carried out with the aim of breaking down the complexity of the samples before the AAS analysis. 10mL of the wastewater was measured into a 50mL beaker and a 10mL of nitric acid, acting as a catalyst, was carefully added to it. The beaker was then placed inside the fume cupboard and heated with the heating mantle for 30 minutes at 100˚C. The cooled mixture was removed from the fume cupboard and then digested. Distill water was added to the making it up to 100mL before it was filtered and the filtrate subjected to AAS analysis.

(ix) AAS analysis: The Flame Atomic Absorption Spectrophotometer (FAAS) with model number TAS-990, of the College of Agriculture, University of Osun, Ejigbo, Osun State, Nigeria, was used. The FAAS's main specifications include: sensitivity of up to ppb level; two channels (independent or simultaneous); wavelength range of between 180 nm and 900 nm; and probe of teflon tubing—1.6 mm OD, 0.8 mm ID. The equipment was calibrated using the prescribed procedures. The five Standard samples of pre-determined concentrations on each of the element were used in the correlations of the absorbance with the concentration. It detected the concentrations of desired Pb^{4+} and Cr^{3+}. The flame used in the analysis was air-acetylene. The temperature formed in the air-acetylene flame was around 2300˚C. The FAAS technique made use of the fact that neutral or ground state atoms of an element can absorb electromagnetic radiation over a series of very narrow, sharply defined wavelengths. The sample in solution was aspirated as a fine mist into a flame where it was converted into atomic vapor. Most of the atoms remained in the ground state and were therefore capable of absorbing radiation of a suitable wavelength (Ojoawo and Udayakumar, 2014). The wavelengths of the metals being analyzed were adjusted and the monochromator then measure the quantities of the absorbed metals as the digested wastewater was sucked by the compressor on the main machine and it later sent signals to the computer.

(x) The adsorption studies

For the study, adsorption isotherm and kinetics of Pb^{4+} and Cr^{3+} were the focus.

(a) Sorption Capacity and Removal Efficiency: The sorption capacity qe (mg/g) and removal efficiency Q were obtained according to the equations (1) and (2), respectively (Song *et al*, 2014):

$$q_e = \frac{(Co - Ce)V}{W} \qquad (1)$$

$$Q = \frac{(Co - Ce) \times 100}{Co} \qquad (2)$$

where V is the volume of the solution, W is the amount of adsorbent, C_0 and Ce are the initial and equilibrium concentration in the solution.

(b) Adsorption Isotherm

Pb^{4+} and Cr^{2+} adsorption by *Carica papaya* were analyzed using Langmuir and Freundlich isotherms. The Langmuir isotherm is used to characterize the monolayer adsorption, which is represented by the following linear form (Ding *et al*, 2012; Ghasemi and Gholami, 2014; Song *et al*, 2014):

$$\frac{Ce}{qe} = \frac{1}{qmaxb} + \frac{Ce}{qmax} \qquad (3a)$$

or

$$\frac{1}{qe} = \frac{1}{Ce\ qmax\ b} + \frac{1}{qmax} \qquad (3b)$$

The essential characteristic of the Langmuir isotherm is expressed in terms of a dimensionless constant separation factor, R_L, which is defined as:

$$R_L = \frac{1}{1+bCo} \qquad (4)$$

where q_e is the equilibrium adsorption uptake of heavy metal ions, q_{max} is the maximum adsorption capacity corresponding to the complete monolayer coverage. b is the Langmuir constant which is related to the energy of adsorption. If $R_L > 1$: unfavourable or non-optimum adsorption; $R_L = 1$: linear adsorption; $R_L = 0$; irreversible adsorption and $0 < R_L < 1$: optimum/favourable adsorption (Chen and Zhao, 2009; Farooq *et al*, 2010).

The Freundlich isotherm is generally applicable to the adsorption as they occur on heterogeneous surface. The linear form is shown:

$$\log qe = \log KF + \frac{1}{n}\log Ce \qquad (5)$$

where KF and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. If $\frac{1}{n} = 0$: irreversible adsorption process; $\frac{1}{n} > 1: non -$ optimum adsorption; and $0 < \frac{1}{n} < 1: optimum\ adsorption\ process$ (Ghasemi and Gholami, 2014).

(c) Adsorption Kinetics

In order to investigate the mechanism of adsorption, kinetic models such as the pseudo-first order and the pseudo-second order kinetic models were applied to study the adsorption dynamics.

The Lagergren's-first-order kinetic model can be expressed in linear form:

$$\log(qe - qt) = \log qe - \frac{k1}{2.303}t \qquad (6)$$

The pseudo-second-order kinetic model is used in the following linear form:

$$\frac{t}{qt} = \frac{1}{k2(qe)(qe)} + \frac{1}{qe}t \qquad (7)$$

where k1 and k2 are the adsorption rate constants of pseudo-first-order and pseudo-second-order kinetic models, respectively, qt is adsorption uptake at time t.

3. RESULTS AND DISCUSSION

(a) Adsorption Isotherm on Pb^{4+} using Langmuir and Freundlich equations

The adsorption isotherm patterns observed using both Langmuir and Freundlich's models are as presented and discussed in this sub-section.

(i) Langmuir isotherm model: The results of adsorption study and batch experiments are as summarized on Table 1. From the results, 0.2g of the adsorbent has the highest removal efficiency of nearly 50%, and the efficiency decreased with increasing dosage. The same 0.2g dosage also has the highest adsorption capacity of 0.114 mg/g, it is therefore selected as the optimum dosage for the study.

Table 1: Results of adsorption and batch experiments for Pb^{4+}

Adsorbent dosage(g)	*Co (mg/l)*	*Ce (mg/l)*	*Co - Ce (mg/l)*	*Q*	*V/W*	*qe mg/g*	*1/qe g/mg*	*1/Ce l/mg*
0.2	0.979	0.524	0.455	46.48	0.250	0.114	8.772	1.908
0.4	0.979	0.533	0.446	45.56	0.125	0.056	17.857	1.876
0.6	0.979	0.546	0.432	44.23	0.083	0.036	27.777	1.832
0.8	0.979	0.602	0.377	38.51	0.063	0.024	41.667	1.661
1.0	0.979	0.515	0.464	47.40	0.050	0.023	43.478	1.942

Then, plotting the graph of 1/qe (mg/g) against $1/C_e$ (mg/l) we have the representation in Figure 1.

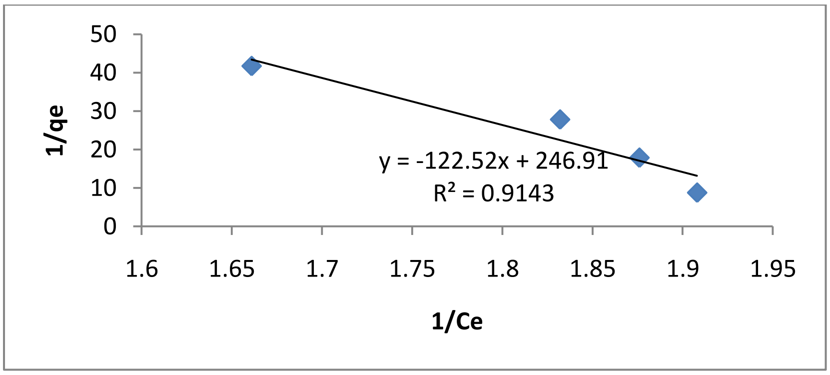

Figure 1: Langmuir Isotherm model graph of 1/qe vs 1/Ce for Pb^{4+}

From the graph in Figure 1 we obtained

$$y = -122.52x + 246.91$$

$$R^2 = 0.9143$$

Using equations (3b) and (4) we have the results of Langmuir isotherm as presented on Table 2. According to the obtained results, the Separation factor, R_L tends toward zero, and correlation coefficient, R^2 = 0.9143, showing an irreversible adsorption process (Chen and Zhao, 2009; Farooq *et al*, 2010).

Table 2: Results of Langmuir isotherm for Pb^{4+}

q_m	K_l	R_L
0.0041	-2.051	0

(ii) Freundlich Isotherm

The linear form of Freundlich equation (5) provided the basis for plotting the graph of log q_e against log C_e,

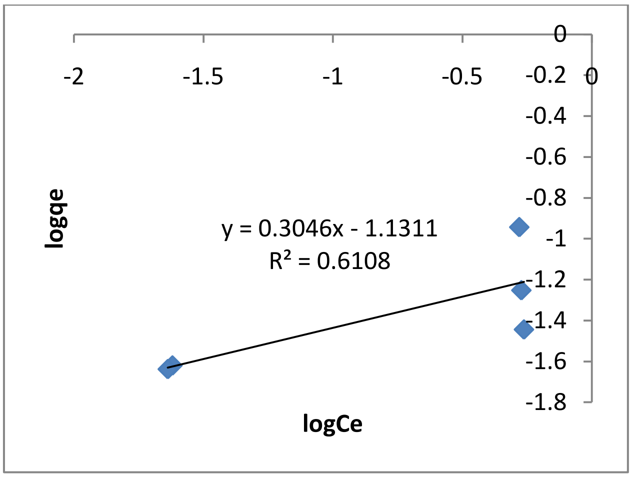

Figure 2: Freundlich Isotherm model graph of log qe vs log Ce for Pb^{4+}

From the graph in Figure 2 we obtained

$$y = 0.304x - 1.131$$

$$R^2 = 0.6108$$

Comparing with the equation (5);

$$m = 1/n = 0.304$$

$$and \;\; K_F = 0.074$$

Therefore the intensity of adsorption = 0.304, since $0 < 1/n < 1$; then the adsorption of Pb^{4+} is found to be optimum in line with the Freundlich's model (Ghasemi and Gholami, 2014).

(b) Kinetics adsorption studies of Pb^{4+}

This reflects the relationship between rate of sorption and time.

(i) Pseudo 1st Order Kinetics:

The results of Pb^{4+} adsorption as subjected to the 1st order kinetic model, using equation 6 above, are as shown in Figure 3 and Table 3 based on the plot of log (q_e-q_t) against time t

From the graph in Figure 3 we obtained;

$$y = 0.0048x - 1.635$$

$$R^2 = 0.4313$$

Comparing this with equation 6, we have; $K_1 = -0.0111$

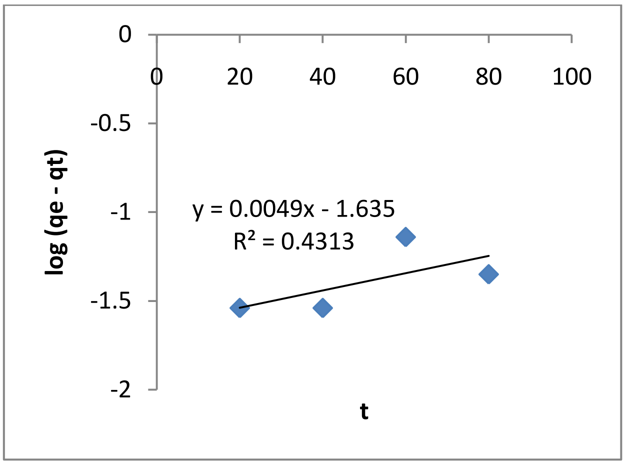

Figure 3: Pseudo 1st Order kinetic model graph of log (qe – qt) vs t for Pb^{4+}

The results of the Pseudo 1st order kinetics model for Pb^{4+} is summarized on Table 3. It is observed that the *Carica papaya* adsorption of Pb^{4+} did not largely follow the 1st order kinetics model as the values of adsorption capacity, qe obtained from both the calculation and experiment are wide apart and the correlation coefficient R^2 is far from unity.

Table 3: Pseudo 1st Order kinetics results for Pb^{4+}

K_1	$q_{e\ calculated}$	$q_{e\ experiment}$	R^2
-0.0111	0.0232	0.114	0.431

(ii) 2nd Order of Kinetics studies

From equation (7), the 2nd order Kinetics model was formed using information on Table 4. This was later translated into a graph t/q_t against t shown in Figure 4.

Table 4: Batch experiment results on adsorption capacity with time Pb^{4+}

t (min)	q_t *(mg/g)*	t/q_t
20	0.085	235.290
40	0.085	470.580
60	0.042	1428.570
80	0.070	1151.08

From the graph in Figure 4 we obtained;

$$y = 18.52x - 104.9$$
$$R^2 = 0.727$$

Comparing this with the equation (7) we have:

$qe = 1/m = 0.054$

$c = 1/K_2 q_e^2$

and $K_2 = -3.270$

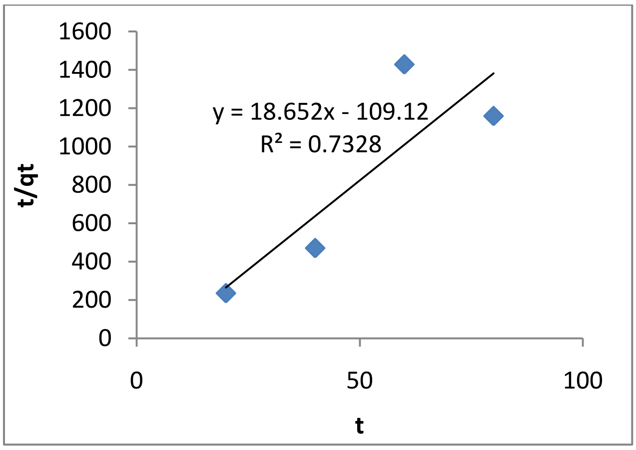

Figure 4: Pseudo 2nd Order kinetic model graph of t/qt vs t for Pb^{4+}

On Table 5, the results of Pseudo 2nd Order kinetics model for Pb^{4+} are summarized. The values of adsorption capacity calculated and from experiment are 0.054 and 0.114 mg/g respectively, while the correlation coefficient, R^2 is 0.727. The adsorption of Pb^{4+} therefore fairly follows the Pseudo Second order kinetics model.

Table 5: Pseudo 2nd Order kinetics results for Pb^{4+}

K_2	$q_{e\ calculated}$	$q_{e\ experiment}$	R^2
3.270	0.054	0.114	0.727

(c) Adsorption Isotherm on Cr^{3+} using Langmuir and Freundlich equations

The remediation efficiency of Cr^{3+} by the adsorbent practically increased with increased dosage, from 46.9 to 68.8% (Table 6).

(i) Langmuir isotherm model: The results of adsorption study and batch experiments for Cr^{3+} are as summarized on Table 6.

Table 6: Results of adsorption and batch experiments for Cr^{3+}

Adsorbent dosage(g)	*Co (mg/l)*	*Ce (mg/l)*	*Co - Ce (mg/l)*	*Q (%)*	*V/W*	*qe (mg/g)*	*1/qe (g/mg)*	*1/Ce (l/mg)*
0.2	1.776	0.790	0.986	55.52	0.250	0.247	4.049	1.266
0.4	1.776	0.943	0.833	46.90	0.125	0.104	9.615	1.061
0.6	1.776	0.650	1.126	63.40	0.083	0.094	10.638	1.539
0.8	1.776	0.699	1.079	60.75	0.063	0.068	14.706	1.439
1.0	1.776	0.555	1.221	68.75	0.050	0.061	16.393	1.802

Then, plotting the graph of 1/qe (mg/g) against 1/Ce (mg/L) as shown in Figure 5.

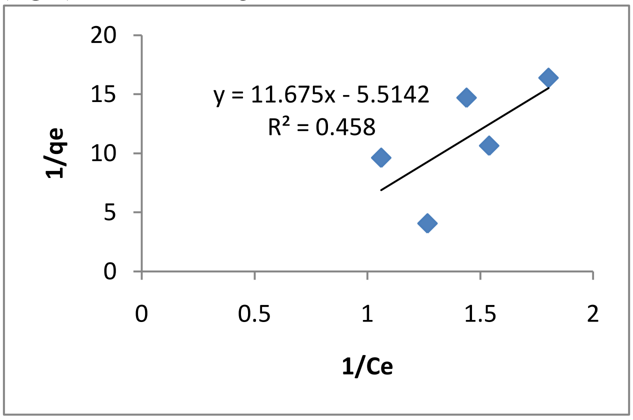

Figure 5: Langmuir Isotherm model graph of 1/qe vs 1/Ce for Cr^{3+}

From the graph in Figure 5 we obtained

$y = 11.675x – 5.5142$

$R^2 = 0.458$

Computing Langmuir parameters using equation (3b)

$1/qe = 1/qm + 1/(qm \times K_1 Ce);$

$1/qm = C = -5.5142$

$qm = -0.181$

and $K_1 = -0.472$

Applying equation (4),

$R_L = 6.20$

The results of Langmuir isotherm are hereby analyzed in the table 7. According to the obtained results of $R_L = 6.20$ and correlation coefficient of $R^2 = 0.458$, the adsorption is non-optimum.

Table 7: Results of Langmuir isotherm for Cr^{3+}

q_m	K_l	R_L
-0.181	*-0.472*	*6.20*

(ii) Freundlich Isotherm model Cr^{3+}

The linear form of Freundlich equation is: log q_e= log K_F + 1/n log Ce

Table 8: Details of isotherm adsorption for Cr^{3+}

Adsorbent dosage (g)	*Equilibrum Conc. C_e*	*Adsorbed substance q_e*	*Log q_e*	*Log C_e*
0.2	0.790	0.247	-0.607	-0.102
0.4	0.943	0.104	-0.983	-0.026
0.6	0.650	0.094	-1.027	-0.187
0.8	0.699	0.068	-1.168	-0.156
1.0	0.555	0.061	-1.215	-0.246

Plotting the graph of log q_e against log C_e as shown in Figure 6, a straight line graph is obtained

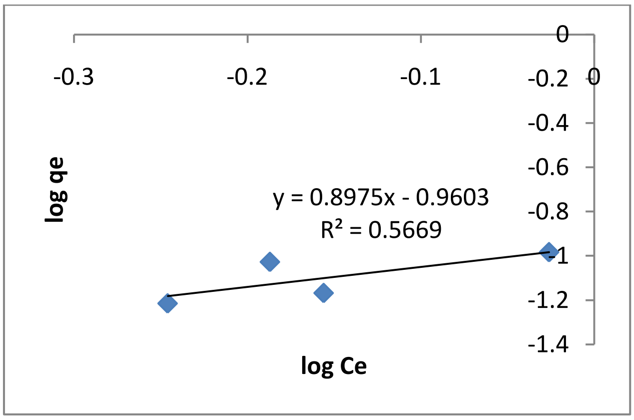

Figure 6: Freundlich Isotherm model graph of log qe vs log Ce for Cr^{3+}

from the graph in Figure 6, we obtained

$$y = 0.8975x - 0.9603$$

$$R^2 = 0.5669$$

Comparing this with Freundlich

where; log K_F = c = 0.9603

and $m = 1/n = 0.8975$

Therefore the intensity of adsorption $1/n = 0.8975$, since $0 < 1/n < 1$; then the Cr^{3+} adsorption is optimum (Ghasemi and Gholami, 2014).

To determine K_F

$$Log_{10}K_{F} = 0.9603$$

$$K_F = 7.998$$

(d) Kinetics adsorption studies of Cr^{3+}

(i) Pseudo 1st Order Kinetics:

The Pseudo 1st Order kinetics equation is: $\log (q_e - q_t) = \log q_e - K_1 t / 2.303$

With the inputs, the adsorption does not follow the 1st order kinetic model.

(ii) 2nd Order Kinetics equation:

The 2nd Order Kinetics equation is: $t/q_t = i/ q_e\, t + 1/(k_2 q_e^2)$

Applying the derived values from Table 9 into this equation, and using this to plot the graph of t/q_t against t (mins) as shown in Figure 7, we determined the pattern of kinetics model.

Table 9: Time sorption capacity of Cr^{3+}

t (min)	*q_t (mg/g)*	*t /q_t*
20	0.294	68.027
40	0.295	135.593
60	0.295	203.389
80	0.295	271.186

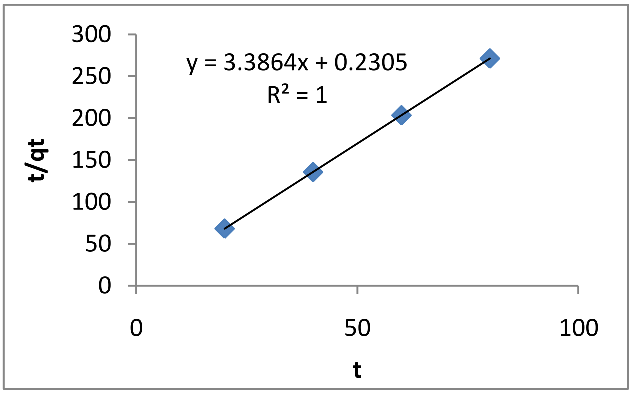

Figure 7: Pseudo 2nd Order kinetic model graph of t/qt vs t for Cr^{3+}

From the graph in Figure 7 we obtained;

$$y = 3.3864x + 0.2305$$

$$R^2 = 1.00$$

Comparing this with equation (7):

$$1/\, q_e = m = 3.3864$$

$$qe \;\; = 1/\, 3.3864 = 0.295$$

$$c = 0.2305 = 1/\, K_2\, q_e^2$$

$$K_2 = 1/\, (\, cq_e^2)$$

$$K_2 = 49.75$$

Table 10 summarizes the results of pseudo 2nd order kinetics for Cr^{3+}. The values of calculated adsorption capacity and the one from the experiment are quite close, while the correlation coefficient $R^2 = 1.00$. The adsorption therefore largely follows the pseudo 2nd order kinetics model.

Table 10: Pseudo 2nd Order kinetics results for Cr^{3+}

K_2	$q_{e\ calculated}$	$q_{e\ experiment}$	R^2
49.75	*0.295*	*0.247*	*1.00*

4. CONCLUSION

Carica papaya as an adsorbent is very efficient in remediating Cr^{3+} and efficient in that of Pb^{4+} from metal-galvanizing wastewater, with adsorption capacity of 0.114 and 0.247mg/g respectively for Pb^{4+} and Cr^{3+}. This study concludes that *Carica papaya* stem is a good sorbent for the removal of Cr^{3+} from aqueous solution of wastewater range from 0 to 2 mg/L with optimum adsorbent dose of 0.2 g/L at $9 < pH < 12$ under the minimum equilibrium time of 2 hours. There is a sharp decrease in adsorption above $pH < 9$. Maximum observed adsorption is about 70% removal of Cr^{3+}. Conversely, the adsorbent is a fairly good sorbent for the removal of Pb^{4+} from aqueous solution of wastewater range from 0 to 1.5 mg/L with optimum adsorbent dose of 0.2 g/L at $3 < pH < 6$ under the minimum equilibrium time of 2 hours. There is a sharp decrease in adsorption above $pH > 6$. Maximum observed adsorption is about 50% removal of Pb^{4+}. The adsorption patterns of Pb^{4+} and Cr^{3+} with *Carica papaya* were both optimum with Freundlich isotherm model. The one of Pb^{4+} largely follows the Pseudo 2nd Order kinetics models, whereas the same model was perfectly observed by the Cr^{3+}adsorption. Considering the cost, ease of preparation and minimal slugde after treatment, the application of *Carica papaya* in remediating from metal-galvanizing industrial wastewater is hereby strongly recommended.

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