International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.8, No.6, pp 324-343, 2015

Kinetic Modeling and Multicomponent Isotherm Studies on Adsorption of Multi Heavy Metal Ions in MSW Leachate by Alcoffine

Senthilkumar.G and Murugappan. A

Environmental Engineering Laboratory, Department of Civil Engineering, Faculty of Engineering and Technology, Annamalai University, Annamalai Nagar – 608002, Tamil Nadu, India

Abstract: Municipal solid waste leachate samples were collected from the leachate pit, of Mayiladuthurai municipal solid waste open dumping site, Nagapattinam District, Tamil Nadu, India. Leachate samples were analyzed and multi heavy metal ions namely Cu, Zn, Pb, Cr and Ni were identified. Pozzolonic material Alcoffine were collected and used as solid adsorbent. Its applicability for adsorption of such a multi heavy metal ions present in MSW leachate was studied by three Multicomponent adsorption isotherm models namely Extended Langmuir Isotherm model, Langmuir - Freundlich Isotherm model and Multicomponent Isotherm model. Kinetic studies were performed with three kinetic models namely pseudo first order, pseudo second order and intra particle diffusion model. Experimental equilibrium metal uptake data were compared with calculated values.
Keywords: Alcoffine, Municipal solid waste leachate, Multicomponent Isotherm models, Kinetics.

Introduction

Rapid industrialization and growth of industries in India has led to migration of people from villages to the urban centre and in turn generate thousands of tones of Municipal Solid Waste (MSW) daily. The quantum is excepted to get increased during the year 2020, when the country attains the status of industrialized nation[1,2,3]. The unscientific disposal of municipal solid waste causes an adverse impact on all components of the environment and human health[4,5,6]. The composition of municipal solid waste was determined on a wet weight basis and it consists mainly of organic fraction 40-60%, paper 3-6% and plastic, glass, metals (< 1%).

In many of the cities, open, uncontrolled and poorly managed dumping is commonly practiced and leads to serious environmental degradation. More than 90% of the MSW in cities and towns are directly disposed of on land in an unsatisfactory manner. The availability of land for the disposal of solid waste is very limited. The refuse after disposal on to the land undergoes a series of biological and chemical reactions as the waste biodegradation progresses. The biodegradability of organic content in the MSW and the compaction of the waste make the landfill environment as anaerobic giving many similarities to the composition of leachate between various landfills. The open dumped wastes undergo various phases of decomposition as initial aerobic phase followed by acetogenic-methonogenic phases of anaerobic digestion and a stabilization phase[7]. Landfill leachate shows significant temporal variability in terms of quantity and composition[8].

The leachate is generated by due to infiltration and percolation of rainwater through the various layers in a landfill. The physical, chemical, and biological processes in the waste transfer pollutants from the solid

waste material to the percolating water[9]. The pollutants present in the MSW landfill leachate includes dissolved organic matter, Inorganic macro components, Heavy metals and xenobiotic organic compounds.

The heavy metal concentration in preliminary phase of waste degradation may be higher and its presence in the leachate will vary widely. The low concentration of heavy metals in methanogenic leachates is not due to lack of heavy metals in the waste. Heavy metal balances for landfills have shown that less than 0.02% of heavy metals received at landfills are leached from the landfill after 30 years[10,11,12]. These pollutants due to migration through soil have every possibility to reach the water table and may contaminate the ground water aquifers. Solid waste dumping in coastal towns has led to heavy metals rapidly leaching into the coastal waters[6,13,14,15,16,17]. Hence to prevent the migration of leachate from the open dumped municipal solid waste landfill a single or double liner barrier system has to be provided on the ground, with a facility to collect the excess leachate and to treat it in the Common effluent treatment plant.

In this investigation an attempt is made to study applicability of Alcoffine, a pozzalonic material for adsorption of multi heavy metal ions in leachate. Leachate samples were collected from the leachate pit of Mayiladuthurai Municipal solid waste open dumping site, Nagapattinam District, Tamil Nadu, India. Alcoffine 1203 is a specially processed product based on slag of high glass content with high reactivity obtained through the process of controlled granulation. ALCCOFINE 1203 have used conforming to ASTM C989-99. Three Multi component adsorption isotherm models namely Extended Langmuir Isotherm model, Langmuir - Freundlich Isotherm model and Multicomponent Isotherm model along with three kinetic models namely pseudo first order, pseudo second order and Intra particle diffusion model were used for modeling the equilibrium data of multi heavy metal ions such as Cu, Zn, Pb, Cr and Ni in leachate by Alcoffine as adsorbent.

Materials and Methods

Table 1: Properties of MSW Leachate

Constituent in MSW Leachate	Concentration
pH	7.61
EC	5.64
Chlorides	1640
Hardness	1040
Turbidity	47
Sulphate	295
Fe	27.96
Ammonia	50
Na	98
Ca	282
K	45
Phosphate	14
COD	3920
Acidity	70
BOD	1224
Cu	1.22
Zn	2.86
Pb	2.62
Cr	1.5
Ni	0.65
Cd	BDL

All values in mg/l except pH and EC

Table 2: Properties of Alcoffine 1203

Parameter	concentration
CaO	61 - 64%
SO3	2-2.4%
SiO2	21-23%
Al2O3	5-5.6%
Fe2O3	3.8-4.4
MgO	0.8-1.4%
pH	7.63
EC (mmhos/cm)	0.22
TDS	143
Cl	16
Hardness	200
Ca	51.30
Na	13.76
K	5.27
SO_4	nil
PO_4	2.0
Nitrate	nil
Fe	0.11
Cd	0.01
Cu	Nil
Zn	0.01
Pb	0.02

All values in mg/l except pH and EC

The collected MSW leachate was analyzed and the contents are given in Table 1. All the analysis was carried out as per the procedure given in APHA 2005 at room temperature. The collected Alcoffine 1203 was oven dried at 105^{o}C for a period of two hours. The oven dried adsorbents under goes for the preliminary physicochemical analysis and the report is shown in Table 2. The heavy metal analysis in MSW leachate was carried out using Atomic Absorption Spectrophotometer (AAS - Make Thermo fisher - Chemito, Model 201). 100 ml of MSW leachate stock solution was taken in 250ml conical flask along with 0.2gms of Alcoffine and kept in rotary shaker (Make: Remi, Model RS24) for a period of maximum of 4hours in order to reach equilibrium. The shaker is maintained at constant rpm of 60. For a periodic time interval of 0, 30, 60, 90, 120, 150, 180, 210 and 240minutes the samples were collected. The samples were centrifuged and the supernatant were kept in AAS and the absorbances were noted at respective wave lengths. The concentration of multi heavy metal ions is calculated from the absorbance using the calibration curve. The amount of metal ions adsorbed on to the Alcoffine is calculated with mass balance equation 1.

$$q_{eq} = \frac{V}{M}(C_i - C_{eq}) \text{----(1)}$$

Where qeq (mg/g) = uptake of metal ions at equilibrium conditions. Ceq (mg/l) = Concentration of metal ions at equilibrium condition. V (l) = Volume of solution taken for analysis. M (g) = Mass of adsorbent used. Ci (mg/l) = Initial concentration metal ion in MSW leachate. The same procedure is repeated with varying Alcoffine dosage of 0.4, 0.6, 0.8, 1.0 and 1.2g. All the experiments and analysis were carried out at a room temperature of 30^{o}C. The solution pH is maintained at 7 in all experiments. The SEM analysis was performed both before and after adsorption and the pictures were given in Figure 1 and Figure 2.

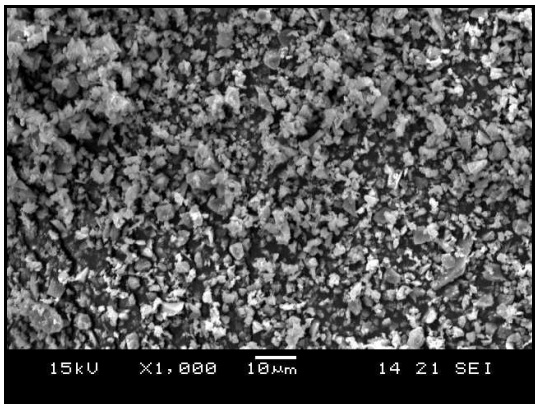

Figure 1: Photographical representation SEM analysis of Alcoffine before adsorption

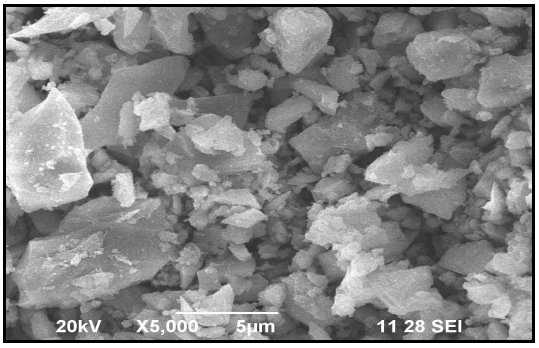

Figure 2: Photographical representation SEM analysis of Alcoffine After adsorption

Results and Discussion

Adsorption Isotherms

Equilibrium studies are carried out to understand the behavior of the adsorbent at equilibrium conditions. Adsorption Equilibria provides the fundamental physicochemical information to assess the applicability of the adsorption process. Moreover the Adsorption Equilibria is the essential to analysis and design of the adsorption process.

An adsorption isotherm is the relationship between the adsorbate in the liquid phase and the adsorbate adsorbed on the surface of the adsorbent at equilibrium at constant temperature. It describes the phenomenon governing the mobility of a substance from the aquatic environments to a solid-phase under equilibrium condition at a constant temperature and pH[18,19,20]. The equilibrium adsorption isotherm is very important to design the adsorption systems. Adsorption equilibrium is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration[18,21,22]. Usually, the mathematical correlation, which provides an important role towards the modeling, operational design and applicability of the adsorption systems, is usually described by graphical expression of adsorbate concentration in the solid-phase against liquid phase[18,23].

Various single component isotherms like Langmuir, Freundlich, Dubinin-Radushkevich, Temkin, Toth, Redlich-Peterson, Sips, Khan and Hill models have been studied but unexpectedly no one would be a successful one, due to the presence of multi heavy metals in the leachate used in this investigation. This unfit nature is the account of presence of other metal ions which may either interact with adsorbate of interest or compete for same binding sites of adsorbent. Due to these constraints, the amount of adsorbent adsorbed either increase, decrease or remain unaltered in the presence of other heavy metal ions. A number of alternates have been proposed to correlate multicomponent adsorption. In the present investigation three multi component adsorption isotherms namely Extended Langmuir Isotherm, Langmuir-Freundlich Isotherm and Multicomponent Adsorption Isotherm has been used to assess adsorbate - adsorbent interactions and nature of adsorption[24]. Table 3 shows the equations and parameters of multicomponent isotherm investigated in this present study.

Extended Langmuir Isotherm

When two or more adsorbable components exist with the possibility of occupying the same adsorption sites, isotherm relationship become more complex. The simplest is the extension of Langmuir type isotherm by assuming no interaction between adsorbate[29]. Commercial application of physical adsorption involves mixture rather than pure components. During the adsorption of a component from the liquid solution containing n number of components, certainly one can increase, decrease or have no influence on the adsorption of other component, depending upon the interactions of the adsorbed molecules. The simple theoretical treatments to the extension of the Langmuir equation by neglecting such an interactions and assumes that the only effect is the reduction of vacant surface area to the adsorption. The extended Langmuir isotherm model was applied to determine the adsorption of multi heavy metal ions in leachate onto the Alcoffine adsorbent.

Table 3: Equations and parameters of Multicomponent Isotherms

Model	Equation	Parameters
Extended-Langmuir Isotherm Model[25]	$q_{eq,i} = \frac{k_i\, C_{eq,i}}{1 + \sum_{i=1}^{n} b_i C_{eq,i}} \quad --(1)$	k and b
Langmuir-Freundlich Isotherm[26,27]	$q_{eq,i} = \frac{k_i\, C_{eq,i}^{n,i}}{1 + \sum_{i=1}^{n} b_i\, C_{eq,i}^{n,i}} \quad --(2)$	k, b and n
Multicomponent Isotherm[26,28]	$q_{eq,i} = \frac{k_i\, C_{eq,i}}{1 + \sum_{i=1}^{n} b_1 C_{eq,i}^{n,i}} \quad --(3)$	k, b and n

Table 4: Extended Langmuir Adsorption isotherm for adsorption of Multi heavy metals in leachate by Alcoffine solid adsorbent

Heavy Metal	Extended Langmuir Adsorption Isotherm Parameters and Constants		
	K	b	R^2
Cu	16.476	0.375	0.768
Zn	4.371	0.916	0.921
Pb	5.089	1.008	0.880
Cr	1.406	3.683	0.933
Ni	4.383	0.144	0.622

The extended Langmuir Isotherm model is given in Table 3. The extended Langmuir parameters k_i and b_i can be obtained by using the fminsearch tool in Matlab10a Version. Table 4 shows the constants and parameters of extended Langmuir isotherm for adsorption of Multi heavy metal ions in leachate by Alcoffine solid adsorbent. The coefficient of correlation for extended Langmuir isotherm is seems to be unfit in general, except zinc and chromium even though the quality of fit is good for all metal ions. Figure 3 shows the plot q_{eq} experimental against q_{eq} by extended Langmuir isotherm.

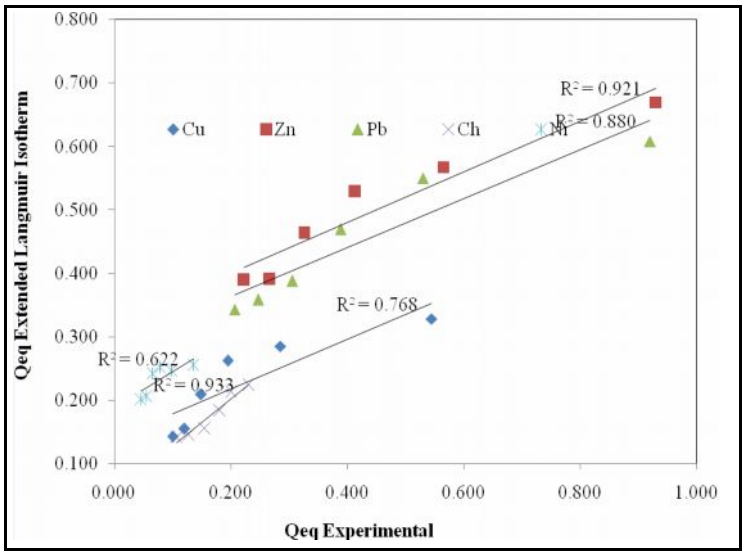

Figure 3: Extended Langmuir Adsorption isotherm for adsorption of Multi heavy metals in leachate by Alcoffine solid adsorbent

Langmuir-Freundlich Isotherm

Table 5: Langmuir-Freundlich Adsorption isotherm for adsorption of Multi heavy metals in leachate by Alcoffine solid adsorbent

Heavy Metal	Langmuir-Freundlich Adsorption Isotherm Parameters and Constants			
	K	b	n	R^2
Cu	11.859	0.024	0.801	0.718
Zn	6.260	2.137	1.612	0.991
Pb	5.017	0.871	0.961	0.867
Cr	1.173	2.059	0.526	0.217
Ni	0.387	0.792	0.024	0.971

A combination of Langmuir and Freundlich isotherm models makes a new model called the Langmuir-Freundlich isotherms model. The Langmuir Freundlich Isotherm parameters Ki, bi and ni are obtained by using the fminsearch tool in Matlab10a Version. Table 5 shows the constants and parameters of Langmuir Freundlich adsorption isotherm. The coefficient of correlation obtained for the comparison of qeq experimental with qeq Langmuir Freundlich isotherm is less for Zn and Cr. Figure 4 show the graphical representation for the plot of qeq experimental with qeq Langmuir Freundlich isotherm.

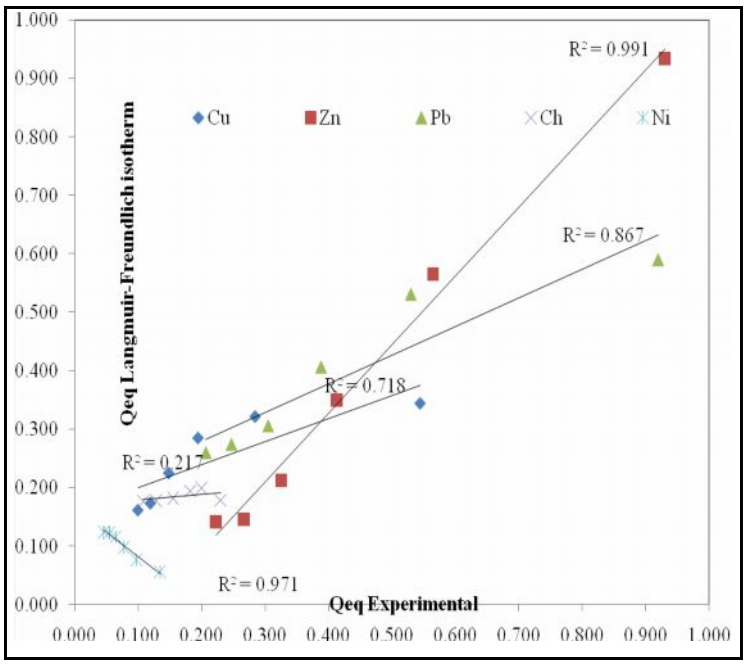

Figure 4: Langmuir-Freundlich Adsorption isotherm for adsorption of Multi heavy metals in leachate by Alcoffine solid adsorbent

Multicomponent Isotherm

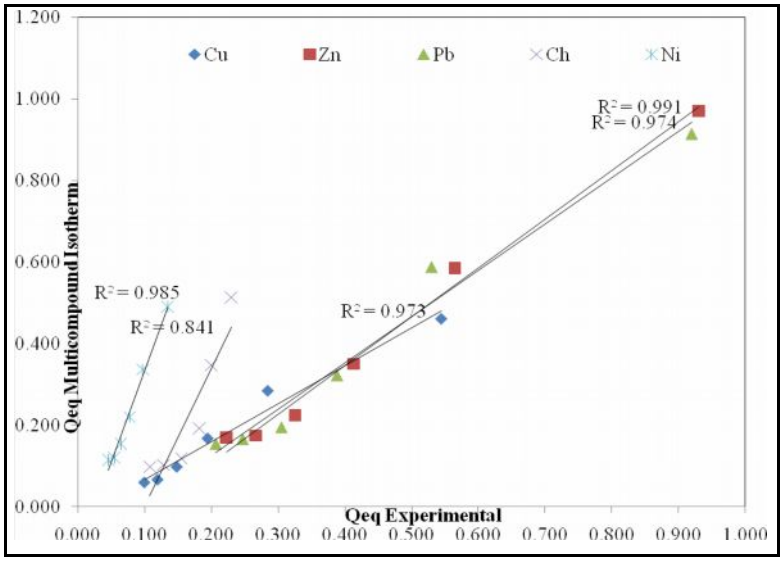

Figure 5: Multicomponent Adsorption isotherm for adsorption of Multi heavy metals in leachate by Alcoffine solid adsorbent

The equation for Multicomponent adsorption isotherm model is given in Table 3. The constants and parameters are given in Table 6 for Multicomponent Adsorption isotherm. Figure 5 shows the graphical fit of qeq experimental with qeq of Multicomponent isotherm. Among the three isotherms the coefficient of correlation seems to be good for all heavy metal ions present in the leachate. Multicomponent Adsorption isotherm model is found to fit for the adsorption of multiheavy metal ions present in leachate by Alcoffine as adsorbent.

Table 6: Multicomponent Adsorption isotherm for adsorption of Multi heavy metals in leachate by Alcoffine solid adsorbent

Heavy Metal	Multicomponent Adsorption Isotherm Parameters and Constants			
	K	b	n	R^2
Cu	6.178	0.222	1.616	0.973
Zn	1.695	1.522	0.330	0.991
Pb	2.046	0.761	0.009	0.974
Cr	0.860	2.035	0.402	0.841
Ni	2.254	0.728	0.373	0.985

Kinetic Studies

Understanding of adsorption mechanism and potential rate controlling steps such as mass transport and chemical reaction processes are essential in kinetic studies. Adsorption kinetics are mainly controlled by various steps, including Diffusion and reaction processes; Step 1. Bulk diffusion i.e., Ion transfer from bulk solution to the boundary film bordering the adsorbent surface. Step 2. Film diffusion i.e., Ion transport from boundary film to the surface of the adsorbent. Step 3. Intra particular diffusion i.e., Transfer of ion from the surface to the intra particular active sites. Step 4. Chemical reaction i.e., Uptake of iron on active sites via chelating, ion exchange or complexation [30]. It describes the ion uptake rate and obviously this rate controls the residence time of ion uptake at the solid liquid interface[31,32,33]. In order to evaluate the kinetic mechanism which controls the process, Pseudo first order model, second order model and intra particle diffusion model have been used to test the experimental data in this study.

Pseudo First Order Kinetic Model

The Lagergren's rate equation is one of the most widely used rate equation to describe the adsorption of ions from liquid phase. The linear form of pseudo first order kinetic model is

$$\log(q_{eq} - q_t) = \log q_{eq} - \frac{k_1}{2.303} t \text{ ----(1)}$$

The values of log (q_{eq} - q_t) was calculated for each time interval at different dosage of adsorbent. Where q_{eq} and q_t signify the amount adsorbed at equilibrium and at any time.

Table 7: Constants and Parameters of Pseudo-first order model for adsorption of multi heavy metals in leachate by Alcoffine solid adsorbent

Adsorbent	Metal	$q_{eq\ Exp}$	K1	log qeq	$q_{eq\ Cal}$	R^2
0.2	Cu	0.545	0.021	-0.177	0.665	0.970
	Zn	0.930	0.014	-0.044	0.903	0.990
	Pb	0.920	0.009	-0.006	0.986	0.990
	Cr	0.230	0.012	-0.537	0.290	0.909
	Ni	0.135	0.014	-0.732	0.185	0.897
0.4	Cu	0.285	0.021	-0.475	0.335	0.937
	Zn	0.565	0.023	-0.168	0.679	0.963
	Pb	0.530	0.014	-0.244	0.570	0.902
	Cr	0.200	0.012	-0.838	0.145	0.909
	Ni	0.098	0.014	-1.038	0.091	0.897
0.6	Cu	0.195	0.014	-0.725	0.188	0.985
	Zn	0.413	0.021	-0.330	0.467	0.950
	Pb	0.388	0.025	-0.227	0.592	0.879
	Cr	0.182	0.016	-0.545	0.284	0.833
	Ni	0.078	0.021	-0.899	0.126	0.777
0.8	Cu	0.149	0.035	-0.689	0.204	0.827
	Zn	0.326	0.028	-0.510	0.309	0.966
	Pb	0.305	0.030	-0.552	0.280	0.971
	Cr	0.155	0.035	-0.66	0.218	0.920
	Ni	0.065	0.037	-1.096	0.080	0.966
1.0	Cu	0.120	0.018	-1.013	0.097	0.907
	Zn	0.267	0.035	-0.695	0.201	0.968
	Pb	0.247	0.030	-1.182	0.065	0.962
	Cr	0.128	0.025	-0.980	0.104	0.972
	Ni	0.055	0.037	-0.706	0.196	0.986
1.2	Cu	0.100	0.025	-1.23	0.058	0.939
	Zn	0.223	0.025	-0.902	0.125	0.928
	Pb	0.207	0.025	-0.968	0.107	0.857
	Cr	0.108	0.023	-1.225	0.059	0.904
	Ni	0.046	0.028	-1.647	0.022	0.855

The experimental data along with constants and parameters of pseudo first order kinetic model for adsorption of multi heavy metal ions in leachate by Alcoffine is represented in Table 7. It provides the experimental uptake of various heavy metal ions such as Cu, Zn, Pb, Cr and Ni with calculated values of various dosage of Alcoffine namely 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2g. Figure 6(a), 6(b), 6(c), 6(d), 6(e) and 6(f) shows the same. The comparison of experimental and calculated equilibrium uptake rate by pseudo first order model shows a slight difference, even though the coefficient of correlation seems to be good in general. This difference is predominant in higher dosage concentration, i.e., above 0.6g of adsorbent dosage. This might be due to the non linearity i.e., exponential trend between the time and equilibrium uptake of metal ion by Alcoffine adsorbent during first 60 minutes of the contact time. In latter stages the increase of metal ion uptake is gradual shows a flat trend. Hence the pseudo first order kinetic model is unfit for adsorption of metal ions in

leachate by Alcoffine. Among the five heavy metals present in the leachate Cu shows the higher uptake based on pseudo first order model.

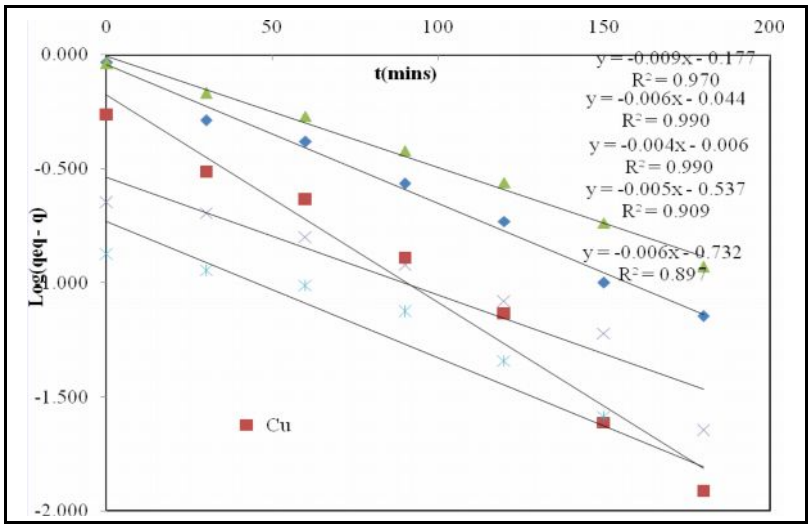

Figure 6(a):Constants and Parameters of Pseudo-first order model for adsorption of multi heavy metals in leachate by 0.2 g Alcoffine solid adsorbent

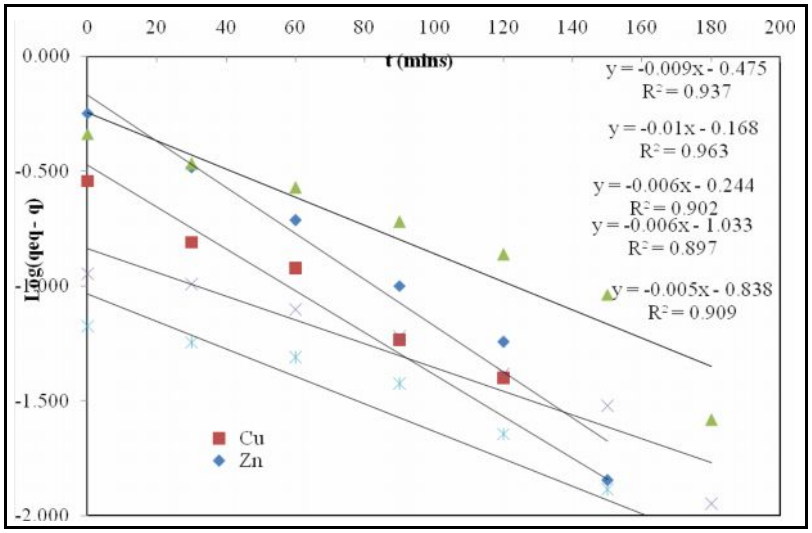

Figure 6(b):Constants and Parameters of Pseudo-first order model for adsorption of multi heavy metals in leachate by 0.4 g Alcoffine solid adsorbent

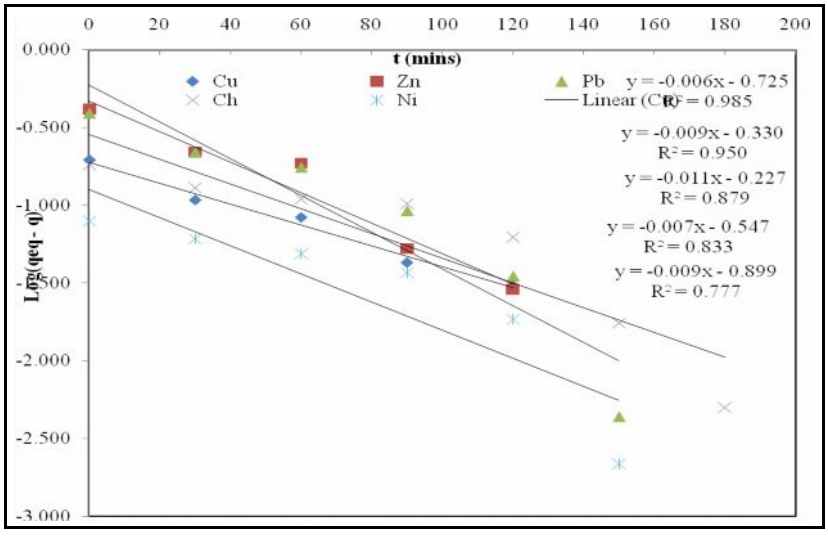

Figure 6(c): Constants and Parameters of Pseudo-first order model for adsorption of multi heavy metals in leachate by 0.6 g Alcoffine solid adsorbent

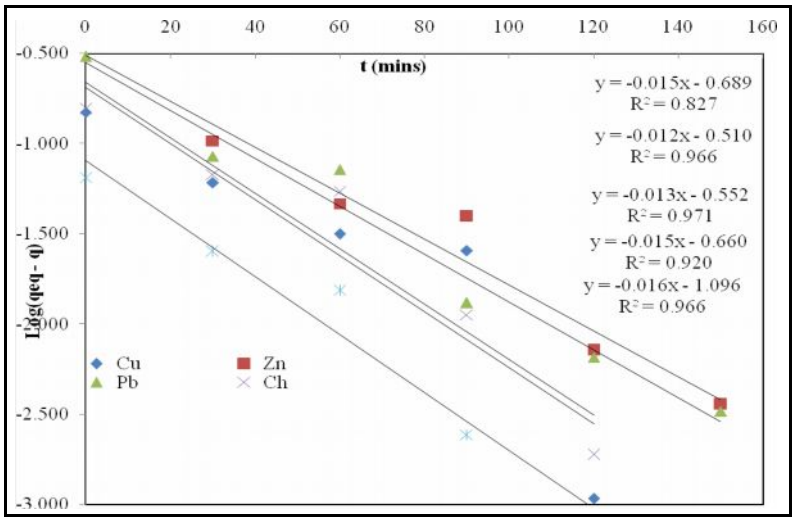

Figure 6(d): Constants and Parameters of Pseudo-first order model for adsorption of multi heavy metals in leachate by 0.8 g Alcoffine solid adsorbent

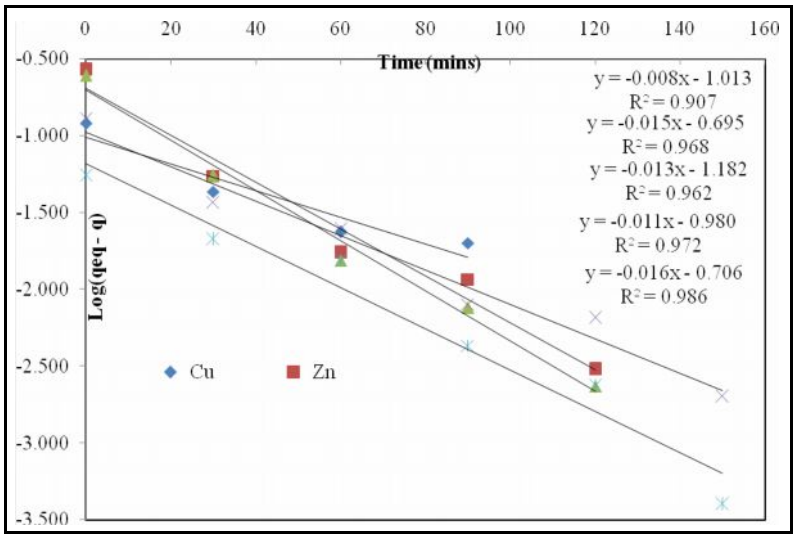

Figure 6(e): Constants and Parameters of Pseudo-first order model for adsorption of multi heavy metals in leachate by 1.0 g Alcoffine solid adsorbent

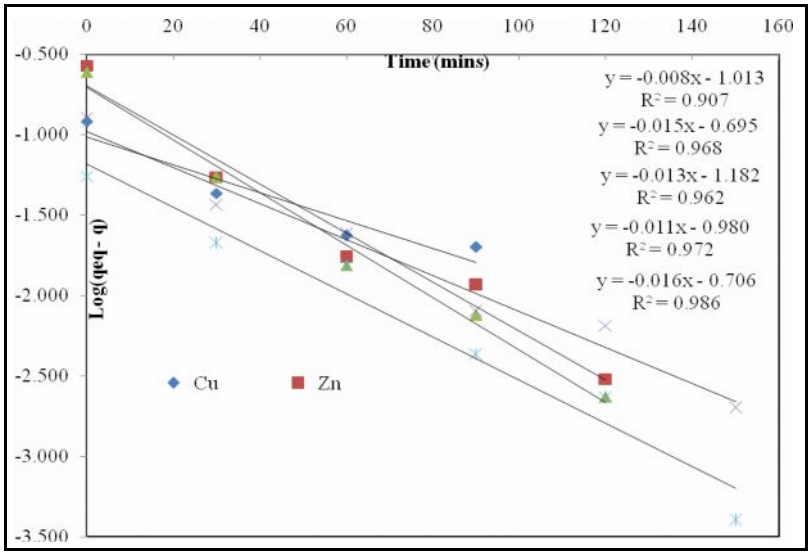

Figure 6(f): Constants and Parameters of Pseudo-first order model for adsorption of multi heavy metals in leachate by 1.2 g Alcoffine solid adsorbent

Pseudo Second order model

The pseudo second order kinetic model is [1 (42,44)]

$$\frac{t}{q_t} = \frac{1}{k_2} q_{eq}^2 + \frac{1}{q_{eq}} t \quad ----(2)$$

Where K_2 is the rate constant of pseudo second order kinetic model and h, the initial adsorption rate which can be expressed as $h = k_2 q_{eq}^2$. Pseudo second order model is based on the adsorption capacity of the solid phase. Contrary to the pseudo first order model, it predicts the behaviour over the whole range of adsorption and is in agreement with an adsorption mechanism, being the rate controlling step[31]. If second order kinetic model is applicable, the plot of t/q against t should give a linear relationship from which the q_{eq} and k_2 can be determined from the slope and intercept of the plot and there is no need to know any other parameter in advance[31].

Although the pseudo first order model shows a good fitting based on the coefficient of correlation with experimental data, the pseudo second order kinetic model describes the kinetic mechanism better than the first order kinetic model. It can be better understood that the adsorption rate of all heavy metal ions in leachate onto Alcoffine, is based on the time factor, which is extended up to equilibrium level. Therefore adsorption mechanism can be approximated more favorably by the pseudo second order kinetic model for all the adsorbent dosage of Alcoffine, investigated in this study. This is evident from the value of h calculated by K_2 and q_{eq}.

Table 8: Constants and Parameters of Pseudo-Second order model for adsorption of multi heavy metals in leachate by Alcoffine solid adsorbent

Adsorbent	Metal	$q_{eq\ Exp}$	$q_{eq\ Cal}$	K_2	R^2	h
0.2	Cu	0.545	0.7037	0.0226	0.961	0.0112
	Zn	0.930	1.2092	0.0117	0.953	0.0171
	Pb	0.920	1.6949	0.0030	0.819	0.0086
	Cr	0.230	1.7007	0.0003	0.159	0.0009
	Ni	0.135	2.2624	0.0001	0.333	0.0005
0.4	Cu	0.285	0.3658	0.0478	0.965	0.0064
	Zn	0.565	0.7107	0.0270	0.971	0.0136
	Pb	0.530	0.8780	0.0056	0.809	0.0043
	Cr	0.200	0.8503	0.0007	0.159	0.0005
	Ni	0.098	1.1299	0.0003	0.333	0.0004
0.6	Cu	0.195	0.2536	0.0643	0.958	0.0041
	Zn	0.413	0.5247	0.0365	0.958	0.01
	Pb	0.388	0.5123	0.0305	0.953	0.008
	Cr	0.182	0.3940	0.0100	0.694	0.0016
	Ni	0.078	0.1848	0.0199	0.712	0.0007
0.8	Cu	0.149	0.0221	72.7	0.998	0.0355
	Zn	0.326	0.0067	240.7	0.994	0.0108
	Pb	0.305	0.0205	78.4	0.996	0.0329
	Cr	0.155	0.0059	272.7	0.985	0.0095
	Ni	0.065	0.0036	447.6	0.994	0.0058
1.0	Cu	0.120	0.1322	0.3596	0.992	0.0063
	Zn	0.267	0.2785	0.5113	0.999	0.0397
	Pb	0.247	0.2556	0.5388	0.999	0.0352
	Cr	0.128	0.1369	0.4806	0.996	0.009
	Ni	0.055	0.0622	0.6419	0.99	0.0025
1.2	Cu	0.100	0.1042	1.2928	0.999	0.014
	Zn	0.223	0.2314	0.6095	0.999	0.0326
	Pb	0.207	0.2133	0.7866	0.999	0.0358
	Cr	0.108	0.1108	1.3444	0.999	0.0165
	Ni	0.046	0.0471	4.2965	0.999	0.0095

Table 8 shows the experimental data along with constants and parameters of pseudo second order kinetic model for adsorption of multi heavy metal ions in leachate by Alcoffine in which the experimental uptake and calculated values are compared. Figure 7(a), 7(b), 7(c), 7(d), 7(e) and 7(f) shows the same. The comparison of experimental and calculated equilibrium uptake rate by pseudo second order model shows a greater coincidence. Also this is supported by the coefficient of correlation which gives excellent linearity. The pseudo second order rate constant K_2 increases with an increase in Alcoffine dosage from 0.2 to 1.2g.

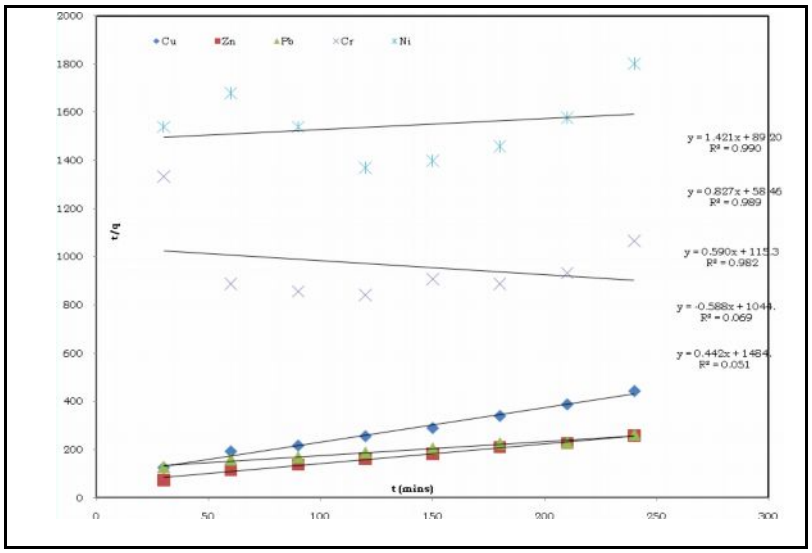

Figure 7(a): Constants and Parameters of Pseudo-Second order model for adsorption of multi heavy metals in leachate by 0.2 g Alcoffine solid adsorbent

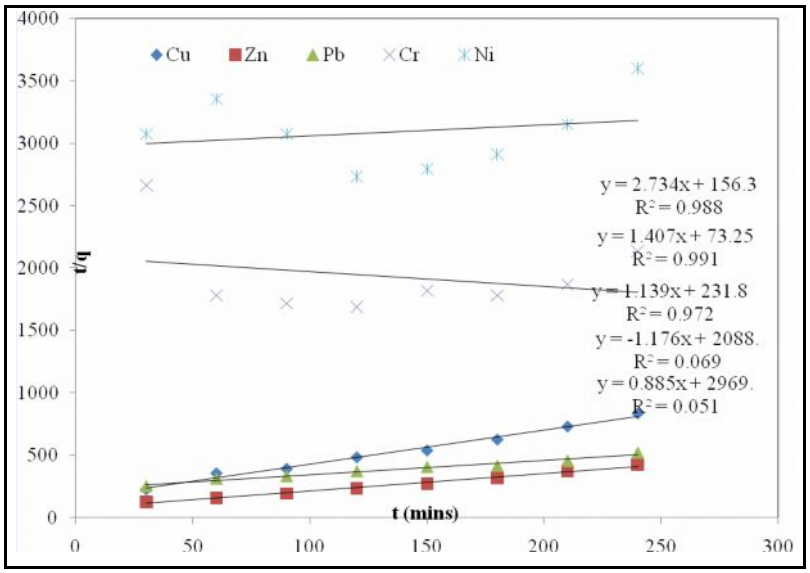

Figure 7(b): Constants and Parameters of Pseudo-Second order model for adsorption of multi heavy metals in leachate by 0.4 g Alcoffine solid adsorbent

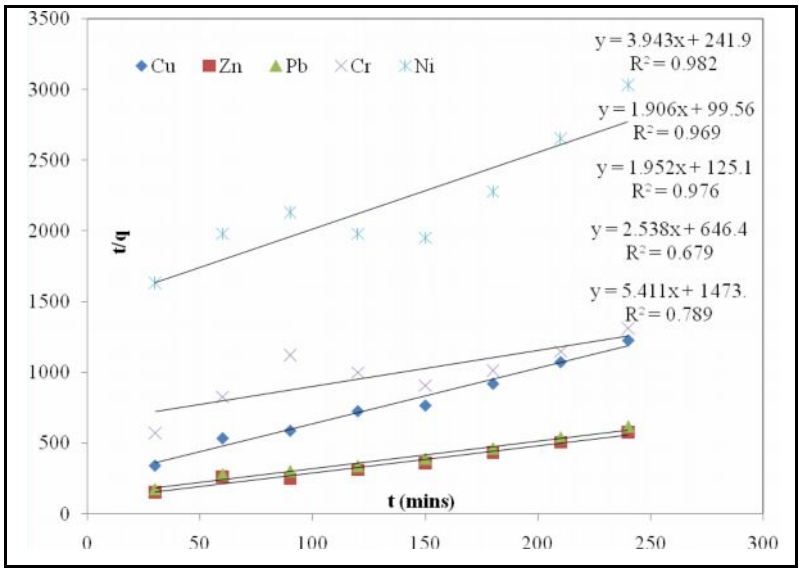

Figure 7(c): Constants and Parameters of Pseudo-Second order model for adsorption of multi heavy metals in leachate by 0.6 g Alcoffine solid adsorbent

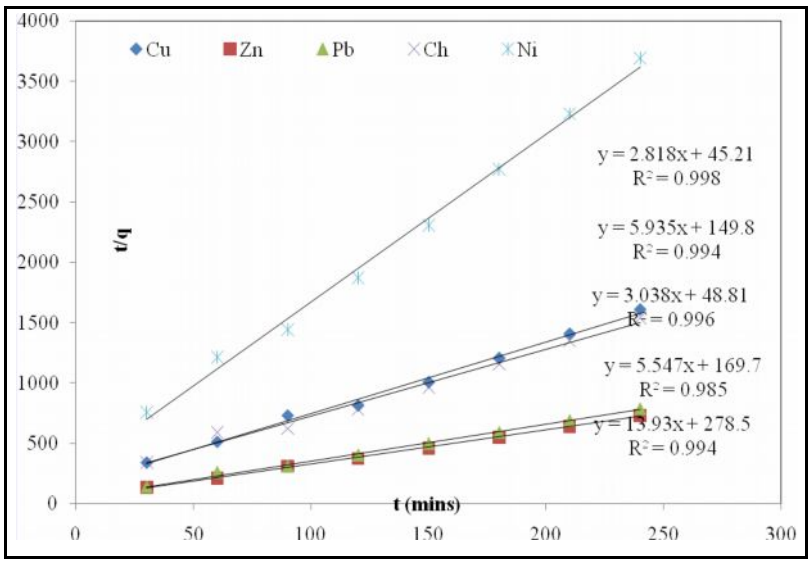

Figure 7(d): Constants and Parameters of Pseudo-Second order model for adsorption of multi heavy metals in leachate by 0.8 g Alcoffine solid adsorbent

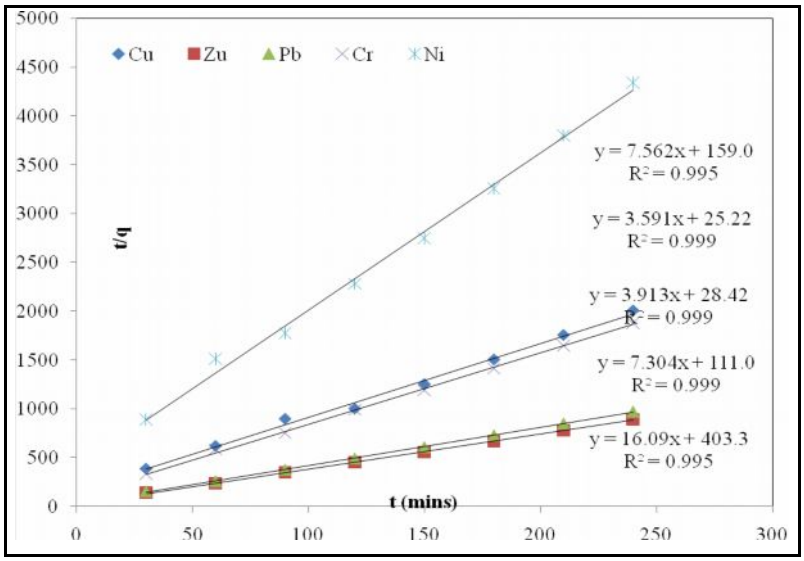

Figure 7(e): Constants and Parameters of Pseudo-Second order model for adsorption of multi heavy metals in leachate by 1.0 g Alcoffine solid adsorbent

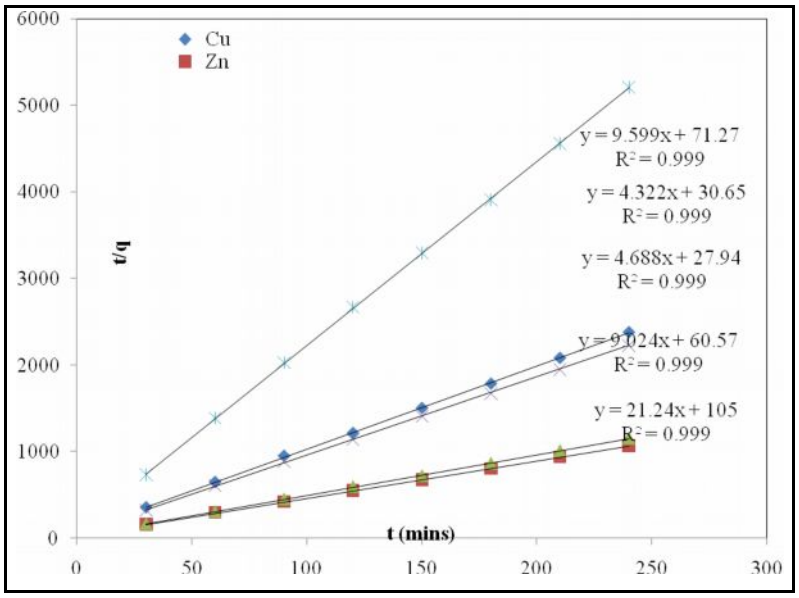

Figure 7(f): Constants and Parameters of Pseudo-Second order model for adsorption of multi heavy metals in leachate by 1.2 g Alcoffine solid adsorbent

Intraparticle Diffusion Model

The possibility of Intraparticle diffusion model[31] is investigated based on the following equation

$$q_t = k_{ID}\sqrt{t} + C \quad ----(3)$$

Where k_{ID} is the Intraparticle diffusion rate constant (mg/g √min) and C is the constant.

Prediction of the rate-limiting step is an important factor to be considered in adsorption processes. For solid–liquid adsorption process, the solute transfer was usually characterized by either boundary layer diffusion or Intraparticle diffusion or both. If the rate limiting step is Intraparticle diffusion, then the graph drawn between (q_t) (mg/g) verses square root of the contact time $\sqrt{t}$ should yield a straight line passing through the origin[32,33].

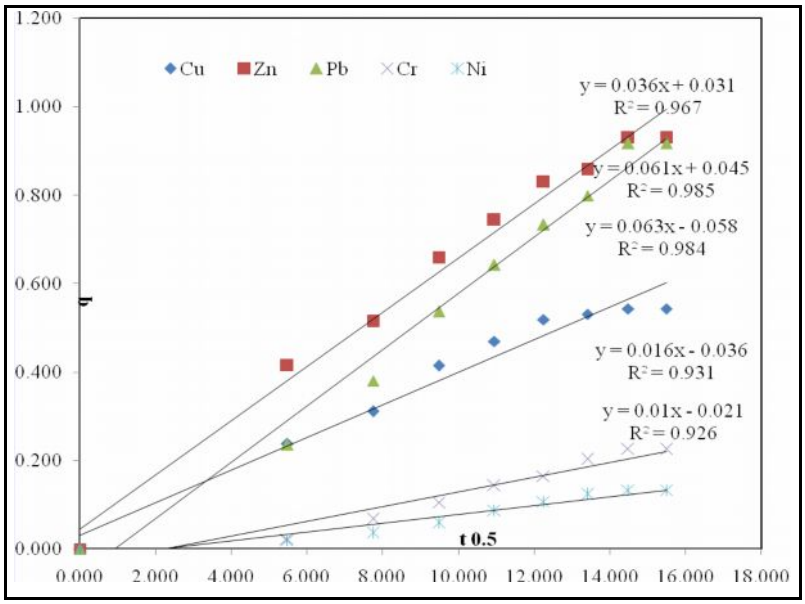

Figure 8(a): Constants and Parameters of Intraparticle Diffusion Model for adsorption of multi heavy metals in leachate by 0.2 g Alcoffine solid adsorbent

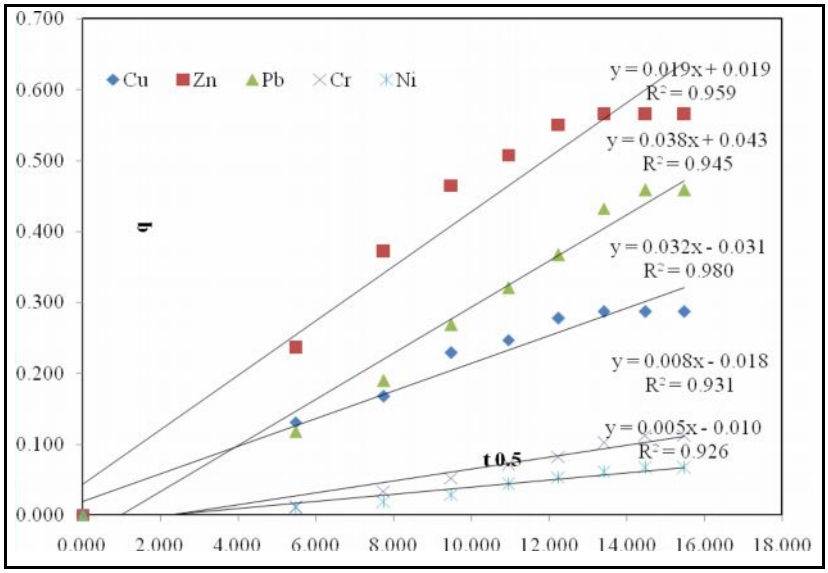

Figure 8(b): Constants and Parameters of Intraparticle Diffusion Model for adsorption of multi heavy metals in leachate by 0.4 g Alcoffine solid adsorbent

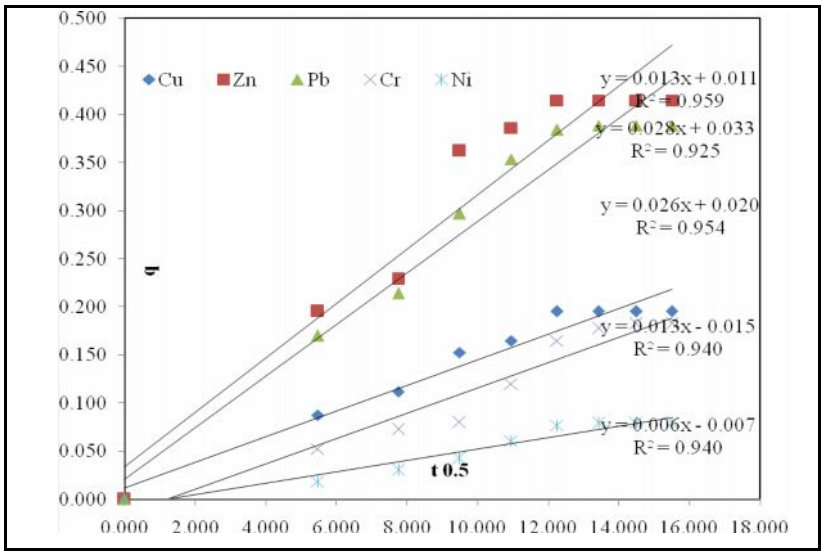

Figure 8(c): Constants and Parameters of Intraparticle Diffusion Model for adsorption of multi heavy metals in leachate by 0.6 g Alcoffine solid adsorbent

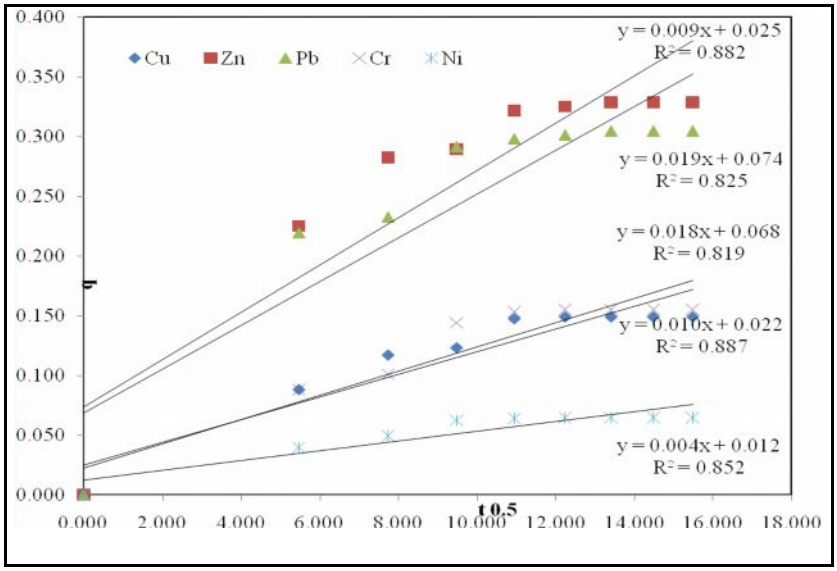

Figure 8(d): Constants and Parameters of Intraparticle Diffusion Model for adsorption of multi heavy metals in leachate by 0.8 g Alcoffine solid adsorbent

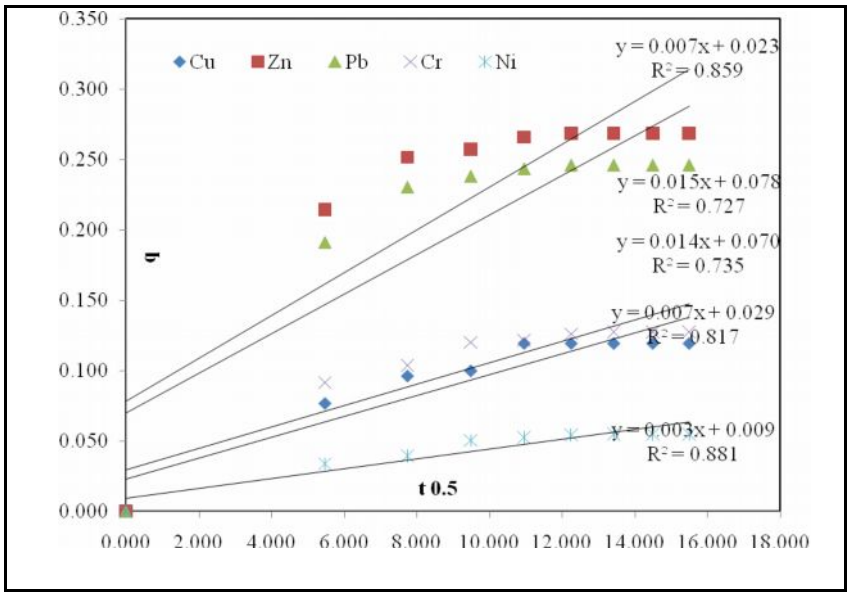

Figure 8(e): Constants and Parameters of Intraparticle Diffusion Model for adsorption of multi heavy metals in leachate by 1.0 g Alcoffine solid adsorbent

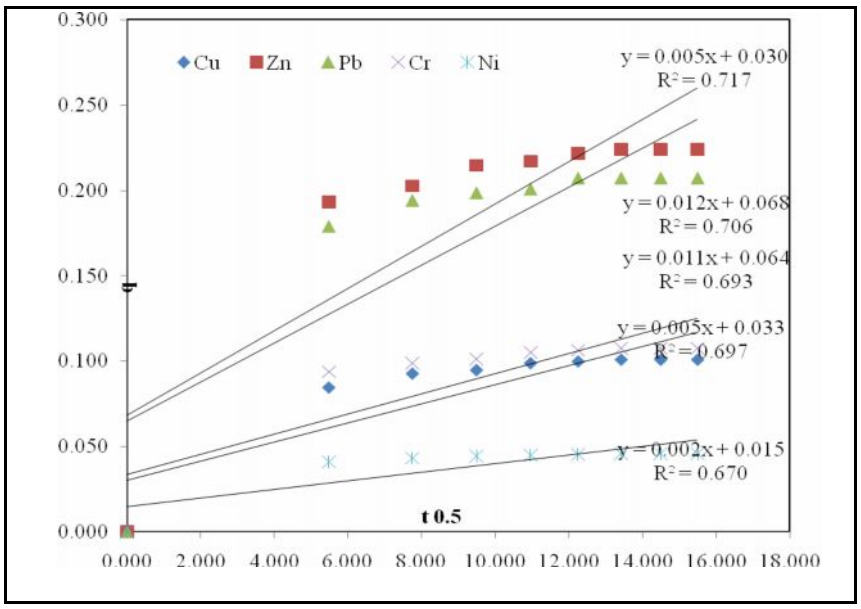

Figure 8(f): Constants and Parameters of Intraparticle Diffusion Model for adsorption of multi heavy metals in leachate by 1.2 g Alcoffine solid adsorbent

Figure 8(a) to Figure 8(f) describes the plot of q_t verses $\sqrt{t}$ and as could be seen that the graph contains two distinct linear regions. It is observed that an initial sharp increasing portion ended with a smooth curve followed by second gradual increasing portion. The two phases in the Intraparticle diffusion model, suggests that the adsorption process proceeds by surface adsorption and the Intraparticle diffusion. The initial steep linear portion of the plot indicates boundary layer effect while the second gradual linear portion is due to Intraparticle or pore diffusion. The slope of second linear portion of the plot has been defined as the Intraparticle diffusion parameter k_{ID} (mg/g $min^{0.5}$).

While considering the entire adsorption time, values of q_t were found not to be linearly correlated with entire values of $\sqrt{t}$. For this case the coefficient of correlation is found to be less. Hence the graph between q_t Vs $\sqrt{t}$ was drawn with an intercept, which results high coefficient of correlation. The value of intercept C gives an idea about the thickness of the boundary layer[31]. Moreover the intercept of the plot is the indication of the boundary layer effect. Larger the intercept, greater is the contribution of the surface adsorption in the rate limiting step[33,34,35].

Table 9: Constants and Parameters of Intraparticle Diffusion Model for adsorption of multi heavy metals in leachate by Alcoffine solid adsorbent

Adsorbent	Metal	K_{ID}	C	R^2
0.2	Cu	0.036	0.031	0.967
	Zn	0.061	0.045	0.985
	Pb	0.063	0.058	0.984
	Cr	0.016	0.036	0.931
	Ni	0.01	0.021	0.926
0.4	Cu	0.019	0.019	0.959
	Zn	0.038	0.043	0.945
	Pb	0.032	0.031	0.980
	Cr	0.008	0.018	0.931
	Ni	0.005	0.010	0.926
0.6	Cu	0.013	0.011	0.967
	Zn	0.028	0.033	0.985
	Pb	0.026	0.020	0.984
	Cr	0.013	0.015	0.931
	Ni	0.006	0.007	0.926
0.8	Cu	0.009	0.025	0.882
	Zn	0.019	0.074	0.825
	Pb	0.018	0.068	0.819
	Cr	0.01	0.022	0.887
	Ni	0.004	0.012	0.852
1	Cu	0.007	0.023	0.859
	Zn	0.015	0.078	0.727
	Pb	0.014	0.070	0.735
	Cr	0.007	0.029	0.817
	Ni	0.003	0.009	0.881
1.2	Cu	0.005	0.030	0.717
	Zn	0.012	0.068	0.706
	Pb	0.011	0.064	0.693
	Cr	0.005	0.033	0.697
	Ni	0.002	0.015	0.670

The constants and parameters of intra particle diffusion model for adsorption of multi heavy metal in leachate by Alcoffine are given in Table 9. It is observed from the Table 9, the R^2 values were found to be close to unity up to a adsorbent dosage 0.6 g, beyond this dosage namely 0.8, 1.0 and 1.2g the R^2 value shows a gradual decline in its trend. This observation indicates that up to 0.6 g of Alcoffine dosage the adsorption mechanism follows pore diffusion, during latter stages the adsorption mechanism follows Intraparticle diffusion model. That is the adsorption of heavy metal ions onto Alcoffine may be controlled due to film diffusion at earlier stages and as the active sites of Alcoffine particles gets loaded with metal ions, the adsorption process may be controlled due to Intraparticle diffusion.

Conclusions

The present studies show the applicability of Alcofine, the pozalonic material for the adsorption of multi heavy metal ions in MSW leachate. Among the three isotherms multicomponent adsorption isotherm model shows a greater fit, rather than extended Langmuir Adsorption isotherm model and Langmuir - Freundlich adsorption model. The coefficient of correlation R^2 found to be high for all the metal ions by Multicomponent Isotherm model. Similarly pseudo second order kinetic model is found to be fit for this

adsorption of multi heavy metal ion in leachate by Alcoffine. From the observation it is found that the uptakes of heavy metal ions under equilibrium condition show a decreasing trend with an increase in adsorbent dosage after 0.6g of Alcoffine. The two phases in the Intraparticle diffusion model, suggests that the adsorption process proceeds by surface adsorption and the Intraparticle diffusion. The initial steep linear portion of the plot indicates boundary layer effect while the second gradual linear portion is due to intraparticle or pore diffusion. The slope of second linear portion of the plot has been defined as the Intraparticle diffusion parameter k_{ID} (mg/g $min^{0.5}$).

While considering the entire adsorption time, values of q_t were found not to be linearly correlated with entire values of $\sqrt{t}$. For this case the coefficient of correlation is found to be less. Hence the graph between q_t Vs $\sqrt{t}$ was drawn with a intercept, which results high coefficient of correlation. It is observed from the Table 3, the R^2 values were found to be close to unity up to a adsorbent dosage 0.6 g, beyond this dosage namely 0.8, 1.0 and 1.2g the R^2 value shows a gradual decline in its trend. This observation indicates that up to 0.6 g of Alcoffine dosage the adsorption mechanism follows pore diffusion, during latter stages the adsorption mechanism follows Intraparticle diffusion model. That is the adsorption of heavy metal ions onto Alcoffine may be controlled due to film diffusion at earlier stages and as the active sites of Alcoffine particles gets loaded with metal ions, the adsorption process may be controlled due to Intraparticle diffusion.

References

1. Sharma, S and Shah, K.W., Generation and disposal of solid waste in Hoshangabad. In: Book of proceedings of the second International Congress of Chemistry and Environment, Indore, India, 2005, 749-751.
2. CPCB (Central Pollution Control Board), Management of Municipal Solid waste, Ministry of Environment and Forests, New Delhi, India, 2004.
3. Shekdar, A.V., Indian Urban Solid Waste Management systems –jaded systems in need of resource augmentation. Journal of Waste Management, 1992, 12(4), 379-387.
4. Sharholy, M., Ahmad,K., Mahmood, G., and Trivedi, R.C., Analysis of municipal solid waste management systems in Delhi – a review. In: Book of proceedings for the Second International congress of Chemistry and Environment, Indore, India, 2005, 773-777.
5. Kansal, A., Solid waste management strategies for India, Indian Journal of Environmental protection, 2002, 22(4), 444-448.
6. Gupta,S., Krishna,M., Prasad, R.K.,Gupta, S., and Kansal, A., Solid waste management in India: options and opportunities. Resource, Conservation and Recycling, 1998, 24, 137-154.
7. Christensen, T.H. and Kjeldsen, P., Landfill emissions and environmental impact: An introduction. in SARDINIA'95*,* Fifth International Landfill Symposium, Proceedings, Volume III*,* Christensen, T.H., Cossu, R., and Stegmann, R., Eds., CISA, Cagliari, Italy, 1995, 3.
8. Donevska. Katerina., Jovanovski. Milorad., and Jovanovski.., Joze, BALWOIS 2010 - Ohrid, Republic of Macedonia, 2010, 25.
9. Christensen, T.H., and Kjeldsen, P., Basic biochemical processes in landfills. Chapter 2.1 in Sanitary Landfilling*:* Process, Technology and Environmental Impact, Christensen, T.H., Cossu, R., and Stegmann, R., Eds., Academic Press, London, UK, 1989, 29.
10. Flyhammer, P., Analysis of the cadmium flux in Sweden with special emphasis on landfill leachate, J. Environ. Qual, 1995, 24, 612.
11. Aulin, C. and Neretnieks, I., Material balance for an industrial landfill. In SARDINIA'95, Fifth International Landfill Symposium, Proceedings, Volume III, Christensen, T.H., Cossu, R., and Stegmann, R., Eds., CISA. Cagliari, Italy, 173, 1995.
12. Belevi, H., and Baccini, P., Long-term behavior of municipal solid waste landfills, Waste Management Res*, 1989,*7, 43.
13. Mor, S., Ravindra, K., Visscher, A.D., Dahiya, R.P., and Chandra, A., Municipal Solid Waste Characterization and its assessment for potential methane generation: a case study. Journal of Science of the Total Environment, 2006, 371 (1), 1-10.
14. Siddiqui, T.Z., Siddique, F.Z., and Khan, E., Sustainable development through integrated municipal solid waste management (MSWM) approach –a case study of Aligarh District. In: Proceedings of National conference of Advances in Mchanical Engineering (AIME – 2006), Jamia Millia Islamia, New Delhi, India, 2006, 1168-1175.

15. Das, D., Srinivasu, M., and Bandyopadhyay, M., Solid state acidification of vegetable waste, Indian Journal of Environmental Health, 1998, 40(4), 343-342.
16. Kansal, A., Prasad, R.K., and Gupta, S., Delhi Municipal waste and environment – an appraisal, Indian Journal of Environmental protection, 1998, 18(2), 123-128.
17. Khan, R.R., Environmental managementof municipal solid wastes, Indian journal of environmental protection, 1994, 14(1), 26-30.
18. Foo, K.Y., and Hameed, B.H., Insights into the modeling of adsorption isotherm systems", Chemical Engineering Journal, 2012, 156, 2–10.
19. Limousin, G., Gaudet, J.P., Charlet, L., Szenknect, S., Barthes, V., and Krimissa, M., Sorption isotherms: a review on physical bases, modeling and measurement, Appl. Geochem, 2007, 22, 249–275.
20. Allen, S.J., Mckay,G., and Porter,J.F., Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems, J. Colloid Interface Sci, 2004, 280, 322–333.
21. Kumar, K.V., and Sivanesan, S., Sorption isotherm for safranin onto rice husk: comparison of linear and non-linear methods, Dyes Pigments, 2007, 72, 130–133.
22. Ghiaci, M., Abbaspur,A., Kia,R., and Seyedeyn-Azad,F., Equilibrium isotherm studies for the sorption of benzene, toluene, and phenol onto organo-zeolites and as-synthesized MCM-41, Sep. Purif. Technol, 2004, 40, 217–229.
23. Ncibi,M.C., Applicability of some statistical tools to predict optimum adsorption isotherm after linear and non-linear regression analysis, J. Hazard. Mater, 2008, 153, 207–212.
24. Saad A., Al-Jlil, andMohammad Sajid Latif., Evaluation of Equilibrium Isotherm Models For The Adsorption Of Cu And Ni From Wastewater On Bentonite Clay, Materials and technology, 2013, 47(4), 481–486.
25. Mckay,G., Use of adsorbents for the removal of pollutants from wastewater, CRC, Press, Inc., 1996
26. Fritz,W., and Schuender,E.U., Simulation adsorption Equilibria of organic solutes in dilute aqueous solution on activated carbon, Chemical Engineering Series, 1974, 29,1279.
27. Liapis,A.I., and Rippin,W.D.T., A general model for the simulation of multi-component adsorption from a finite batch, Chemical Engineering science, 1977, 32, 619.
28. Yon, C.M., and Turnock,P.H., Multicomponent adsorption equilibria on molecular sieves, American Institute Chemical Engineers, Symposium, 1971, 67, 75.
29. Motoyuki Suzuki., Adsorption Engineering,1989,56.
30. Vadivelan, V., Kumar, K.V., 2005. "Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk", Journal of Colloid and Interface Science, 2005, 286, 90-100.
31. Mohanty, K., Das. D., and M.N. Biswas., Adsorption of phenol from aqueous solutions using activated carbons prepared from Tectona grandis sawdust by ZnCl2 activation. Chem. Eng. J., 2005, 115(1-2), 121-131.
32. Allen, S.J., Mckay.G., and Khader, K.Y.H., Intraparticle diffusion of basic dye during adsorption on to sphagnum peat. Environmental Pollution, 1989, 56(1), 39-50.
33. Weber, W.J., and Morris,J.C., Kinetics of adsorption on carbon from solution, Journal of Sanitary Engineering Division, American Society of Civil Engineers, 1963, 8, 31-59.
34. Ho, Y. S., Removal of copper ions from aqueous solution by tree fern, Water Resource, 2003, 37, 2323-2330.
35. Santhi,T., Manonmani. S and Smitha,T., Removal of Malachite green from aqueous solution by activated carbon prepared from the epicarp of Ricinus communis by adsorption, Journal of Hazardous Material, 2010,179, 178-186.

*****