Cadmium (Cd) is an environmental pollutant. Adsorption and desorption of Cd in soil control the availability and accumulation of Cd in plants. Cadmium adsorption in soils is affected due to several factors including soil pH, texture, calcium carbonate contents and ionic composition in soil solution. This experiment was conducted to study the adsorption-desorption behavior of Cd in the presence of Ca in soil. Soil was taken from research area of Institute of Soil and Environmental Sciences (UAF). Soil (3g) was taken in 50 ml centrifuge falcon tubes spiked with the combination of 0, 10, 20, 40, 60, 80 and 100 mg/kg Cd with 20 and/or 30 mg/kg Ca. To achieve equilibrium and maximum adsorption, suspension was kept for seven days and shaken for 30 minutes twice a day. After equilibrium is attained, solution was filtrated and the residual soil was kept for desorption study. For desorption of Cd, 0.01 M sodium nitrate solution (30 ml) was prepared and added to the falcon tubes containing residual soil from adsorption study. To attain the desorption equilibrium, falcon tubes was shaken twice a day (30 minutes each shaking) for period of 1 day. Suspension was filtered using Whatman 42 filter paper. The filtrate was analyzed for Cd concentration using atomic absorption Spectrophotometer ( S Adsorption parameters of Cd in soil was studied using Freundlich model in Plangmuir equation. From data it was concluded that adsorption of Cd was decreased as level of Ga marcased from 10 mg kg<sup>-1</sup> to 30 mg kg<sup>-1</sup>. At Ca-10 mg kg<sup>-1</sup> maximum adsorption was observed (6-90 mg kg<sup>-1</sup>) and at Ca-20 adsorption <sup>1</sup>) while minimum also ption was observed at Ca-30 (3-82 mg kg<sup>-1</sup>). If we was (5-of mg kg compare desorption of all treatments, at Ca-10 minimum desorption was observed (2-7 mg kg<sup>-1</sup>) and at Ca-20 desorption rate was (3-11 mg kg<sup>-1</sup>) while maximum desorption was observed at Ca-30 which was (5-14 mg kg<sup>-1</sup>). It was concluded that maximum adsorption was observed at Ca-10 mg kg<sup>-1</sup> while maximum adsorption was observed at Ca-30 mg kg<sup>-1</sup>.

#### **CHAPTER 1**

#### INTRODUCTION

Heavy metals are naturally occurring elements that have a high atomic weight and a density at least 5 times greater than that of water (Fregusson *et al.*, 2016). Their multiple industrial, domestic, agriculture, medical and technological applications (Bradl*et al.*, 2018) have led to their wide distribution in the environment, raising concerns over their potential effects on human health and the environment.

Their toxicity depends on several factors including the dose, route of exposure, and chemical species as well as the age, gender, genetics and nutritional status of exposed individuals. Because of their high degree of toxicity, arsenic (As), cadmium (Cd), lead (Pb) and mercury (Hg) rank among priority metals. These metallic elements are considered systematic toxicants that are known to induce multiple organ damage, even at lower level of exposure (Duffus*et al.*, 2016).

Heavy metal contamination of soils is widespread problem around the globe in the industrial area. Most of the heavy metals are metabolically non-essential area thus they are toxic for living organisms though at small concentration. By continuous the or untreated waste water, heavy metal accumulates in soil (Huimin *et al.* (10)).

Heavy metals are toxic more an inpollutants and carrie of anthropogenic and natural origin. The natural contribution of heavy metals is much but human activities have main role in contribution of heavy metals. Phen accumulation in the soil is mainly through disposal of the sewage sludge, iron foundries, metal contaminated industrial effluents, municipal and pesticide waste through mining and smelting use of phosphatic fertilizers (Khan *et al.*, 2017), Ni-Cd batteries, plating, pigments, pesticides (Sterckeman *et al.*, 2018), plastics and many other industrial processes (Antosiewicz *et al.*, 2017).

Pakistan is situated in semi-arid to arid regions and thus is confronted with severe shortage of good quality of water. Due to this situation farmers use waste water to irrigate the crops (Yang *et al.*, 2018). In Pakistan, untreated water irrigates almost 32,500 ha (Murtaza *et al.* 2016). In Pakistan, now a days irrigation of agricultural land with canal water is limited as well as its increasing population leads to the shortage of surface water which makes more use of un-treated water to irrigate the crops, which ultimately pollute the soil with heavy metals.

Agricultural soils polluted with toxic metals have become the major problem all over the world and imposed a harmful impact on health of humans and its accumulation in the food chain

# **REVIEW OF LITERATURE**

Heavy metal ions are the most toxic inorganic pollutants which occur in soils and can be of natural or of anthropogenic origin (Siegel, 2002). Some of them are toxic even if their concentration is very low and their toxicity increases with accumulation in water and soils. Adsorption is a major process responsible for accumulation of heavy metals. The most important interfaces involved in heavy metal adsorption in soils are predominantly inorganic colloids such as clays (Bradl, 2002) metal oxides and hydroxides (Demirata *et al.*, 2002), and metal carbonates and phosphates. Therefore, the study of adsorption processes is of utmost importance for the understanding of how heavy metals are transferred from a liquid mobile phase to the surface of a solid phase. Research work of different research highlighting adsorption and desorption of metals in general and that of Cadmium in particular is explained below;

Olaofe *et al.* (2015) studied the adsorption of four different metals such as Pb, Cl, Cu and Zn collected from four different places using batch experiment. They use study the effect of different factors that affected the sorption of heavy mean index. By using regression equation, data of adsorption were correlated with ad order isotherm. When graph protted between adsorbate and mass of clay two, discontrations were shown firstly at low concentration straight line plot and at high concentration flat to the user observed. It was concluded that adsorption data better correlate to Langmuir than Freundlich isotherm and all parameters in these isotherms were deliberated. It was concluded that adsorption data correlated with three functions such as Olaofe proposed function, Simple Elovich and power function. In these three functions all parameters were discussed. From results it was concluded that natural clay can be used as adsorbent.

Sulaiman (2015) studied the effect of different factors affecting bio-sorption of Cu ion from aqueous solution. For removal of heavy metals from waste water bio sorption is considered important process. In waste water copper exist in form of Cu (II) while copper carbonate exists in form of organic complexes. According to WHO copper carbonate concentration in waste water has reached 0.12g which reduced the water quality and it is nontoxic element. Effect of different factors such as biosorbent concentration, contact time and metal concentration were concludedon removal of Cu. From results it was concluded that all factors have effect on removal of Cu from industrial waste water.

surface bases on correlation coefficient ( $r^2$ ). The empirical data of adsorption process on single substance of Cd as adsorbate and sands white and black as adsorbent with batch operation were used. The binary metal ions in solution was mixed with the sand then shaken in 100 rpm. The kinetics adsorption capacity was than measured with the pseudo order model to evaluate the interaction type from the r2 indicator. The result found that the Cd with  $r^2 = 0.9656$  and  $r^2 = 0.9989$ for first and second order respectively, for black sand and  $r^2 = 0.9070$  and  $r^2 = 0.9999$  for first and second order respectively, for white sand. It was indicated that the interaction type of metal ions on sand surface was occurred together as physical and chemical interaction.

Bostani et al. (2018) investigated the adsorption behavior of particular heavy metals (Cu, Pb, and Ni) under single and multi-metal treatments by a light textured soil (calcareous) amended with biochars of plant residue (wheat straw, corn straw, licorice root pulp and rice husk each at 3% w/w). The Freundlich isotherm best defined the heavy metal adsorption signifying multilayer adsorption. The heavy metal adsorption capacity followed the order viz., Pb > Chi Ni for all treatments under both adsorption conditions which was linked vipothe under radius, hydrolysis constant, and electronegativity of particular metals in the part of adsorption capacity decreased simultaneous due to the presence of multiple metals and the area or sation was in the order of Ni > Pb > Cu. The biochard for straw (BCS) has the baximum adsorption capacity (Freundlich 1.41 Ni - (23 and Pb = 2.73) and average distribution coefficient (Kd Kf (m, , , , , , ) Cor medium (L kg-1) for Cu = 1.61.00, Ni = 59.30 and Pb = 2602.00), indicating the BCS is the best effective treatment for heavy metals stabilization in the soil. This was related with the chemical properties of the BCS (high amounts of P and CaCO<sub>3</sub>) and the highest increase pH value of soil. Yumi et al. (2018) studied the effect of free iron oxides on the adsorption of Cd (II) and Cu(II) from aqueous media on natural allophane (NA). The objective of this research was to obtain natural allophane with (NA-FeOx) and without (NA) iron oxides from a Southern Chilean Andisol and determine the influence of the natural free iron oxide coatings on the adsorption of cationic pollutants Cd (II) and Cu (II) in aqueous media. From the kinetic studies, equilibrium adsorption was achieved within 60 min and was almost independent of the presence of the iron oxides. Among the kinetic models evaluated, the pseudo-second order model presented a better correlation with the experimental data. The adsorption studies revealed that NA has a greater adsorption capacity of both Cd<sup>+2</sup> and Cu<sup>+2</sup> compared to NA-FeOx. Langmuir and Freundlich adsorption models fitted the experimental data well, suggesting that the adsorption process is a combination of physical and

is not distinctive empirical model (EM) has additional mechanisms such as competition for sorption site or solid phase heterogeneity while mechanistic model did not have this mechanisms. Basic difference between two approaches is that empirical model have no electrostatic term while mechanistic model (MM) have this electrostatic term.

### **Adsorption Isotherm**

They are used to determine the interaction that occur between absorbate molecule and absorbent molecule. For determination of this interaction two important molecule are used such as Freundlich (1906) and Langmuir (1918) isotherm model.

## Langmuir Isotherm Model

This model is based on the assumption that at surface of absorbent, monolayers of absorbate took place which indicate that on one adsorption (Ad) site only one molecule will be absorbed or with the distance intermolecular forces will be decrease Crini *et al.* (20) Found Kanan *et al.* (2002) give an assumption that adsorbent surface are hereingeneous and holds equivalent adsorption sites. Equation of Langmuir isotherm more is shown in equ (c)

Values of linear expression  $q_m$  and  $K_L$  are expressed from intercept of plot between  $C_e/q_e$  versus  $C_e$ 



#### Effect of soil pH

Soil pH is important factor that effect then cadmium adsorption and desorption. Gomes *et al.* (2001) reported that pH of equilibrium solution significantly decreased during Cd<sup>+</sup> hosorption for both soils. The pH of REQ soil decreased more than the RAR solution the same Cd<sup>2+</sup> loading. For the same soil, equilibrium solution pH decreased with increasing Cd<sup>2+</sup> adsorption (Yu *et al.*, 2002) reported that heavy metal comanitation potentially causes voll acrdification, and the more the heavy metal input the neuronaction will a multinomial regression equation with correlation coefficients. In equilibrium solution pH generally increased with desorption and was lower when Cd<sup>2+</sup> concentration in the equilibrium solution increased.

#### Effect of CaCO<sub>3</sub>

Plassa *et al.*(2000) stated that carbonate dissolution increases when the pH of soil decreases as ionic exchange is the principle retention mechanism of heavy metals. Due to the presence of carbonates at elevated pH retention of cadmium also increases. Heavy metals are retained by soil mainly as carbonate salt when the calcium carbonate (CaCO<sub>3</sub>) contents in soils are high. The mobility of heavy metal such as Cd in soil is controlled by its adsorption/desorption on surface of soil mineral. It includes clays, metal oxides and hydroxides, carbonate contents as well as organic matter (Zhao *et al.*, 2014). Sorption of heavy metal increase is due to several mechanism such as physical, chemical sorption and precipitation (Xiong *et al.*, 2005). Calcium carbonate content in the soil increases soil pH by following hydrolysis reaction.

$$CaCO_3 + HOH = Ca^{+2} + HCO_3 + OH^{-1}$$

Due to the presence of  $CaCO_3$  weak base  $Ca(OH)_2$  is formed that may rise the pH and sorption of heavy metal.

#### **Effect of Complex Formation**

Metal cations form complexes with inorganic and organic ligands resulting has a lower positive (+ve) charge than the free metal ion and carry a net negative (-ve) charge. The real effect of complex formation on sorption depends on the several properties. These properties includes the type and amount of ligands present, soil surface properties, soil solution composition, pH and redox condition which have effect on sorption, Metal adsorption and mobility is mostly affected by complex formation between metals and organic ligand. Competition between the metal binding site and soluble organic ligand determines either the complex will be formed between the metal and soluble organic matter or not. The ectent of complexation between a net 1) no soluble organic ligand for the metal. Metals mobility in soil is not a complex is repeated by overcash and Pal (1979).

While the order of metal mobility is reported by khan et al. (1982)

Cu>Ni>Pb>Ag>Cd.

Copper (Cu) and Nickel (Ni) has high mobility because they have higher ability to form complex with soluble soil organic matter (SOM). In the presence of dissolved organic matter (DOM) mobility of copper (Cu), nickel (Ni) and lead (Pb) increases it is also reported by Amrhein *et al.* (1992).

#### **Effect of Time Adsorption**

Time also has an effect on adsorption of cadmium (Cd). When contact time increase adsorption capacity of Cd also increases. Adsorption capacity of Cd at prolonged contact time initially increases rapidly then decreases slowely because of large quantity of unsaturated functional group

# **MATERIALS AND METHODS**

An experiment was conducted to study the effect of Ca<sup>2+</sup> on adsorption and desorption of Cd using Freundlich and Langmuir Isotherm. All the basic analysis of soil, and experiment was conducted in soil and water chemistry Laboratory, Institute of Soil and Environmental Sciences, University of Agriculture, Faisalabad.

#### **3.1. Soil Collection and Preparation**

Soil was collected from research area of Institute of Soil and Environmental Sciences University of Agriculture, Faisalabad. Soil samples was air dried, grinded and sieved using 2 mm

Ing 2 mm. Ing 2 mm. Different physico-chemical properties of soils were characterized before starting the experiment (Table 3.1) 3.2.1. Particle Size Analysis 9 Hydromet

Hydrometer method was used to determine the particle size of the soils. Weighted 40 gram of air-dried soil added into 600 ml of beaker then added 60 ml of dispersing solution covered the beaker and left for overnight. Next day transferred the beaker material into the soil stirring cup and 3 quarters of water was added in to stirring cup. Then the suspension was stirred at high speed for 3 minutes. Then material of stirring cup was washed into a 1000 ml graduated cylinder which have 1 L capacity after hydrometer was put in cylinder and make the volume of 1 L with distilled water. After hydrometer was removed and materials of graduated cylinder was shaken with the help of metal plunger. When suspension was uniform, hydrometer was inserted into cylinder after 40 sec hydrometer reading was recorded (HR1). Removed the hydrometer form cylinder, shook the material with plunger then after 2 hours second hydrometer reading was recorded. Hydrometer was calibrated at 20 C° temperature HR1 and HR2 were corrected if temperature was up and down from 20 C°. If temperature was above then 20 C° for each degree added a factor of 0.4 to the

### **CHAPTER 4**

#### **RESULTS AND DISCUSSION**

This study was conducted to study the adsorption-desorption behaviour of Cd in soil. The salient results obtained during the experiment are explained below;

#### **4.1 Adsorption study**

Adsorption data of cadmium was analyzed according to Freundlich and Langmuir Isotherm. In Freundlich model, the parameters like  $\log (x/m)$  and  $\log (c)$  was plotted against each other to calculate the adsorption parameters. The amount of Cd adsorbed per unit soil (x/m) increased progressively with an increase in added Cd and this increase was linear. At Ca-10 mg kg<sup>-1</sup> Cd<sub>10</sub> was added into soil, amount of  $Cd_{10}$  adsorbed was 6.41 mg kg<sup>-1</sup> with  $Cd_{20}$ , the about of Cd adsorbed was 14.11 mg kg<sup>-1</sup> and 32.28 mg kg<sup>-1</sup> Cd adsorbed with Cd<sub>40</sub> Subject with Cd<sub>60</sub> and Cd<sub>80</sub>, Cd adsorption was 54.71 and 73.62 mg kg<sup>-1</sup>, respectively Gd 90.215 mg kg<sup>-1</sup> adsorption took place at Cd1<sub>00</sub>. When compared the copyrol with other treatment, it was concluded that the minimum adsorption took plate in control and ad option was maximum with Cd<sub>100</sub>. When compared the advertision % of Cd wither spectro the added Cd, it was observed that, Cd adsorption % increased with increasing he level of the added Cd. When soil was equilibrated with Cd<sub>10</sub>, Cd adsorption % was (64.11%), with  $Cd_{20}$  and  $Cd_{40}$ , Cd adsorption % was (70.56%) and (80.76%) and Cd adsorbed with  $Cd_{60}$  was (91.18%) while (92.03%) and (90.23%) of Cd adsorbed with  $Cd_{80}$ and  $Cd_{100}$  respectively. When we compared all the treatments, it was concluded that the maximum Cd adsorption % took place with  $Cd_{100}$  while the minimum Cd adsorption % took place with  $Cd_{10}$ . Similarly, when we compared the % of Cd solution concentration with respect to the added Cd, it was observed that with increasing the level of added Cd, % of Cd solution concentration was increased. When soil was equilibrated with Cd<sub>10</sub> Cd<sub>20</sub>, % of Cd solution concentration was the minimum (64.11%) and (70.56%), after % of Cd solution concentration was going to increase, with  $Cd_{40}$  and  $Cd_{60}$  % Cd solution concentrations was (80.79%) and (91.19%), after with  $Cd_{80}$ and Cd<sub>100</sub>, % Cd solution concentration was (92.03%) and (90.23%) respectively. When we compared all the treatments, it was concluded that with  $Cd_{10}$  % Cd solution concentration was the

Logarithmic relationship (adsorption isotherm) between equilibrium solution Cd concentration (ECdC) and Cd adsorbed per unit weight of soil (x/m).

# Table.4.8 Cd adsorption parameters of the Freundlich adsorption equation atCa-20

Description	Proportionality	Exponent (1/n)	Correlation
	constant (K <sub>f</sub> )		coefficient (R <sup>2</sup> )
Units	Mgkg <sup>-1</sup>	mgL <sup>-1</sup>	0.709
			K
Value	1.012	0.256	<b>CO</b> . <b>U</b>
		otesale.	

Hence it is concluded from adsorption ea of Ca20 rate of adsorption was 0.256 while extent of adsorption was 1.012.





Table.4.13 Amount of Cd adsorption and adsorption percentage at Ca-30

Figure.4.7 Relationship between ECdC and Cd adsorbed per unit of soil (x/m) at Ca30

# 4.3.2 Langmuir Model

The Langmuir adsorption isotherm is used to describe the equilibrium between adsorbate and adsorbent system.

 $x/m = K_L b (ECdC) / [1+K_L b (ECdC)]$ 

Table.4.16 Parameters	for th	e Linear	r Form o	f Langmuir	model
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Amount of Cd added (mg L <sup>-1</sup> )	ECdC (mg L <sup>-1</sup> )	x/m (mg Cd kg <sup>-1</sup> Soil)	C/x/m= ECdC/x/m
0	0.303	0	0
10	0.510	3.23	0.158
20	0.714	otesale	0.079
40	w from 6	0	0.054
50	Pass	39.26	0.039
80	1.946	59.71	0.033
100	2.357	82.71	0.028

### 4.4.2 Langmuir Model

Table.4.20 Cd desorption parameters of the Langmuir desorption equation atCa10



Figure.4.12 Logarithmic relationship (desorption isotherm) between equilibrium solution Cd concentration (ECdC) and Cd desorbed per unit concentration of Cadmium (x/m) at Ca10

Concentrations	ECdC	x/m	C/x/m=ECdC/x/m	b	KL	$x/m=K_L*b(ECdC)/[1+(K_L)(ECdC)]$	%ad
			-				
0	0.214d	0	0	9.76	0.058	1.011	0
						<b>K</b>	
10	0.409cd	3.21	0.127	976	0.658	1.766	32.1
			Notes				
20	0.615c	f † 10	0.147	9.16	0.058	2.433	20.85
	ew		730				
prev		20					
40	1.025b	5.59	0.183	9.76	0.058	3.433	14.75
60	1.436ab	7.61	0.189	9.76	0.058	4.263	12.68
	1.8470	0.05	0.204	0.76	0.058	4.974	11.21
80	1.047a	9.05	0.204	9.70	0.038	4.0/4	11.51
100	2.258a	10.21	0.221	9.76	0.058	5.362	10.21

# Table.4.23 Calculation of Desoprtion of Langmuir Model at Ca-20

Concentrations	ECdC	x/m	C/x/m=ECdC/x/m	b	KL	$x/m=K_L*b(ECdC)/[1+(K_L)(ECdC)]$	%ad
0	0.303e	0	0	17.39	0.011	0.057	0
10	0.510d	4.02	0.124	1239		0.097	32.3
20	0.714c	ſŕØ	0.127 <b>£</b> 78 <b>O</b>	17.39	0.011	0.136	45.45
Prev	1.1246	8.07 6.07	0.185	17.39	0.011	0.213	515 7
60	1.535ab	8.13	0.189	17.39	0.011	0.289	65.43
80	1.946a	11.98	0.162	17.39	0.011	0.364	74.63
100	2.357a	13.16	0.179	17.39	0.011	0.439	82.71
		13.16					

 Table.4.26 Calculation of Desorption of Langmuir Model for Ca-30

period twice daily. After attaining equilibrium, soil suspension will be filtrated with Whatsmann 40 filter paper to get the filtrate. Filtrate will be analysed by Atomic Absorption Spectrophotometer. Same tubes will be taken for this experiment which will be used for adsorption study. Desorption filtrate was analyzed using AAS According to linear form of Freundlich and Langmuir equation data of adsorption and desorption will be plotted. The data of study was statistically concluded by using software STATISTIX 8.1.

From data it was concluded that adsorption of Cd was decreased as level of Ca increased from 10 mg kg<sup>-1</sup> to 30 mg kg<sup>-1</sup>. At Ca-10 mg kg<sup>-1</sup> maximum adsorption was observed (6-90 mg kg<sup>-1</sup>) and at Ca-20 adsorption was (5-86 mg kg<sup>-1</sup>) while minimum adsorption was observed at Ca-30 (3-82 mg kg<sup>-1</sup>). If we compare desorption of all treatments, at Ca-10 minimum desorption was observed (2-7 mg kg<sup>-1</sup>) and at Ca-20 desorption rate was (3-11 mg kg<sup>-1</sup>) while maximum desorption was observed at Ca-30 which was (5-14 mg kg<sup>-1</sup>). It was concluded that maximum adsorption was observed at Ca-10 mg kg<sup>-1</sup> while maximum adsorption was observed at Ca-30 mg kg<sup>-1</sup> Calcium is a very important macro-nutrient, and can also be used observed the uptake of heavy metals from soil. Amendments containing Ca van base that role in the rehabilitation of Cd contaminated soils. Cd solubility decreased by Ca. Ca is thorget to be a tough opponent of Cd on exchange site of soil. Captures an important more to recure Cd phytotoxicity in plants and as a result growth and Cd adsorption and increase the desorption of Cd in soil.