Advances In Multidisciplinary & Scientific Research
A Multidisciplinary & Interdisciplinary Journal
Vol. 4 No. 2, June 2018

Performance evaluation of Azadirachta Indica (Neem Tree) bark in the remediation of $Pb4^+$ and $Cr3^+$ from galvanizing industrial wastewater

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ABSTRACT

The menace of wastewater pollution in the 21st century is becoming alarming. Application of the low-cost adsorbents for wastewater treatment has received more attention this moment in environmental history than never. Most industrial wastewater has not been receiving adequate treatment prior to disposal into the nearby stream, and this is a potential threat to plants and animals feeding therefrom. There is therefore the need to proffer an effective solution to this pollution problem. An approach of bioremediation with a cost-effective plant waste is considered apt, with the application of Azadirachta indica (Neem tree) bark as adsorbent in this study.

Galvanizing/wire-gauze industrial wastewater effluents were collected and subjected to Atomic Absorption Spectrophotometry (AAS) analysis to determine the concentrations of heavy metals. Phytochemical and Proximate analyses of the adsorbent were performed while adsorption study with the effects of adsorbent dosage, contact time, stirring speed and pH on the adsorption process during the wastewater treatment was carried out. The adsorption isotherms and kinetic models that best described the adsorption of Pb^{4+} and Cr^{3+} were established.

The respective initial concentrations of Cr^{3+}, Fe^{2+}, Pb^{4+}, Mn^{2+}, Cu^{3+}, Zn^{2+}, and Cd^{2+} in the wastewater were 1.8, 1.4, 1.0, 0.6, 0.4, 0.3, and 0.1 mg/l. The % of alkanoid, saponin, tannin, flavonoid and phytate in the adsorbent were 0.09, 0.1, 0.2, 0.3 and 0.03 respectively. Its proximate analysis yielded 4.7, 0.9, 10.0, 13.3, 12.0 and 59.3% for moisture, crude protein, crude fat, crude fibre, ash and carbohydrate in that order. The adsorption capacities were found as 0.099 and 0.20 mg/g respectively for Pb^{4+} and Cr^{3+} with optimum adsorbent dose of 0.2 g/L in both cases. The maximum observed adsorption is about 50 and 67% respectively for Pb^{4+} and Cr^{3+}. The adsorption patterns of Pb^{4+} and Cr^{3+} with Azadirachta Indica were both optimum with Freundlich isotherm model. Adsorption of Pb^{4+} largely follows the Pseudo 2nd Order kinetics model, whereas the same model was perfectly observed by the Cr^{3+} adsorption.

It is concluded that Azadirachta Indica bark is very efficient in remediating Cr^{3+} and efficient in that of Pb^{4+} from metal-galvanizing wastewater. Considering the cost, ease of preparation and minimal slugde after treatment, its application in remediating Cr^{3+} from metal-galvanizing industrial wastewater is hereby strongly recommended.

Keywords: Remediation, Adsorption, Isotherm, Kinetics, wastewater

Keywords: Smart city, smart mobility, transportation, development, urban liveability

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Aims Research Journal Reference Format:
*S.O. Ojoawo, A.A. Adegbola, O.S. Olaniyan, R.A. Olaoye, J.R. Oluremi, S.O. Ajamu, A.A. Ademola & I.A. Ademola (2018): Performance evaluation of Azadirachta Indica (Neem Tree) bark in the remediation of $Pb4^+$ and $Cr3^+$ from galvanizing industrial wastewater. Advances in Multidisciplinary & Scientific Research Journal. Vol. 4. No.2, Pp 73-88.

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1. INTRODUCTION

Wastewater from metal finishing industries contains high concentrations of contaminants which are hazardous to the environment and pose potential health risks to the public. With increasingly stringent regulations governing wastewater discharge and greater quantities of wastewater being produced, there is a growing need for more efficient and cost effective methods to remove heavy metals (Amer, 1998). Wastewater from metal finishing industries contains contaminants such as heavy metals, organic substances, cyanides, and suspended solids, at levels which are hazardous to the environment and pose potential health risks to the public. Heavy metals, in particular, are of great concern because of their toxicity to human and other biological life. Heavy metals typically present in metal finishing wastewater are cadmium, chromium, copper, lead, nickel, silver, tin, and zinc.

A major consequence of industrialization and industrial production is the generation and release of toxic waste products including trace heavy metals like Cd, Pb, Mn, Cu, Zn, Mg, Cr, Fe, and Ni, which are polluting our environment (Faur-Brasquet *et al.,* 2002; Baysal *et al.,* 2013). These received widespread attention because of their persistent nature, toxicity, carcinogenicity or mutagen city even at very low concentrations (Rahul *et al.*, 2014**)**. The increase in usage of heavy metals in industrial activities such as foundry, steel rolling, metal galvanizing, has caused their existence of them in waste water (Amit and Minocha, 2006). For example lead and cadmium are the main pollutant of wastewater from industries such as electroplating, plastic and paint manufacturing, mining, metallurgical process, petrochemical process, batteries, paper and pulp (Iqbal and Edyvean, 2004).

One of the contributors for this rise in the concentration level is the extensive development of heavy & manufacturing industries that uses metals and related compounds (Olayinka *et al.,* 2007). Discharge of treated industrial wastewater containing metal ions such as nickel, lead, copper, zinc, chromium and aluminum are common in nearby water sources like river (Iqbal and Edyvean, 2004) This may affect the quality of aquatic & human life . Wastewater effluents are generated from metal galvanizing works across the globe and their disposal has greatly contributed to the pollution of the environments. Heavy metals are major toxicants found in industrial wastewaters; they may adversely affect the biological treatment of wastewater. The toxicity of such wastewater has been observed to have a negative effect on all living things. Since there is scarcely adequate treatment, this results in nutrient depletion, the accumulation of toxic compounds in biomass and sediments, loss of dissolved oxygen in water and other pollution challenges.

The removal of heavy metals from wastewater is beneficial to the environment. Heavy metals are toxic to aquatic organisms even at very low concentrations. Most of these minerals were present in our environment only in minute amounts until recent centuries, when the orientation toward industrialization and production brought about our many technological advances (Samara, 2006). At present, these toxic metals have polluted our atmosphere, waters, soil, and food chain. (Ko *et al.,* 2000). There is therefore an urgent need to device a suitable mean of reducing the pollution and bringing the concentration of the pollutants into bearable minimum level.

Some conventional methods of heavy metals removal in wastewater include ion-exchange, electro-winning, coagulation, cementation, reverse osmosis/electrodialysis, electro-coagulation, precipitation, and membrane separation (Kang *et al.,* 2007; Sag and Kutsal, 2001; Wang and Tang, 2001; Ahalya *et al.,* 2003; Wickramasinghe *et al.*, 2004; Wan Ngah and Hanafiah (2008); Baysal *et al.,* 2013). These methods are however characterized by disadvantages such as secondary pollution, high cost, high energy input, large quantities of chemical reagents, and poor treatment efficiency at low metal concentrations (Ahluwalia and Goyal, 2007; Gao *et al.,* 2008). A proven alternative treatment approach, with capacity to overcome most of the identified flaws of the conventional methods, has been found in adsorption through bioremediation (Bailey *et al.,* 1999; Sag and Kutsal, 2001; Volesky, 2007; Turker, 2007; Wan *et al.,* 2008; Sud *et al.,* 2008; Demirbas, 2008).

Natural adsorbents like *Azadirachta indica* (Neem tree) have gained popularity in recent research activities due to the fact that they are more readily available, require little processing, low-cost, usually byproduct of waste materials from waste industries and isolated organisms are cultivated or propagated for biosorption purposes using inexpensive materials (Sag and Kutsal, 2001; Sekhar *et al.,* 2003; Baysal *et al.,* 2013).

The aim of this research is to study the attenuation of toxic heavy metal ions by Neem bark from metal galvanizing wastewater. The specific objectives are to identify the heavy metal pollutants in the metal galvanizing industrial wastewater and determine their initial concentrations; to characterize the physical and chemical properties of *Azadirachta indica* bark for suitability in wastewater remediation; to study the application of *Azadirachta indica* bark as an adsorbent on the wastewater using factors that include adsorbent dosage, contact time, stirring speed and pH; and to determine the adsorption isotherms and kinetic models that best describe the adsorption of the two most prominent heavy metals in the wastewater.

2. METHODOLOGY

(a) Collection of wastewater

The wastewater used for this research was obtained from Spintex Galvanizing Industry Nigeria Limited, Lagos. Samples were collected into a sterilized 10-litre plastic keg and transferred immediately to the laboratory for analyses under room temperature.

(b) Collection and preparation of *Azadirachta Indica* Tree Bark

The *Azadirachta indica* bark was obtained from the Teaching and Research Farm of Ladoke Akintola University of Technology, Ogbomoso, Oyo State, Nigeria. The Preparation of the Neem bark was in line with Rahul *et al.,* 2014. The peeled bark was washed several times with de-ionized water to remove dust particles and soluble impurities. This was later oven-dried at 35^{0}C to remove the adherent moisture content. The dried tree bark was crushed with a clean domestic mortar and grinded in a mill to produce the adsorbent. The powdery adsorbent produced was further dried. It was then sieved to obtain particle sizes of 250 - 350 µm prior to its application.

(c) Proximate and phyto-chemical analyses of Neem Bark Tree

The proximate analysis and phyto-chemical characterization of adsorbent were carried out using the procedures of Sharma and Bhattacharyya, 2005. In the proximate analysis, values of crude protein, crude fat, crude fibre, ash, carbohydrate and moisture contents were determined. For phyto-chemical analysis, alkanoids, saponin, tannin, flavonoid and phytate compositions of the adsorbent were carried out.

(d) One-factor-at-a-time (OFAT) Experimental Adsorption study

Four different types of experiments were conducted in order to determine the effects of contact time, pH, adsorbent dosage and rotating/stirring speed on the adsorption of heavy metals using the prepared *Azadirachta Indica* (neem tree) bark powder (Ojoawo *et al.,* 2016a).

(i) **Preliminary adsorption study:** Five conical flasks of 100ml volume were taken and labeled from 1 to 5.Then in each of the flasks 50ml of the untreated foundry effluent shall be put. After this 0.2, 0.4, 0.6, 0.8 and 1.0 g of the *Azadirachta Indica* (neem tree) bark powder were added to the 5 respective conical flasks. The flasks was then placed in a rotary mechanical shaker and agitated at a speed of 150 rpm for 1 hour at a room temperature of 32^{0}C. The filtrate from each flask was collected in a test tube and subjected to AAS analysis to determine the heavy metal concentrations.

Calculations:

The adsorption capacity (qe) is calculated from the formula:

$$qe = \frac{(Co-Ce)V}{W} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \; 1$$

where qe is the adsorption capacity (*in mg/g*), C_o is the initial concentration of the heavy metal ion (*in mg/L*), C_e is the concentration after adsorption (in mg/L), V is the volume of the measured wastewater for the experiment (*in L*), and W is the weight of adsorbent substance (*in g*).

(ii) **Contact time effect study:** Six conical flasks with 50 ml of the untreated industrial effluent added had 0.2g of adsorbent into each of them. The flasks were then placed in a mechanical shaker one after the other and agitated at 150 rpm for different selected contact times of 20, 40, 60, 80, 100 and 120 minutes. Filtrates from the content of each flask were subjected to AAS analysis.

(iii) **Study on agitation rate:** For rotating speed effect on the treatment process, 1 g each of the adsorbent was added 5 conical flasks of 50 ml wastewater. The conical flasks were placed in a mechanical shaker in turns and rotated at the selected speed ranging from 150 to 350 rpm at intervals of 50 rpm.

(iv) **pH effect study on the treatment process:** The effect of pH on the adsorption of heavy metal ions were studied over a pH range of 2 to 6. Three conical flasks were filled with 50 ml of the untreated foundry effluent. 1 g of the adsorbent was added to each of them. The pH of the contents in the three conical flasks shall be adjusted and maintained at 2, 4 and 6 respectively. The flasks contents were then agitated in a mechanical shaker at 150 rpm for an hour. The filtrates of each flask were subjected to AAS analysis.

(v) **Percent removal of adsorbate/biosorption:** The percentage biosorption of heavy metal for the experiment

Calculation:

$$\%\,Biosorption = \frac{1-F}{I} \times 100\%. \quad \ldots\ldots\ldots\ldots\ldots\ldots \; 2$$

where I = Initial metal concentration
F = Final metal concentration

(vi) **Final Effluent tests:** This is the last test that was carried on the wastewater filtrate samples after the treatment. To obtain the filtrate, the final effluent was centrifugated in a microfuge and filtered through a Whatman No 42 filter paper. The collected filtrate was subjected to AAS analysis while the settled pellets were oven-dried at 105^0C.

(e) The adsorption studies

(i) **Adsorption Isotherm:** Metal adsorption by *Azardiracha Indica* 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):

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

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

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

$$R_L = \frac{1}{1+bCe} \qquad \text{........................... } \textit{(4)}$$

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:

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

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

(ii) **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:

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

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

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

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.

(f) Digestion of samples

Digestion analysis was carried out on the wastewater sample with the aim of breaking down the complexity of the sample before the AAS analysis. 10ml of the wastewater was taken and another 10ml of HNO_3 and HCl was added to it at 3: 2 and 80 ml of distilled water was also added to it make up 100ml and poured inside a beaker. The nitric acid and hydrochloric acid act as a catalyst on the wastewater for rapid reaction. The sample in the beaker was placed inside the fume cupboard and was heated with the heating mantle for 30 minutes at 100˚C.

After the time duration, the sample was removed from the fume cupboard and then digested. Distill water was added to the sample making it up to 100mL before it was filtered and the filtrate was poured inside a container for the AAS analysis.

(g) Atomic absorption spectrophotometer (AAS) analysis

Atomic absorption spectrophotometer analysis was a laboratory technique used for establishing the concentration of different heavy metals in a particular industrial wastewater sample. It was widely used for the determination of the initial concentrations of the heavy metals in the wastewater sample and the final concentrations after the bioremediation processes.

3. RESULTS AND DISCUSSION

(a) Physico-chemical composition analysis of Neem tree bark *(Azadirachta Indica)*

The fresh neem tree bark was prepared and analyzed to determine the physical and chemical properties it constitutes as presented in Table I.

Table I: Neem bark physico-chemical properties

	PROXIMATE ANALYSIS
Moisture (%)	4.67
Crude Protein (%)	0.87
Crude Fat (%)	9.95
Crude Fibre (%)	13.26
Ash (%)	12.00
Carbohydrate (%)	59.25
	PHYTOCHEMICAL ANALSIS
Alkaloid (%)	0.085
Saponin (%)	0.102
Tannin (%)	0.154
Flavonoid (%)	0.320
Phytate (%)	0.025
	HEAVY METAL ANALYSIS
Cu^{3+} (ppm)	0.13
Mg^{2+} (ppm)	0.55
Mn^{2+} (ppm)	0.24
Fe^{2+} (ppm)	4.65
Zn^{2+} (ppm)	6.47
Ca^{2+} (ppm)	413.64

(b) Initial concentration of Heavy Metals in the Samples

AAS detected the initial concentrations of Cu^{3+}, Fe^{2+}, Zn^{2+}, Pb^{4+} and Cr^{3+} present in the wastewater samples, The concentration unit for the metals analyzed was in part per million (ppm). It is noted that Pb, Cr, and Fe all have higher concentrations in galvanized wastewater the results, while in the adsorbent, traces of Hg^{2+}, Cd^{2+}, Pb^{4+} and Cr^{3+} were not detected, as shown in Table 4.2 below. Since Hg^{2+} is not easily come across in day to day activities, and Cd^{2+} concentration is relatively negligible, the adsorption studies in this paper has therefore been based on Pb^{4+} and Cr^{3+}.

Table II: Concentrations of the initial heavy metals in the wastewater samples

S/N	Metal	Wastewater Concentration (*in ppm*)	*Azadirachta Indica* Concentration (*in ppm*)	Total Concentration (*in ppm*)
1.	Cu^{3+}	0.369	0.130	0.499
2.	Mn^{2+}	0.620	0.240	0.860
3.	Fe^{2+}	1.371	4.650	6.021
4.	Zn^{2+}	0.288	6.470	6.758
5.	Hg^{2+}	1.500	N.D	1.500
6.	Cd^{2+}	0.038	N.D	0.038
7.	Pb^{4+}	0.979	N.D	0.979
8.	Cr^{3+}	1.776	N.D	1.776

Note: *N.D = Not Detected*

(c) Adsorption studies of Pb^{4+} and Cr^{3+}

The adsorption isotherm patterns observed using both Langmuir and Freundlich's models, and the kinetics using the pseudo 1st and 2nd order models are as presented and discussed in this sub-section.

(i) **Langmuir isotherm model of Pb^{4+}:** The summary of results of adsorption study and batch experiments is presented on Table III. From the results, 0.2g of the adsorbent has the highest adsorption capacity of 0.099 mg/g and a reasonable removal efficiency of more than 40%. The removal efficiency after 0.6g dosage decreased with increasing dosage; therefore 0.2g dosage is selected as the optimum dosage for the study.

Table III: 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	0.580	0.399	40.76	0.250	0.099	10.10	1.72
0.4	0.979	0.524	0.455	46.48	0.125	0.057	17.54	1.91
0.6	0.979	0.518	0.461	47.09	0.083	0.038	26.32	1.93
0.8	0.979	0.561	0.418	42.70	0.063	0.026	38.46	1.78
1.0	0.979	0.580	0.399	40.76	0.050	0.020	50.00	1.72

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

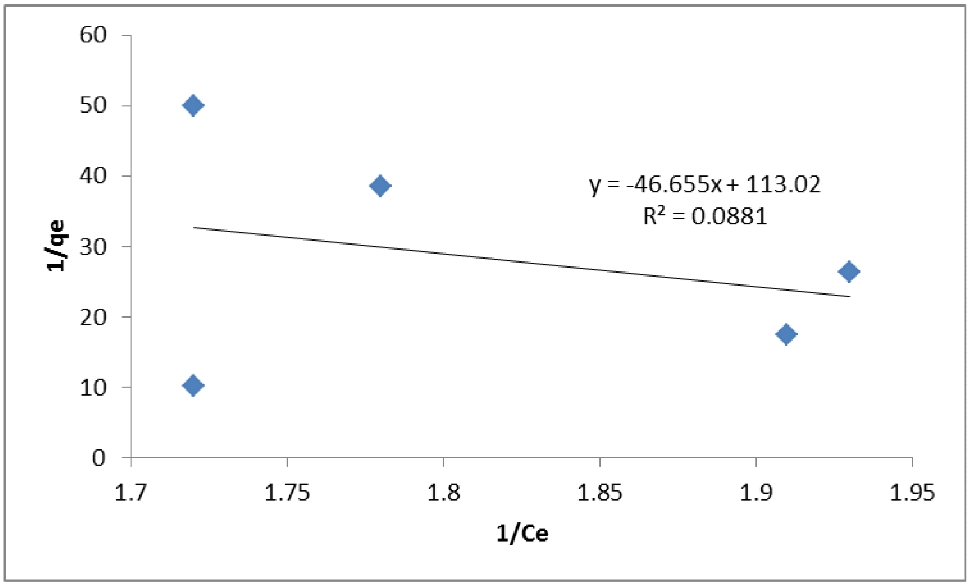

Figure 1: Langmuir Isotherm model graph of 1/qe vs 1/Ce for Pb^{4+}

From the graph in Figure 1 we obtained

$$y = -46.655x + 113.02$$
$$R^2 = 0.0881$$

Using equations (3b) and (4) in section 3.7 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, $R^2 = 0.0881$, showing an irreversible adsorption process (Chen and Zhao, 2009; Farooq *et al*, 2010).

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

q_m	b	R_L
0.0088	2.422	0

(ii) Freundlich Isotherm of Pb^{4+}

The linear form of Freundlich equation (5) in section 3 provided the basis for plotting the graph of log q_e against log C_e,

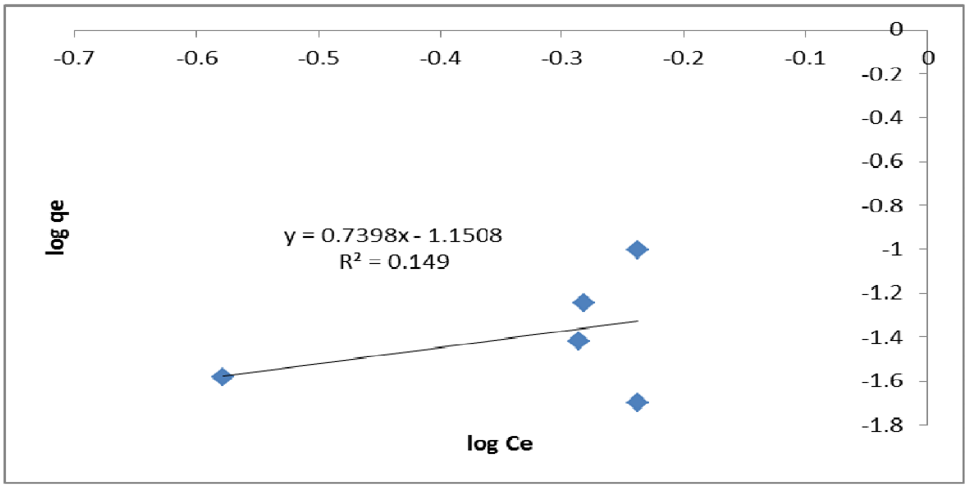

Figure 2: Freundlich Isotherm model graph of log qe vs log Ce for Pb^{4+}

From the graph in Figure 2 we obtained

$y = 0.7398x - 1.1508$
$R^2 = 0.149$

Comparing with the equation (5);
$m = 1/n = 0.7398$
and $K_F = 0.0707$

The intensity of adsorption ($1/n$) = 0.7398. Since $0 < 1/n < 1$; then the adsorption of Pb^{4+} is found to be in an optimum state in line with the Freundlich's model (Ghasemi and Gholami, 2014).

(iii) Pseudo 1st Order Kinetics of Pb^{4+}

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

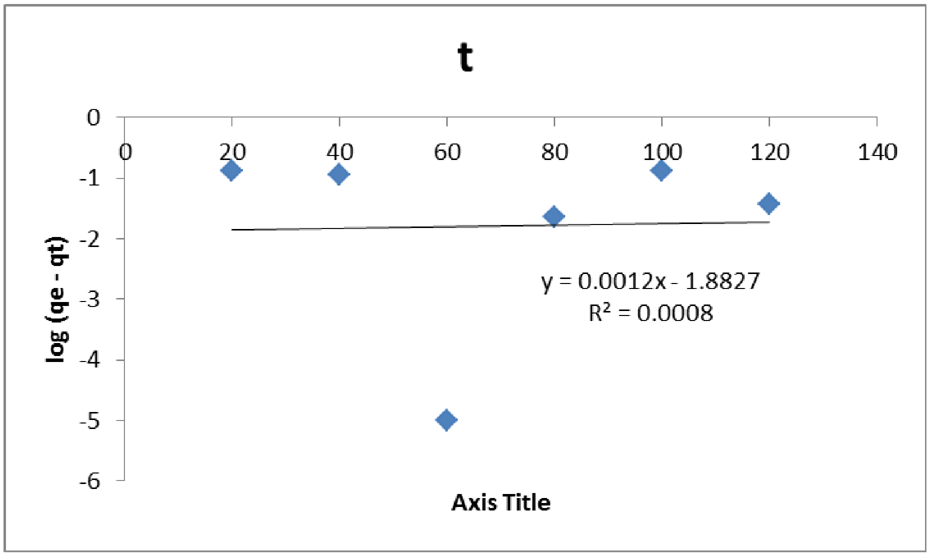

Figure 3: Pseudo 1st Order kinetic model graph of log (qe – qt) vs t for Pb^{4+}

From the graph in Figure 3 we obtained;
$y = 0.0012x - 1.8827$
$R^2 = 0.0008$

Comparing this with equation 6 in section 3,

we have; $K_1 = -0.0028$

The results of the Pseudo 1st order kinetics model for Pb^{4+} is summarized on Table V. It is observed that the *Azadirachta Indica* 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 very far from unity.

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

K_1	$q_{e\ calculated}$	$q_{e\ experiment}$	R^2
-0.0111	0.0990	0.0131	0.0008

(iv) 2nd Order of Kinetics studies of Pb^{4+}

From equation (7) in section 3, the 2nd order Kinetics model was formed using information on Table VI. This was later translated into a graph t/q_t against t shown in Figure 4.

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

t (min)	q_t *(mg/g)*	t/q_t
20	*0.228*	*87.720*
40	*0.213*	*187.793*
60	*0.099*	*606.060*
80	*0.121*	*661.157*
100	*0.228*	*438.596*
120	*0.137*	*875.912*

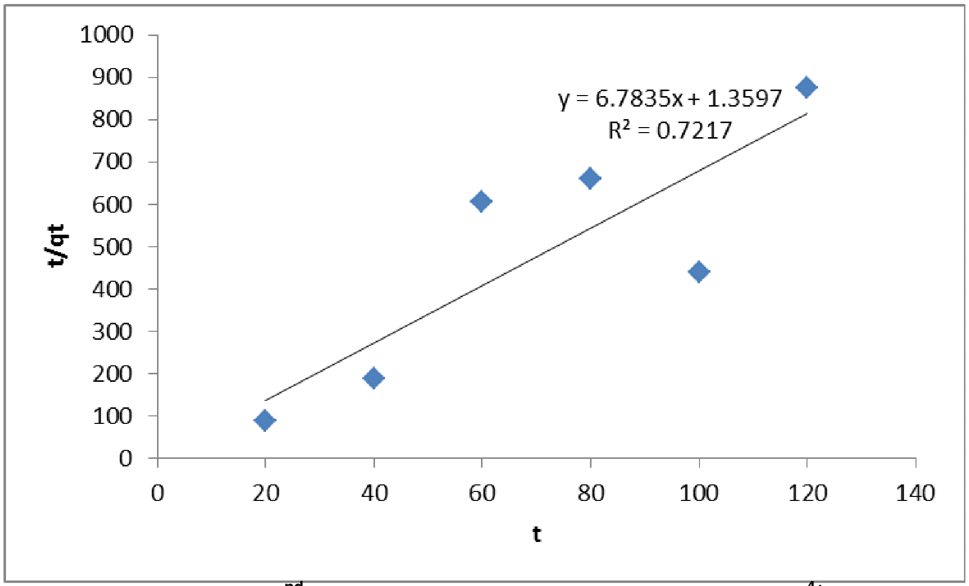

Figure 4: Pseudo 2nd Order kinetic model graph of t/qt vs t for Pb^{4+}

From the graph in Figure 4 we obtained;

$y = 6.7835x + 1.3597$
$R^2 = 0.7217$

Comparing this with the equation (7) in section 3 we have:

$1/m = q_e$
$q_e = 0.1474$
$c = 1/K_2 q_e^2$
and $K_2 = 33.84$

On Table VII, the results of Pseudo 2nd Order kinetics model for Pb^{4+} are summarized. The values of adsorption capacity calculated and from experiment are 0.1474 and 0.099 mg/g respectively, while the correlation coefficient, R^2 is 0.7217. The adsorption of Pb^{4+} therefore sufficiently follows the Pseudo Second order kinetics model.

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

K_2	$q_{e\ calculated}$	$q_{e\ experiment}$	R^2
33.84	*0.1474*	*0.099*	*0.7217*

(v) Langmuir isotherm model of Cr^{3+}: The results of adsorption study and batch experiments for Cr^{3+}, indicating the remediation efficiency is as summarized on Table VIII.

Table VIII: 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	0.975	0.801	45.10	0.250	0.20	4.99	1.03
0.4	1.776	0.929	0.847	47.69	0.125	0.11	9.45	1.08
0.6	1.776	0.883	0.893	50.28	0.083	0.07	13.49	1.13
0.8	1.776	0.836	0.940	52.93	0.063	0.06	16.89	1.20
1.0	1.776	0.603	1.173	66.05	0.050	0.06	17.05	1.66

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

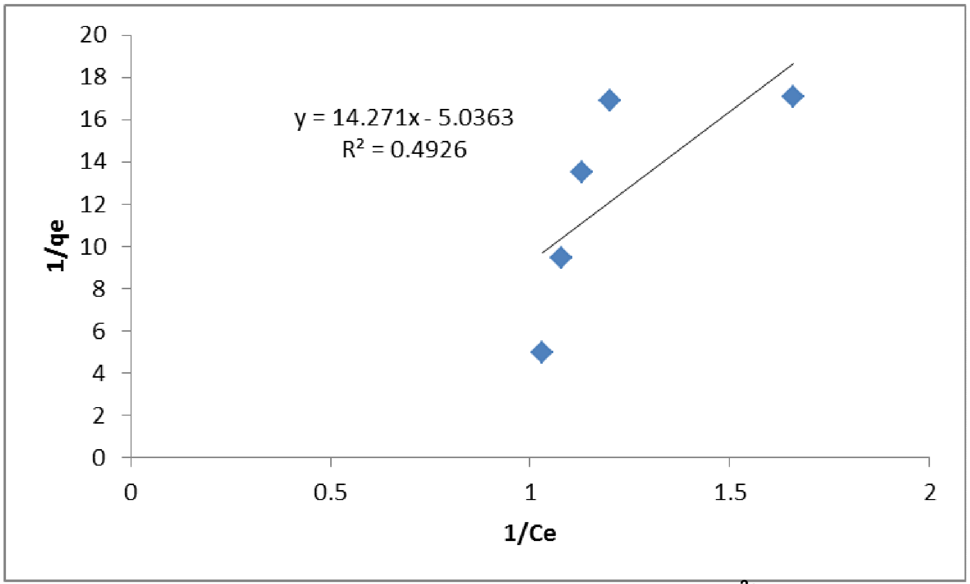

Figure 5: Langmuir Isotherm model graph of 1/qe vs 1/Ce for Cr^{3+}

From the graph in Figure 5 we obtained

$y = 14.271x – 5.0363$
$R^2 = 0.4926$

Computing Langmuir parameters using equation (3b) in section 3.7
$1/qe = 1/qmax + 1/(qmax\ b\ Ce);$
$1/qmax = C = -5.0363$
$qmax = -0.199$
and $b = -0.352$

Applying equation (4) in section 3,
$R_L = 2.67$

The analysis of results of Langmuir isotherm is presented in the Table IX. According to the obtained results of $R_L = 2.67$ and correlation coefficient of $R^2 = 0.4926$, the adsorption is non-optimum and unfavourable.

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

q_{max}	b	R_L
-0.199	-0.352	2,67

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

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

Table X: 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	0.975	0.20	-0.699	-0.011
0.4	0.929	0.11	-0.959	-0.032
0.6	0.883	0.07	-1.155	-0.054
0.8	0.836	0.06	-1.222	-0.078
1.0	0.603	0.06	-1.222	-0.220

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

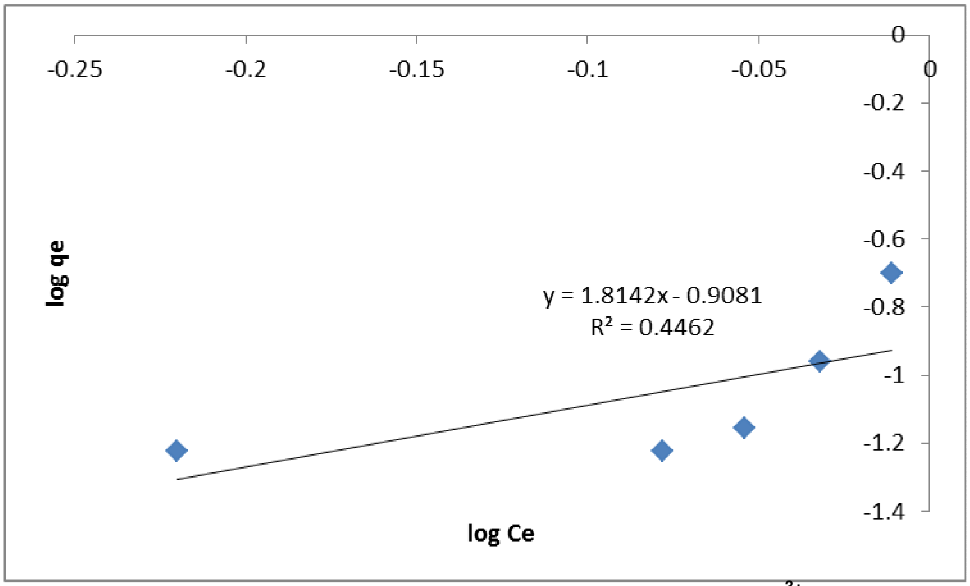

Figure 6: Freundlich Isotherm model graph of log qe vs log Ce for Cr^{3+}

From the graph in Figure 6, we obtained
$y = 1.814x - 0.9081$
$R^2 = 0.4462$

Comparing this with Freundlich equation
where; $\log K_F = c = -0.9081$
and $m = 1/n = 1.814$

Therefore the intensity of adsorption $1/n = 1.814$, since $1/n > 1$; then the Cr^{3+} adsorption is non-optimum (Ghasemi and Gholami, 2014).

To determine K_F
$\log_{10} K_F = -0.9081$
$K_F = 0.124$

(b) Kinetics models of Cr^{3+}

(i) Pseudo 1st Order Kinetics:

The Pseudo 1st Order kinetics equation is: $\log (q_e - q_t) = \log q_e - K_1 t / 2.303$
Table XI gives the details of the parameter inputs for Cr^{3+}.

Table XI: Details of adsorption kinetics for Cr^{3+}

Time (mins)	*qe (mg/g)*	*q_t (mg/g)*	*(q_e - qt)*	*Log (q_e - qt)*
20	0.20	0.137	0.063	-1.201
40	0.20	0.120	0.080	-1.097
60	0.20	0.200	0.010	-2.000
80	0.20	0.137	0.063	-1.201
100	0.20	0.137	0.063	-1.201
120	0.20	0.153	0.047	-1.328

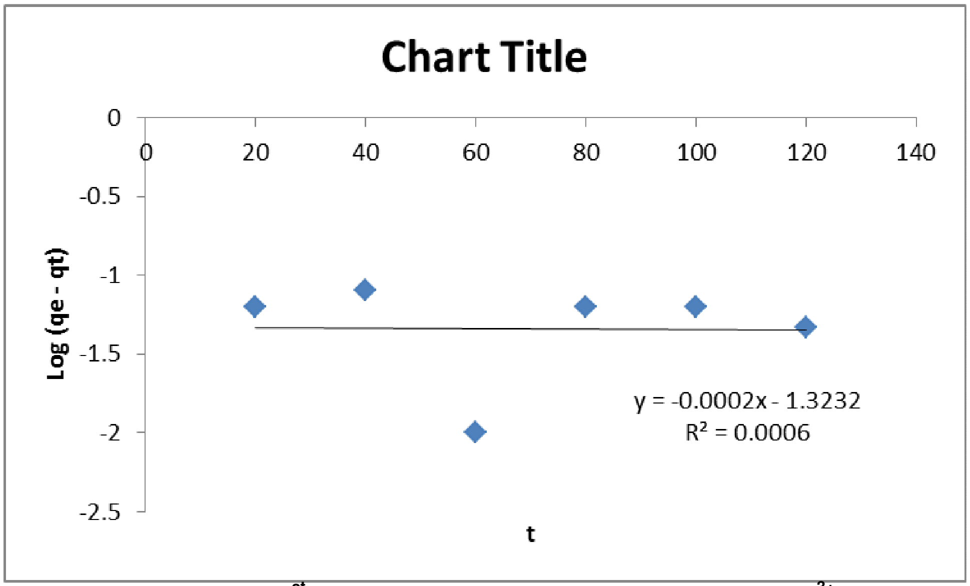

Figure 7: Pseudo 1st order model graph of log (qe – qt) vs t for Cr^{3+}

From the graph in Figure 7, we obtained

$y = -0.0002x - 1.3232$
$R^2 = 0.0006$

Comparing this with equation 6
where; $m = -0.0002$ and $c = -1.3232$
Then *$k1 = 0.00046$*

Log qe = -1.3232, *from where qe = 0.0475*

The results of the Pseudo 1st order kinetics model for Cr^{3+} is summarized on Table XII. It is observed that the *Azadirachta Indica* adsorption of Cr^{3+} like that of Pb^{4+} also did not significantly 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 very far from unity.

Table XII: Pseudo 1st Order kinetics results for Cr^{3+}

K_1	$q_{e\ calculated}$	$q_{e\ experiment}$	R^2
0.00046	*0.0475*	*0.200*	*0.0006*

(ii) Pseudo 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 XIII into this equation, and using this to plot the graph of t/q_t against t (mins) as shown in Figure 8, we determined the pattern of kinetics model.

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

t (min)	*q_t (mg/g)*	*t/q_t*
20	0.137	145.99
40	0.120	333.33
60	0.200	300.00
80	0.200	583.94
100	0.137	729.93
120	0.137	875.91

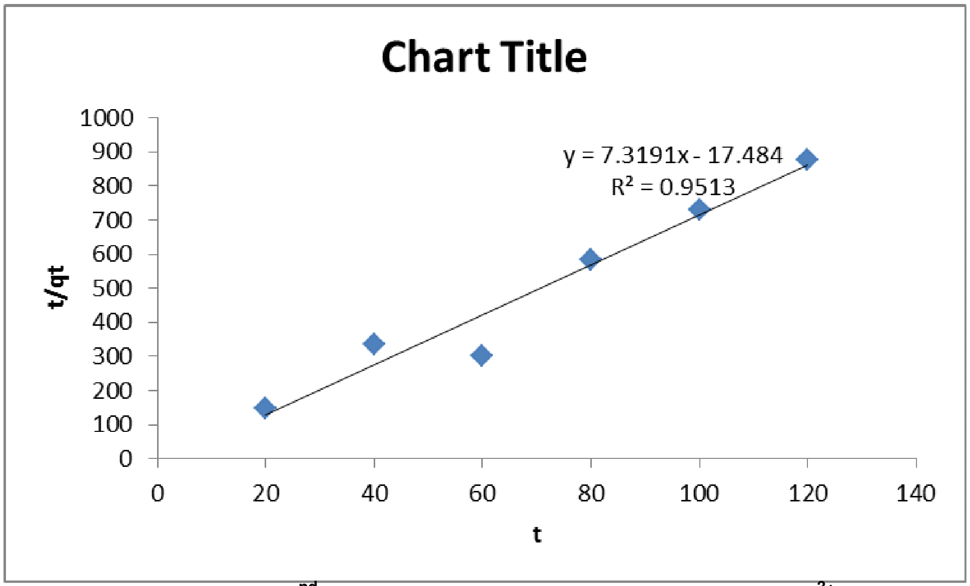

Figure 8: Pseudo 2nd Order kinetic model graph of t/qt vs t for Cr^{3+}

From the graph in Figure 8 we obtained;
$y = 7.3191x - 17.484$
$R^2 = 0.9513$

Comparing this with equation (7) in section 3.7:
$1/q_e = m = 7.319$ *and* $c = -17.484$
$q_e = 1/7.319 = 0.137$

$c = -17.484 = 1/K_2 q_e^2$
$K_2 = 1/(cq_e^2)$
$K_2 = -3.06$

Table XIV summarizes the results of pseudo 2nd order kinetics for Cr^{3+}. The values of calculated adsorption capacity and the one from the experiment are somewhat close, while the correlation coefficient $R^2 = 0.9513$. The adsorption therefore largely follows the pseudo 2nd order kinetics model.

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

K_2	$q_{e\ calculated}$	$q_{e\ experiment}$	R^2
-3.06	0.137	0.200	0.9513

4. CONCLUSION

Azadirachta Indica tree bark which is cheap and abundant in nature 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 0.099 and 0.20 mg/g respectively for Pb^{4+} and Cr^{3+}. This study concludes that *Azadirachta Indica* bark 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. Maximum observed adsorption is about 67% 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 *Azadirachta Indica* 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 sludge after treatment, the application of *Azadirachta Indica* in remediating Cr^{3+} from metal-galvanizing industrial wastewater is hereby strongly recommended.

Acknowledgements
The authors express profound gratitude to Tertiary Education Trust Fund (TETFUND) of Nigeria and the Authorities of Ladoke Akintola University of Technology, Ogbomoso for the Institution-Based Research Grant (PV No: 00011244), under which this research was executed. We also appreciate Mrs. Olubunmi T. Ojoawo for assistance on typesetting and formatting of the manuscript.

REFERENCES

1. Ahalya, N., Ramachandra, T. V., & Kanamadi, R. D. (2003). Biosorption of heavy metals. *Research Journal of Chemistry and Environment*, 7, 71-79.
2. Ahluwalia, S. S. and Goyal, D. (2007). Microbial and plant derived biomass for removal of heavy metals from wastewater. *Bioresource Technology*, 98, 2243-2257.
3. Amer, S.I (1998) Treating Metal Finishing Wastewater. *Environmental Technology*, Aquachem Inc.
4. Amit, B and Minocha, A.K (2006) Conventional and Non-Conventional absorbent for removing pollutants fron water: a review, *Indian Journal of Chemical Technology*, Vol 13, pp 203-217.
5. Bailey S.E., T.J. Olin, R.M. Bricka, D.D. Adrian, (1999) A review of potentially low cost sorbents for heavy metals, *Water Resources*. 33 2469–2479.
6. Baysal, A., Ozbek, N., and Akman, S. (2013). Determination of trace metals in wastewater and their removal processes. (*In Intech Open Science, Wastewater treatment technologies and recent analytical developments*. Retrieved September 20, 2014 from http://dx.doi.org/10.5772/52025. 145 – 171.
7. Chen, H. and Zhao, J. (2009) Adsorption study for removal of Congo red anionic dye using organo-attapulgite. *Adsorption*, 5 (4), 381 – 389.
8. Demirbas, A. (2008). Heavy metal adsorption onto agro-based waste materials: a review. *Journal of Hazardous Materials*, 157, 220-229.
9. Ding, Y., Jing, D., Gong, H., Zhou, L., and Yang, X. (2012) Biosorption of aquatic cadmium (II) by unmodified rice straw. *Bioresource Technology*, 114, 20 – 25, doi:10.1016/j.biotech.2012.01.110.
10. Farooq, U., Kozinski, J.A., Khan, M.A., Athar, M. (2010) Biosorption of heavy metal ions using wheat-based biosorbents – a review of the recent literature. *Bioresource Technology*, 101, 5043 – 5053.
11. Faur-Brasquet C, Kadirevelu K, Le Cloirec P (2002). Removal of metal ions from aqueous solution by adsorption onto activated carbon cloths adsorption completion with organic matter. *Carbon*, 40: 2387- 2392.
12. Gao, H., Liu. Y.G., Zeng, G.M., Xu, W.H., Li, T., and Xia, W.B.(2008). Characterization of Cr (VI) removal from aqueous solutions by a surplus agricultural waste-rice straw. *Journal of Hazardous Materials*, 150, 446-452.
13. Ghasemi, S and Gholami, R.M (2014) Copper removal by Eucalyptus sawdust and determination of isotherms and kinetics of adsorption process. *Journal of Advances in Environmental Biology*, 8 (21), 105 – 113.
14. Iqbal, M. and Edyvean, R.G.J. (2004) Biosorption of lead, copper and zinc ions on loofa sponge immobilized biomass of *Phanerochaete chrysosporium*, Minerals Engineering, 17, 217 - 223.
15. Kang S., J. Lee, K. Kima, (2007) Biosorption of Cr (III) and Cr (VI) onto the cell surface of pseudomonas aeruginosa, *Biochem. Eng. J.* 36, pp 54 – 68.
16. Ko, D. C. K., Porter, J. F. and Mckay, G, (2000) Optimized Correlation for the Fixed Bed Adsorption of Metal Ions on Bone Char, *Chem. Eng. Sci.,* 55, 5819 – 5829.
17. Ojoawo, S.O, Rao, C.V and Goveas, L.C. (2016a) Bioremediation of Zn, Cu, Mg and Pb in fresh domestic sewage by *Brevibacterium* sp. *International Journal of Environmental Research*, Iran. 10 (1): 139-148.
18. Olayinka, K.O, Alo, B.I, Adu, T (2007). Sorption of Heavy Metals from Electroplating Effluents by Low Cost Adsorbents II: Use of Waste tea, Coconut shell and Coconut husk. *J. Appl. Sci.*, 7(16): 2307-2308.

19. Rahul N. Jain1, S. B. Patil2, D. S. Lal (2014). Adsorption of Cr-(Vi) from aqueous environment using Neem leaves powder. *IJRET: International Journal of Research in Engineering and Technology.* EISSN: 2319-1163 | PISSN: 2321-7308.
20. Sag, Y. and Kutsal, T. (2001). Recent trends in the biosorption of heavy metals: a review. *Biotechnology and Bioprocess Engineering*, 6, 376-385.
21. Samara SA (2006). Toxicity Heavy Metals. *E.Medicine.* pp.1-2.
22. Sekhar, K.C., Kamala, C.T., Chary, N.S., and Anjaneyulu, Y. (2003). Removal of heavy metals using a plant biomass with reference to environmental control. *The International Journal of Mineral Processing*, 68, 37-45.
23. Song, C., Wu, S., Cheng, M., Tao, P., Shao, M., and Gao, G.(2014) Adsorption studies of coconut shell carbons prepared by KOH activation for removal of Lead (II) from aqueous solutions. *Sustainability,* 6, 86 – 89; doi:10.3390/su6010086.
24. Sud, D., Mahajan, G., and Kaur, M.P. (2008.) Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions: a review. *Bioresource Technology*, 99 (13), 6017-6027.
25. Turker, A. R. (2007). New sorbents for solid-phase extraction for metal enrichment. *Clean*, 35, 548-557.
26. Volesky, B. (2007). Biosorption and me. *Water Research*, 41, 4017-4029.
27. Wan Ngah, W.S. and Hanafiah, M.A.K.M (2008) Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. Available online at www.sciencedirect.com, *Bioresource Technology*. 99, pp 3935–3948.
28. Wang, D. S. and Tang, H. X. (2001). Modified inorganic polymer flocculants-PFSi: its precipitation, characterization and coagulation behavior. *Water Research*, 35, 3473-3581.
29. Wickramasinghe, S. R., Han, B., Zimbron, J., Shen, Z., and Karim, M. N. (2004). Arsenic removal by coagulation and filtration: comparison of groundwaters from the United States and Bangladesh. *Desalination*, 169, 231-244.