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Adsorption Capacity of Heavy Metals on Different Types of Soil

DeepikaDhawan, PhD student, I K Gujral Punjab Technical University, Jalandhar, India

Dr. A.P. Singh, Dean Academics, I K Gujral Punjab Technical University, Jalandhar, India

Dr. S.K. Singh, Professor, Punjab Engineering College (Deemed to be University), Chandigarh, India

Abstract -Due to quick industrial development and urbanization, there is a tremendous increase in the production of liquid and solid wastes, and as a result, contamination of soils is on an increase worldwide. Increasing deposition of heavy metals on land has given rise to considerable concern about its impact on the environment in general and there is also possibility of transfer of heavy metals into groundwater systems through leaching. Individual adsorption of heavy metals (Cd, Pb & Cr) onto soil having different texture (Sand, Silt and clay) has been studied using batch adsorption experiments. Langmuir and Freundlich models were considered for heavy metal adsorption and parameter determination in such models have been analyzed. The adsorption isotherms could fit well in Langmuir (R^2 values ranges in between 0.951-0.999) as compared to Freundlich isotherms (R^2 values range in between 0.631-0.962). This comparative study was conducted to determine the retention capacity of soil to adsorb heavy metals. The influence of pH and different metal concentration has also been taken into consideration. The experimented results revealed that maximum adsorption has been taken place at pH 5.0 as compared to pH 7.0 mg/l. The two common sequence were found Cr<Cd<Pb for sand & silt and Pb<Cd<Cr for clay.

Keywords: Adsorption Istotherms, Cd, Cr, Freundlich, Heavy Metals, Langmuir, Pb

I. INTRODUCTION

Industrial and other related activities have caused a major heavy metal contamination by hosting heavy metals directly into the neighbouring environment, henceforth the natural world around us as a whole or in a particular geographical area, gets affected by human activity [1]. The cumulative volume of waste water discharged from various industries and the definitive disposal of the solid waste containing metals have been challenging environmental issues in different regions of Punjab.

Soil is defined as the upper layer of earth in which plants grow, a black or dark brown material typically consisting of a mixture of organic remains, clay, and rock particles and has certain characteristics as well which are discussed in the Table 1.

Table 1Comparative Characteristics of Sand, Silt and Clay

S.No.	Characteristics	Sand	Silt	Clay
1.	Size(mm)	4.75-0.075	0.075-0.002	<0.002
2.	Pore Size	Large	Medium	Very Small
3.	Water Holding Capacity	Low	Medium	High
4.	Fertility	Very Low	Moderate	High
5.	Tillage	Easy	Moderate	Difficult
6.	Chemical Activity	Inactive	Slightly Active	Very Active
7.	Total pore space	Least	Medium	Highest

Heavy metals are not biodegradable and persist in nature for a longer period, they mount up within the organism and can cause poisoning, illness and neurological disorders. Heavy metal pollution has received much attention with respect to accumulation in soil, water bodies and uptake by plant [2, 3]. Being at the interface between the atmosphere and the earth's crust as well as the substrate for natural and agricultural ecosystem, the soil is open to inputs of heavy metals from many sources.

A. Heavy Metals and Contamination

The term heavy metal refers to metallic elements that are denser than other common metals. They are natural components of Earth's crust[4]. To a smaller extent they enter our body via food, water and air. Some heavy metals are beneficial to maintain the metabolism of the human

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body but at higher concentrations they can lead to poisoning. Some metals are beneficial to organisms in traces. But if excessive levels of heavy metals enter environment through human activities they can lead to poisoning, they put in danger health and survival of humans and other organisms.

The effects of heavy metals vary from short term to long term. Cadmium is very toxic at extremely low levels. Long term exposure results in renal dysfunction in humans. At high exposure can cause obstructive lung disease. The symptoms of effects include nausea, dyspnea, vomiting, abdominal cramps and muscular weakness depending on the severity of exposure [5]. Cadmium health hazards result from inhalation of fumes, dusts, and ingestion of contaminated food [6]. Lead is the most substantial toxin of the heavy metals [5]. Lead poisoning also causes inhibition of the production of haemoglobin; dysfunctions in the kidneys in all age groups, reproductive systems, cardiovascular system and acute and chronic damage to the central nervous system (especially hazardous to infants and children) [6,7]. Breathing high levels of chromium can cause irritation to the lining of the nose and breathing problems, such as asthma, cough and shortness of breath. Long term exposure results in damage to liver, kidney circulatory and nerve tissues [7].Primary sources of heavy metals contamination and permissible limits are discussed in Table 2&3.

Table 2Primary Sources of Heavy Metals

Heavy Metal	Sources
Cadmium (Cd)	Electroplating, Mining, Smelter, Battery Crushing units, Plastics, Welding, Pesticides
Chromium (Cr)	Mining, Textile, Dyeing, Tannery, Electroplating industries
Lead(Pb)	Refinery, Smelter, Fuel Combustion, Lead Based Paints, Lead plumbing pipes, Automobiles exhaust,

Table 3Permissible Limits for Heavy Metals

Metal	Primary Drinking water standard (mg/l)	Common range in soil (mg/kg)
Cadmium (Cd)	0.005	0.01-0.7
Chromium (Cr)	0.1	1-1000
Lead (Pb)	0.015	2-200

B. Behaviour of Metals in Soil

The behaviour of heavy metals in soil depends not only on the level of contamination as stated by total content, but also on the form and origin of the metal, and the properties of the soil themselves. Soil has important possible pathways for metal transport to surface water, groundwater, plants, animals and man. Soil due to its ability to bind contaminants by different physico-chemical forces (Figure 1) act as a major sink for the contaminants [8]. When the capacity of soils to retain toxic metal is reduced due to continuous loading of wastewater results in release of heavy metals into groundwater or soil solution for plant uptake [9]. Transportation of heavy metals from top soils to deeper soil layers is done through various processes like advection, dispersion, diffusion [10].

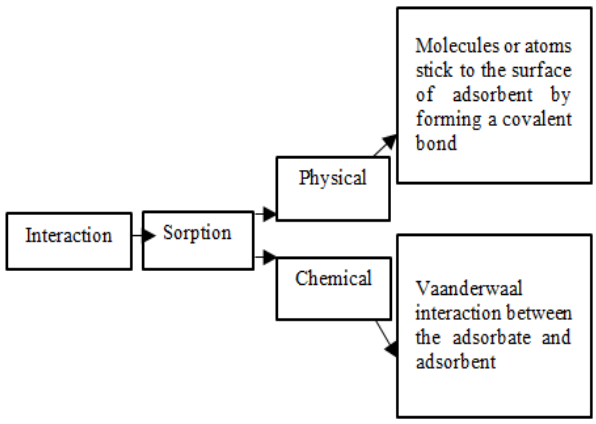

Fig.1. Types of Physico-chemical interactions between adsorbate and adsorbent

C. Adsorption Isotherms

Sorption is a physical and chemical process by which one substance becomes attached to another. It is of two types one is adsorption and another is absorption. Adsorption is the adhesion of adsorbate (chemical constituent) onto the surface of adsorbent [11]. This particular process forms a film of the adsorbate on the surface of the adsorbent. Adsorption is a surface-based process while absorption involves the whole volume of the material (Figure 2).

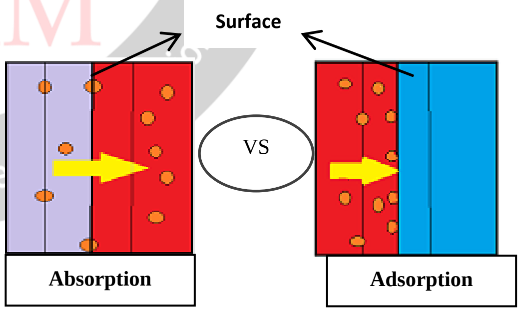

Fig.2. Diagrammatic view of Absorption and Adsorption

Adsorption procedures control the providence and bioavailability of heavy metals in soils. In this comparative study, adsorption characteristics of soil samples from various locations were studied by means of batch process. Concentration of the heavy metal in the liquid phase and the solid phase at equilibrium and at constant temperature are commonly based upon mathematical relationships are described as empirical

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models [12]. This equilibrium can be defined by the equality of the chemical potentials of the two phases defines the equilibrium [12]. These relationships are called isotherms. Most commonly used isotherms are the Langmuir and Freundlich isotherm. The batch adsorption studies have been widely used by various researchers to check the retention capacity of heavy metals onto soil [11].

Isotherms relate metal uptake per unit weight of adsorbent to equilibrium adsorbate concentration in the liquid phase. The Langmuir isotherm was established on the assumptions that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface, the energy of adsorption was constant and there was no movement of adsorbate in the plane of the surface. The Langmuir equation [13] is given by

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L}\frac{1}{C_e} \quad \text{.... (1)}$$

Where, C_e was the equilibrium concentration (mg/l), q_e was the amount adsorbed at equilibrium time (mg/g), q_m and K_L are Langmuir constants related to adsorption capacity (mg/g) and energy of adsorption (L/mg), respectively. The data for Langmuir adsorption isotherm and regression analysis of the data were shown in Table 4 & 5, fitted well in Langmuir adsorption isotherm.

Freundlich isotherm is generally described for mathematical explanation of adsorption in aqueous system and defines heterogeneous surface energies. The Freundlich equation [13] is given by

$$S = Kf\left(C_e\right)^b \quad \text{.... (2)}$$

Where, S indicates the adsorption degree (mg/g), $C_e$indicates the equilibrium concentration (mg/l) and K_f indicates the Freundlich partition coefficient (L/g) and b indicates the empirical constant of the Freundlich isotherm, is a dimensionless parameter that varies between 0 and 1 [14].K_f was the capacity of adsorbent and b indicated the favorability.

This work examines the retention of three heavy metals i.e. cadmium, lead and chromium onto soils that varies in texture using batch experiments. A study was done in thermodynamic equilibrium used batch experiments. Metal uptake by the soil was calculated. The experiments were conducted to determine the impact of initial concentration on metal retention, how the metals are retained by various texture of soil and compare the results. In this paper Langmuir and Freundlich isotherm models were applied to the data to obtain the corresponding correlation coefficients. The study will also be helpful in understanding the leaching behavior as leaching of metal will be inversely proportional to their adsorption capacity.

II. METHODOLOGY

A. Soil Sampling

Three types of soil of different textures i.e. clay, silt and sand were selected for batch studies. Bulk sub-surface soil samples (0-30cm) were collected with different type of texture. Collected samples were grounded, air- dried and passed through a 2-mm sieve for further physicochemical properties, as shown in Table 4.

Table 4Physico-Chemical Characteristics of Soil

S.No.	Parameters	Unit	Sand	Silt	Clay
1.	pH	--	8.2	7.8	7.4
2.	Organic Matter	%	0.207	0.63	1.02
3.	Bulk Density	gm/cc	1.6	1.47	1.79
4.	Sand	%	89	19	18
5.	Silty	%	6	54	33
6.	Clay	%	5	27	49
7.	CEC	meq/100gm	12.1	23.2	38.2
8.	Calcium Carbonate	%	8.9	6.2	16.3

B.Batch Equilibrium Tests

A preliminary study was conducted to select the concentration of heavy metals in the solution. Firstly, Stock solutions (1000 mg/l) for Pb, Cd and Cr were prepared in nitrate salts of metals in double distilled water and all intermediate standards of lower concentration were prepared. Pb, Cd and Pb solutions were adjusted with 0.1 N HCL and 0.1 N NaOH to pH 5.0 and 7.0. Batch sorption experiments (Figure 3) were conducted at room temperature by equilibration 2 g of soil with 20 ml of 10, 30, 50, 70, 90 and 100 mg /l of Cd $(NO_3)_2$, Cr $(NO_3)_3$ and $Pb(NO_3)_2$ by using 0.01 M NaNO3 as background electrolyte with a fixed ionic strength, soil samples were shaken for 24 hour [15]. After 24 hours samples were centrifuged and the supernatant was filtered using Whatman No. 42 Filter paper. Cd,Cr and Pb concentrations of filtered extract were measured using Elico SL 150 atomic absorption spectrophotometer. The amounts of adsorbed metals were derived as the difference between the amount of each metal initially present in the solution and the amount remaining in the solution after equilibrium. The amount of metal adsorbed at equilibrium was calculated using the below formula:

$$q_e = \frac{C_o - C_e \times V}{m}$$

Where,

C_o = Initial concentration of metal ion in the solution

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(mg/l).

C_e = Final concentration of metal ion in the solution (mg/l).

m = Mass of adsorbent (gms).

V = Volume of solution (liter).

q_e= Amount of metal ion adsorbed per gram of adsorbent (mg/g).

(a)

(b)

(c)

Fig.3. Batch equilibrium Experiment-(a) On shaker to attain equilibrium (b) Filtration of samples after 24 of equilibrium (c) Analysis of heavy metals using AAS

III.RESULTS AND DISCUSSION

A. Effect of pH

The important parameter in the adsorption process is the pH of the solution. Experiments were conducted on pH 5.0 and pH 7.0 and study reveals that retention of heavy metals was strongly dependent on pH of the solution. The maximum retention of heavy metals found linear on pH 5.0 for all three heavy metals and further increase in pH results in decreased adsorption.

B. Heavy Metals

For all three soils, sorption data of Cd, Pb and Cr were fitted in both Langmuir and Freundlich to envisage the behaviour of heavy metals sorption by the soils. The data attained were fitted in the equations 1 & 2 for studying the sorption relationship.

The Langmuir and Freundlich constants that were derived from these isotherms are given in Table 5&6. The Langmuir and Freundlich isotherms models better defined the sorption process. Comparatively, the results indicated that all the soils under study were following Langmuir adsorption isotherm better than that of Freundlich adsorption as indicated by higher R^2 values ranging from 0.758-0.998 at pH 7.0 and 0.951-0.999 at pH 5.0. The sequence of adsorption capacity for all three heavy metals was Clay> Silt >Sand. The adsorption capacity was higher for clay soil for all three studied heavy metals and least for the sandy soil; this may be due to higher clay content, organic matter and CEC.

The two adsorption sequences were found one was Cr<Cd<Pb for sand and silt at both pH i.e. 5.0 and 7.0 and second is Pb<Cd<Cr for clay at both pH i.e. 5.0 and 7.0.

It was interesting to note that the adsorption behaviour of all three metals having similar behaviour on sand and silt. The position of cadmium in the all sequence remains the same in all sequences.

The presence of Cr as one of the most retained cation in clay, in spite of its lower electronegativity value (1.6), seems to be related to the fact that this metal was applied in its trivalent form, which is how it appears predominantly in clay soil. Cadmium and lead ions are adsorbed less on clay soil because they are characterized by larger ionic radii and their introduction in interlayers and complexation with surface sites is limited by steric hindrance and lower electrostatic attraction.

From the results it is evident that the total capacity of sand and silt follows the same order towards the studied metals.

In general, Clay soil was found to have a good adsorption capacity towards all studied metals. To prevent groundwater and subsoil by leachates having heavy metal contamination clay are extensively used as Landfill barrier in landfills. The groundwater quality is less effected where areas having clay soil.

Based on isotherm parameter values obtained, the metal adsorption affinity of heavy metals to the studied soils at pH 5.0 was higher as compared to pH 7.0.

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Table 5Freundlich and Langmuir Constants of Cd, Pb &Cr Adsorptionin Soils at 7.0

	Freundlich' s Constants				Langmuir's Constants		
S.No.	Soil Type	K_f(L/g)	b	R^2	q_m(mg/g)	K_L	R^2
Cd							
1.	Sand	0.170	0.281	0.660	0.786	0.212	0.758
2.	Silt	0.182	0.578	0.765	1.505	0.058	0.979
3.	Clay	0.971	0.638	0.908	10.215	0.011	0.949
Pb							
4.	Sand	0.235	0.498	0.858	0.923	0.378	0.988
5.	Silt	0.898	0.654	0.955	1.548	1.473	0.998
6.	Clay	0.190	0.478	0.599	2.819	0.802	0.969
Cr							
7.	Sand	0.098	0.471	0.850	0.549	0.054	0.973
8.	Silt	0.111	0.539	0.882	1.292	0.103	0.988
9.	Clay	0.987	0.847	0.962	14.706	0.010	0.995

TABLE 6 Freundlich and Langmuir Constants of Cd, Pb &Cr Adsorption in Soils at 5.0

	Freundlich' s Constants				Langmuir's Constants		
S.No.	Soil Type	K_f(L/g)	b	R^2	q_m(mg/g)	K_L	R^2
Cd							
1.	Sand	0.128	0.541	0.921	0.863	0.147	0.999
2.	Silt	0.120	0.775	0.948	2.665	0.041	0.995
3.	Clay	0.993	0.680	0.927	22.124	0.005	0.951
Pb							
4.	Sand	0.136	0.438	0.938	1.128	0.078	0.995
5.	Silt	0.278	0.803	0.954	3.153	0.107	0.993
6.	Clay	0.893	0.528	0.631	11.710	0.165	0.997
Cr							
7.	Sand	0.122	0.539	0.912	0.667	0.096	0.999
8.	Silt	0.118	0.830	0.933	2.372	0.017	0.988
9.	Clay	0.999	0.847	0.962	24.499	0.005	0.988

Figure 4 -7 shows the Langmuir and Freundlich isotherms with cadmium at pH 7.0 and pH 5.0 for all three soils, figure 8-11 shows the Langmuir and Freundlich isotherms with lead at pH 7.0 and pH 5.0 for all three soils, figure 12-15 shows the Langmuir and Freundlich isotherms with chromium at pH 7.0 and pH 5.0 for all three soils, respectively.

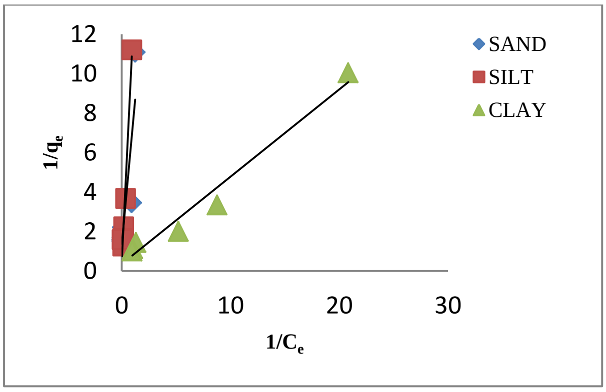

Fig.4. Langmuir Isotherm with Cadmium at pH 7.0

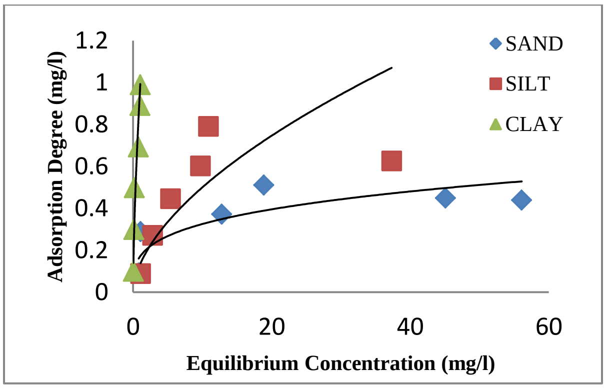

Fig.5. Freundlich Isotherm with Cadmium at pH 7.0

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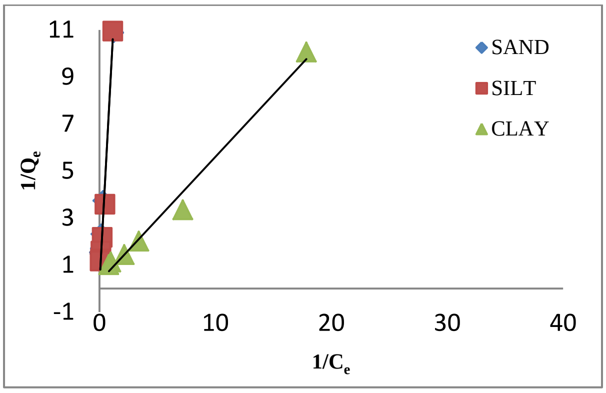

Fig.6. Langmuir Isotherm with Cadmium at pH 5.0

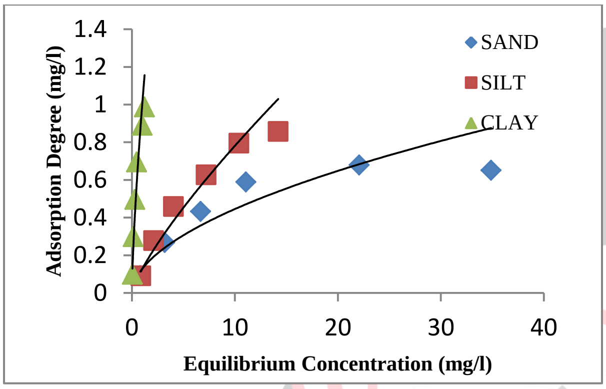

Fig.7. Freundlich Isotherm with Cadmium at pH7.0

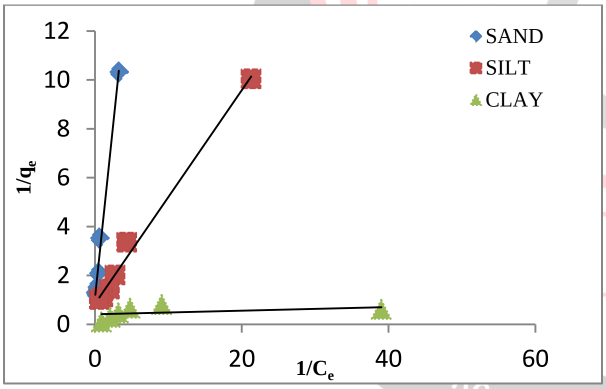

Fig.8.Langmuir Isotherm with Lead at pH 7.0

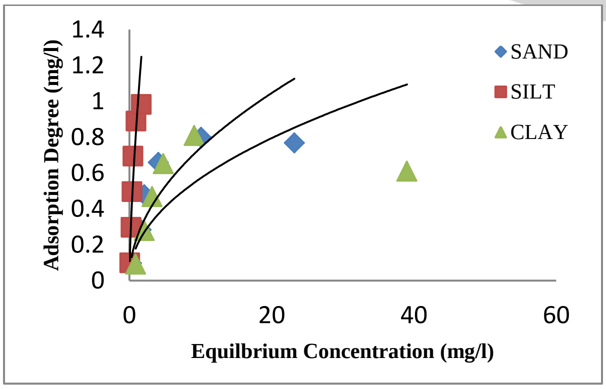

Fig.9. Freundlich Isotherm with Lead at pH 7.0

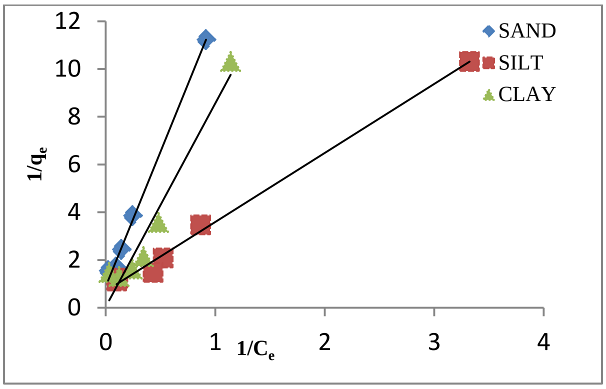

Fig.10. Langmuir Isotherm with Lead at pH 5.0

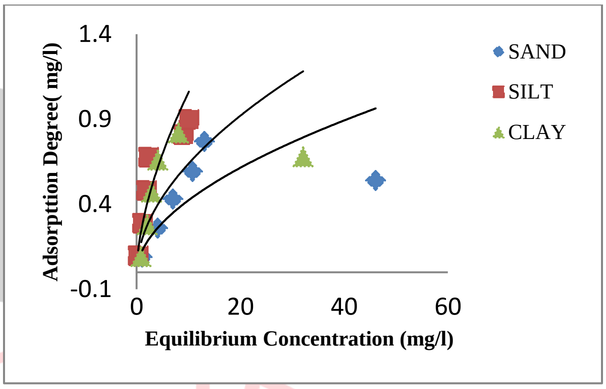

Fig.11.Freundlich Isotherm with Lead at pH 5.0

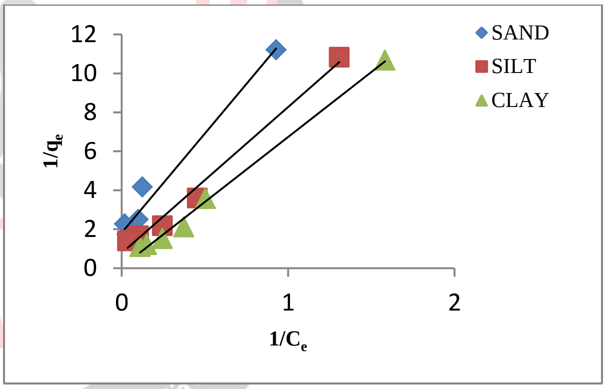

Fig.12. Langmuir Isotherm with Chromium at pH 7.0

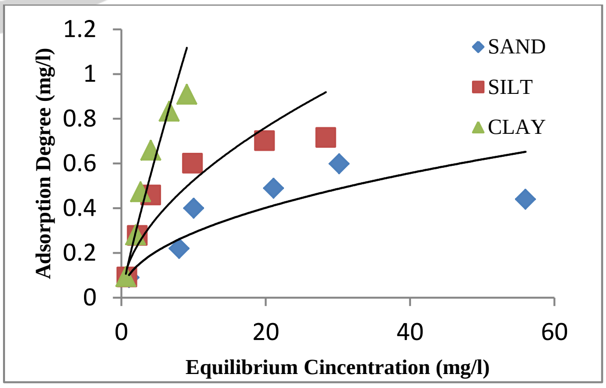

Fig.13.Freundlich Isotherm with Chromium at pH 7.0

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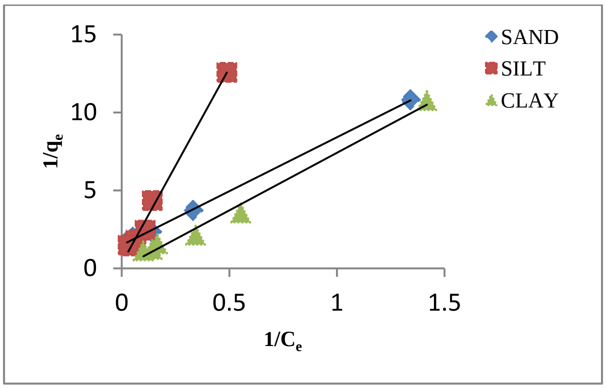

Fig. 14.Langmuir Isotherm with Chromium at pH 5.0

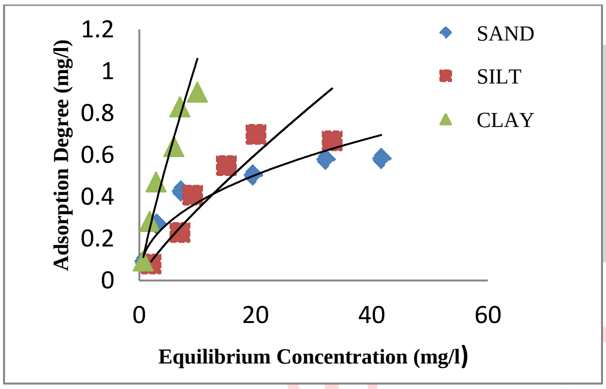

Fig. 15.Freundlich Isotherm with Chromium at pH 5.0

IV. CONCLUSIONS

The results evidenced that the sorption capability of clay towards each metal is higher than the silt and sand. The studied metals are adsorbed on clay in the following order: Cr^{3+}>Cd^{2+}>$Pb^{2+}$and for sand and silt in the following order: Pb^{2+}>Cd^{2+}>Cr^{3+}.A highly significant correlation coefficient obtained for Langmuir at both pH 7.0 and 5.0 as compared to Freundlich isotherm, conforms to the Langmuir isotherm. Maximum adsorption obtained at pH 5.0 for all three heavy metals onto all three studied soils. This study will be helpful in assessing the potential hazards due to contamination with heavy metals. It also helps in planning and execution of formulating the reclamation process for the contaminated site with heavy metals.

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