

ADSORPTION CHARACTERISTICS OF Cu (II), Fe (II), Cd (II) and Cr (III) IONS IN AQUEOUS SOLUTION USING MANGO LEAF AS BIOSORBENTS

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1. INTRODUCTION

1.1 Background of Study

In new era of science and technology, the world has seen major transformations in numerous aspects of life. At the heart of this tremendous advancement lies the rapid industrialization takes place at various parts of the globe. Even though the world having many distinguished benefits for mankind, this kind of revolution has also caused significant degradation to the environment, and leading to detrimental effects to human and animal life. One widespread phenomenon which has drawn in much attention is the contamination of toxic metals such as copper, lead, zinc, nickel and chromium in the aqueous environment, which are sourced from chemical industries such as petrochemicals, refineries, fertilizers, pulp and paper [1]. Heavy metal contamination cause serious health problems such as cancer and brain damage due to the accumulation in living tissues and organs [2]. Generally, metals could be divided into four distinguished categories which are toxic metals, strategic metals, precious metals and radionuclides. Among are the ones associated for causing serious environmental threats, and making its removal from the aqueous environment is essential. From the various types of toxic metals present in wastewater, copper was chosen for this Biosorption studies with regard to its wide usage in industries and potential pollution impact. Copper is listed as one of the pollutants found in wastewater [2]. In industrial waste copper is mainly appears in the form of the bivalent Cu (II), which is according to Ullman's encyclopedia and it is also a more toxic than other metals. This is because it's more solubility in water, and also the bivalent copper could easily absorb into living organisms. High doses of copper in the aqueous environment generate toxicological concerns as it could be deposit into the brain, liver, pancreas and myocardium [3]. Thus, Cu (II) concentrations in wastewater should be reduced to at least 1.0

to 1.5 mg/L. The increase of metal bearing effluents into the aqueous medium has caused progressive developments in wastewater treatment.

Current developed methods include filtration, ion exchange, membrane separation, nutrient stripping and adsorption [4]. However, these methods have some limitations due to technical and economic constraints. The ion exchange process needs a high operational cost because it involves the use of excessive amounts of reagent for its resin regeneration. Meanwhile, the membrane process application is limited by the condition of the membrane used. This membrane tends to be unstable in salty or acidic conditions and fouls, if organic or inorganic substance present in the wastewater. The major disadvantage for the precipitation, it generates a toxic sludge as by-products that requires careful disposal as per regulations. For electrolysis, its inefficiency at low concentrations which causes incomplete metal ion recovery is one of its disadvantages [5]. Due to these factors research has been conducted in adsorption method, to study the use of natural adsorbents as an alternative to remove the effluents from wastewater on the view of economic and environmental concern.

The most current technique employed in removal of metals from wastewater is biological adsorption or bio sorption. "Bio sorption" is the term given to the passive sorption and/or complexation of metal ions by biomass [6]. It is a reversible process where concentration of metal ions in solution decreases due to adsorption on the solid phase until a dynamic equilibrium exists between the aqueous and solid phase. This technology which utilizes natural biomass materials is very effective for the detoxification of metal-bearing industrial effluents. The bio sorption process involves several mechanisms that differ qualitatively and quantitatively by depending on the origin of the biomass, the species were used and it's processing [7]. These mechanisms are generally based on physicochemical interactions between metal ions and functional groups present on the cell surface, which includes ion exchange, complexation, electrostatic attraction and micro precipitation [8]. Various types of biomass have been used as the bio sorbent for the removal of toxic metals. Among these, plant leaves are chosen in this study as they are proposed to be natural, simple and cheap bio sorbents for the efficient removal of several heavy metal ions. They can be found easier, potentially renewable source, nontoxic and biodegradable. After the bio sorption, they are expected to precipitate and become sediments which can be disposed safely. A research was conducted by [9] used much plant leaves for the bio sorption of cadmium, lead and copper

ions. Thus results were proved that the performance of the dried leaves is close to the efficiency of using activated carbon. The results also showed that oven dried leaves have better performance compared to the naturally dried ones [10]. The functional group which is commonly found in plant leaves is carboxylate. Available literature involves the use of mango leaf powder for the bio sorption of heavy metals is quite limited [11-17]. The maximum adsorption capacity for the mango leaf powder with lead was found to be 31.54 mg/g [17]. Demonstrated the use of mango tree bark as biosorbents which is suitable for the removal of Hg^{2+} and Cr^{3+} from aqueous solutions [18]. Thus, there is no studies were found in literature by involving mango leaf powder for the removal of copper ions.

Although the presence of iron supports many biological and enzymatic functions of plants and animals, but its rapid corrosive property makes it more exposed to environment [19]. Also irons launch some troubles in water supplies. It is one of the earth's most plentiful resources as it makes up at least 5% of the earth's crust. Iron get dissolves and seep into aquatic systems like ground and river water bodies by rain water infiltrates into the soil. Iron is mainly present in water in two forms, either soluble ferrous iron or insoluble ferric iron. Water containing ferrous iron is clear and colorless because the iron is completely dissolved. Ferrous iron further oxidized to ferric iron by dissolved oxygen in water.

Metal was discovered in 1797 by the French chemist, Louis Nicolas Vauquelin. And it was named chromium because of many different characteristic colors of its compounds (Greek word "chroma" meaning color) [20]. The presence of heavy metals in the environment is of major concern because of their toxicity to many life forms. Heavy metals like mercury, lead, cadmium, copper, chromium and nickel are toxic even in extremely minute quantities [21]. Since the majority of heavy metals do not degrade into harmless end products, their concentrations must be reduced to acceptable levels prior to discharge of industrial effluents. Otherwise, they could pose threats to public health and affect the aesthetic quality of potable water. According to the World Health Organization (WHO), the metals of most immediate concern are aluminum, chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, mercury, and lead [22].

Chromium contamination of soil and groundwater is one of the significant environmental problems today. Chromium is believed to be the second common inorganic contaminant after lead. The toxicity of chromium does not reside solely with the elemental form but varies

greatly among a wide variety of chromium compounds. Oxidation state and solubility are crucial factors in this regard [23]. Chromium occurs in the environment primarily in two valence states, the oxidized hexavalent chromium, Cr (VI), and the less oxidized trivalent chromium, Cr (III). Under common environmental conditions of pH Cr (III) compounds are sparingly soluble in water, whereas Cr (VI) compounds are quite soluble. Chromium (III) is considered to be essential to mammals for glucose, lipid, and protein metabolism and hence is an essential dietary element [23].

Cadmium is widely used and extremely toxic in relatively low dosages, is one of the principal heavy metals responsible for causing kidney damage, renal disorder, high blood pressure, bone fracture and destruction of red blood Cells [24]. The toxic elements discharged in the effluents will be absorbed and accumulated by microorganisms. The World Health Organization (WHO) has set a maximum guideline concentration of 0.003mg/L for Cd in drinking water [25]. Given contained cadmium contamination and the low drinking water guideline, there is considerable interest in the development of techniques to remove cadmium from contaminated water before they are discharged into receiving bodies.

Several methods utilized to remove metals from aqueous solutions/wastewater include: reduction followed by electrochemical precipitation, chemical precipitation, chemical oxidation–reduction, ultra-filtration, ion exchange, reverse osmosis, solvent extraction, electro-dialysis, electrochemical, coagulation, evaporation and adsorption [26]. The conventional treatment methods become less effective and more expensive when situations involving high volumes, low metal concentrations, and disposal of residual metal sludge are encountered. In addition, these methods are not suitable for small-scale industries [27]. Among these methods, adsorption has been developed as an efficient method for the removal of heavy metals from contaminated water and soil. A variety of adsorbents, including clays, zeolites, dried plant parts, agricultural waste biomass, biopolymers, metal oxides, microorganisms, sewage sludge, fly ash and activated carbon have been used for removal of copper, iron, chromium and cadmium [28].

The present work was carry out by different operating parameters for adsorption of copper; Iron, Chromium and cadmium, such as contact time, pH, initial concentration, temperature and adsorbent dose were investigated in the batch mode of study. The kinetic data were fitted

to pseudo-first, pseudo second-order models and Intraparticle diffusion model and the isotherm equilibrium data were fitted to Langmuir and Freundlich isotherms.

1.2 Statement of the Problem

Heavy metals are those metallic elements with a highly relative atomic mass. The term is usually applied to common for transition metals such as copper, lead, iron and zinc etc. Heavy metals are natural components of the environment but they are of concern lately because they are being added to soil, water and air in an increasing amount as a consequence of growth in population, expansion of industrial activities, etc. Human activities such as mining, smelting, refining, energy production, industrial and vehicular emissions, agricultural operations, sewage discharge, and disposal of wastes are rapidly increasing environmental pollution. Heavy metals are present in all phases of the environment air, water, and land.

The metals are accumulating in the top soil, thus endangering crops and vegetables. Besides plants, other items in the food chain may also get contaminated. In many developing countries including Ethiopia the levels of air pollutants are increasing rapidly in urban area. Petrol and Diesel engine motor vehicles emit a wide variety of pollutants principally benzene, carbon monoxide, lead, organic compounds, oxides of nitrogen, sulphurdioxide, and other suspended particulate matter like smoke, metals (Cd, Co, Cu, Zn, etc.) and inert dust. Plants have a higher capacity to take up metals from soils or atmosphere for their physiological needs. While this may not have any adverse effect on plant itself, it may expose to the consumer to have a higher intake of concerned metals. Since plants are the major source of human food chain, a study of metal content in plants and crops indicates the extent of heavy metal contamination in human beings by consuming them. Chemical contamination from sources such as industries, vehicles and pesticides can affect the safety of food. Vegetables take up metals by absorbing them from contaminated soils, as well as from deposits on different parts of the vegetables exposed to the air from polluted environments.

The aim of the present study was to explore the adsorption of ions such as copper, iron, chromium and cadmium in aqueous medium by using powdery Mango leaves used as an adsorbent, collected from Arba Minch Area, Arba Minch, Ethiopia.

1.3 Objective of the Study

1.3.1 General Objective

- ❖ The main objective of this study is to evaluate the adsorption characteristics of Cu (II), Fe (II), Cd (II) and Cr (III) from aqueous media using Mango Leaf powder.

1.3.2 Specific Objective

- ❖ To examine the effect of adsorbent dosages.
- ❖ To determine the effect of initial metal concentrations.
- ❖ To determine the effect of initial pH of solution.
- ❖ To study the effect operating temperature.
- ❖ To study the thermodynamic parameters (ΔG° , ΔH° and ΔS°)
- ❖ To study adsorption isotherm (Langmuir and Freundlich) of Cu (II), Fe (II), Cd (II) and Cr (III) ion from an aqueous solution on Mango leaf powder.
- ❖ To study kinetics of Cu (II), Fe (II), Cd (II) and Cr (III) ion from aqueous solution on Mango leaf powder.

1.4 Significance of the Study

The study of adsorption thermodynamics' is significant as it provides valuable insights into the reaction pathways and the mechanism of reactions. Therefore, it is important to be able to predict the rate at which pollutant can be removed from aqueous solutions in order to design appropriate adsorption treatment plants.

To develop the adsorption kinetics knowledge of the rate law describing the sorption system is required.

To investigate the adsorption capacity of the adsorbent is very important that the high adsorption capacity and its affinity for heavy metal ions can help to solve many adsorption challenges in the industry and in water purification processes.

2. EXPERIMENTAL

2.1 . MATERIALS AND METHODS

2.1.1 Preparation of Biosorbent

Mature and fresh mango leaves was collected from trees located in Arbaminch area by random method of sample collection, and washed thoroughly by using distilled water to clean them from dust and soil impurities. The cleaned leaves were dried in sun light for few days on a perforated tray until the leaves turned brownish in color. It was then dried further in an oven for 24 hours until the leaves became crisp. The crispy dried leaves were ground well by a mechanical grinder and sieved until achieve the particle size of adsorbent become 250 μ m. Thus the resulting Mango leaf powder (MLP) was kept in a glass bottle, which is ready for further experiments.

2.1.2 Preparation of Adsorbate solutions

The copper, iron, cadmium and chromium stock solution (1000 mg/L) was prepared using analytical grades of $\text{Cu}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Cr}_2(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The solutions of heavy metal ions with necessary dilutions have been prepared and obtain 50 mg/L, 75 mg/L, and 100 mg/L of copper, iron, and cadmium and chromium solution respectively. About 5, 10, 15, 20, and 25mg/L of Cu (II) Fe (II), Cr (III) and Cd (II) standard solutions were also prepared for calibration purpose. The required pH of the Cu (II), Fe (II), Cd (II) and Cr (III) solution was adjusted by adding 0.1 M HCl or 0.1 M NaOH, and it was measured by using pH meter.

2.2. Instrumentation

The removal efficiency of adsorbent (mango leaf powder) involves determination of copper, iron, cadmium and chromium in the effluent solutions before and after adsorption takes place. This was done by using Atomic Absorption Spectroscopy (AAS) BUCK SCIENTIFIC MODEL 210 VGP, East Norwalk, USA. It is equipped with deuterium arc background corrector, nebulizer and hollow cathode lamp corresponding to metal of interest, and in this case copper, iron, cadmium and chromium used in air-acetylene flame environment.

Concentrations of copper, iron, cadmium and chromium were determined in the filtrates by using four series of standard copper, iron, cadmium and chromium solutions in the range of 5 – 25 mg/L. The dilute solutions were prepared by diluting the stock solution of copper, iron, cadmium and chromium with distilled water. A blank (distilled water) and standards were run in AAS and five points of calibration curves were established. Then the sample solutions were aspirated in to the AAS instrument and direct readings of total copper, iron, cadmium and chromium concentrations were recorded. The amount of Cu, Fe, Cd and Cr get adsorbed by adsorbent, and it was calculated from the difference between the before and after adsorption.

2.3 Biosorption experiments

Batch mode experiments for Cu (II), Fe (II) Cr (III) and Cd (II) were carried out in 250 mL conical flask at room temperature (30 ± 2)^oC. Copper, Iron, Chromium and Cadmium biosorption as a function of equilibrium time, pH, amount of adsorbent and initial concentration was studied.

In order to optimize contact time, 2 g of the biosorbent was stirred with 100 mL of 50 mg/L of Cu(II),Fe(II) Cr(III) and Cd(II) solution at different time intervals (0, 15, 30, 45, 60, 80, 100, and 120 min). At the end of the stirring period the samples were centrifuged at 8000 rpm for 10 min and filtered through Whitman No. 1540.090 filter paper. The concentrations of Cu, Fe, Cr and Cd in the filtrate were determined using atomic absorption spectroscopy. The same experiment was repeated using 75 and 100 mg/L of Cu (II), Fe (II) Cr (III) and Cd (II) solutions.

To study the effect of pH on Cu(II),Fe(II) Cr(III) and Cd(II) biosorption, the initial pH of 100mL of 100mg/L Cu(II),Fe(II) Cr(III) and Cd(II) solutions were adjusted to different pH values (2, 3, 4, 5, 6, 7, 8, 9 and 10) using 0.1 M NaOH and 0.1 M HCl. About 0.4 g

biosorbent was equilibrated with these solutions for 60 min and the filtrates were analyzed for the effect of pH on Cu (II), Fe (II) Cr (III) and Cd (II) biosorption.

The effect of adsorbent dosage was also studied by varying the amount of adsorbent (0.4, 0.6, 0.8, and 1.0 g/L) on an initial concentration of 100 of 100mg/L at pH 4.5 for a contact time of 120 min. In another set each 100 mL of Cu(II),Fe(II) Cr(III) and Cd(II) solutions at varying concentrations (50,75 and 100 mg/L) were introduced into the conical flask containing 0.4 g of the adsorbent and stirred for 120 min and the filtrates were analyzed for the effect of Cu(II),Fe(II) Cr(III) and Cd(II) concentration.

The amount of material (adsorbate) adsorbed per unit mass of adsorbent (in mg/g) is given:

$$q = \frac{C_o - C_t}{m} \text{-----} (2.1)$$

Where, C_o is the initial concentration of adsorbate (mg/L) and C_t is the concentration of adsorbate at time t (mg/L). The adsorption efficiency can be expressed as percentage adsorption of metal ion as:

$$\% \text{ adsorption} = \frac{C_o - C_t}{C_o} \times 100 \text{-----} (2.2)$$

Where, C_o and C_t are the initial adsorbate concentration (mg/L) and the adsorbate concentration at time, t (min) respectively.

2.4 Equilibrium Studies

Equilibrium data is commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems. Also, the study of adsorption isotherm has been a greater importance and significance in water and wastewater treatment by the batch absorption technique, as they provide an approximate estimation of the adsorption capacity of adsorbent. The equilibrium data between the metal ions on the MLP and for the removal of metal ions by adsorbent at 30±1⁰C were estimated through testing the Langmuir and Freundlich isotherms.

The Langmuir equation is valid for a monolayer sorption on a homogenous surface with a finite number of identical sites and when there are no interactions between the sorbed species.

The linear form of Langmuir equation is given in equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \text{-----} (2.3)$$

Where C_e (mg/L) is the equilibrium concentration of adsorbate, q_e (mg/g) is the quantity of adsorbed material (mg/g) at equilibrium, K_L is the Langmuir equilibrium constant related to the energy of sorption (Lmg^{-1}) and q_m is the maximum amount of metal ions per unit weight of MLP to form a complete monolayer on the surface bound at high C_e . It is also represents a practical limiting adsorption capacity when the surface is fully covered with the metal ions and assists in the comparison of adsorption performance, particularly in cases where the sorbent did not reach its full saturation in experiments [29-31].

The empirical Freundlich equation applies to multilayer sorption on a heterogeneous surface and can only be employed in the low intermediate concentration ranges.

The Freundlich equation is given in equation:

$$\log q_e = \frac{1}{n} \log C_e + \log K_f \quad \text{-----} \quad (2.4)$$

Where, Freundlich constants K_f ($mg.g^{-1}$) and n (value between 0 and 1) are the measures of adsorption capacity and intensity of adsorption respectively [30, 32-39].

2.5 Thermodynamic study

Thermodynamic parameters such as Gibbs free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) change of adsorption can be evaluated from the following equations:

$$K_c = \frac{C_{Ae}}{C_e} \quad \text{-----} \quad (2.5)$$

$$\Delta G^0 = -RT \ln K_c \quad \text{-----} \quad (2.6)$$

$$\log K_c = \frac{\Delta S^0}{2.303RT} - \frac{\Delta H^0}{2.303RT} \quad \text{-----} \quad (2.7)$$

Where K_c is the equilibrium constant, C_e is the equilibrium concentration in solution (mg/L) and C_{Ae} is the solid-phase concentration at equilibrium (mg/L). ΔG^0 , ΔH^0 and ΔS^0 are changes in Gibbs free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/mol/K), respectively; R is the gas constant (8.314 J/mol/K) and T is the temperature (in Kelvin scale).

2.6 Kinetic study

In order to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, a suitable kinetic model is needed to analyze the data. Any

kinetic or mass transfer representation is likely to be global. From a system design point of view, a lumped analysis of kinetic data is sufficient for practical operations.

The sorption kinetics may be described by a pseudo first-order equation [40].

$$\log(q_e - q_t) = \log q_e - \frac{K_{ad}}{2.303t} \quad \text{----- (2.8)}$$

Where q_t and q_e are the amount of metal ion adsorbed (mg/g) at time t and at equilibrium respectively and k_{ad} is the rate constant of the pseudo-first-order adsorption process (min^{-1}).

The adsorption kinetics may also be described by a pseudo second-order equation [41].

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad \text{----- (2.9)}$$

Where $h = k_{qe}^2$ ($\text{mg g}^{-1}\text{min}^{-1}$) can be regarded as the initial adsorption rate as $t \rightarrow 0$ and k is the rate constant of pseudo-second-order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$).

The equations (2.8) and (2.9) cannot identify the diffusion mechanisms. So, the Intra- particle diffusion model [42 43 and 44] was also evaluated experimentally. The initial rate of the Intraparticle diffusion is given by the following equation:

$$q_t = f \left(t^{\frac{1}{2}} \right) \quad \text{----- (2.10)}$$

The rate parameters for Intraparticle diffusion (k_p) at different initial concentrations are determined using the following equation.

$$q_t = k_p t^{\frac{1}{2}} \quad \text{----- (2.11)}$$

Where k_p is the Intraparticle diffusion rate constant, ($\text{mg/gmin}^{1/2}$).

3. RESULTS AND DISCUSSION

3.1 Adsorption studies of Cu (II), Fe (II), Cr (III) and Cd (II).

3.1.1 Effect of contact time

In order to optimize equilibrium time for the removal of Cu (II), Fe (II), Cr(III) and Cd(II) by adsorption between adsorbates and biosorbent. It was carried out by keeping the initial concentration of Cu (II), Fe (II), Cr (III) and Cd (II) is 50mg/L with 2g adsorbent (for each ion) at different time intervals (15 – 120 min).

The percent removal of Cu (II), Fe (II), Cr (III) and Cd (II) by adsorption is described in tables. 3.1-3.4 and the plot of percent adsorption of Cu (II),Fe (II) ,Cr(III) and Cd(II) on these various initial concentration at different time intervals Fig. 3.1-3.4.The data reveals that the rate of percent Copper ,Iron ,Chromium and Cadmium removal is higher at the beginning. This is probably due to larger surface area of the biosorbent being available at the beginning for the adsorption of Cupper, Iron, Chromium and Cadmium ions [45].

Table 3.1. Effect of contact time of Cu (II) at different time intervals (initial concentration 50 mg/L, adsorbent dose 2 g, initial pH 4.5).

Experiment no.	Contact time (min)	Absorbance	Final conc.(mg/L)	% Removal
1	0	0	0	0
2	15	0.378	11	78

3	30	0.256	7.5	85
4	45	0.196	5.7	88.6
5	60	0.096	2.80	94
6	80	0.087	2.53	94.4
7	100	0.064	1.8	96
8	120	0.0302	0.877	98



Fig.3.1 Effect of contact time of Cu (II) at different time intervals (initial concentration 50 mg/L, adsorbent dose 2 g, initial pH 4.5).

Table 3.2. Effect of contact time of Fe (II) at different time intervals (initial concentration 50 mg/L, adsorbent dose 2 g, initial pH 4.5).

Experiment no.	Contact time(min)	Absorbance	Final con.mg/L	% Removal
1	0	0	0	0
2	15	0.378	13.5	73
3	30	0.231	8.25	83.5
4	45	0.153	5.46	89.1
5	60	0.082	2.9	94.2
6	80	0.065	2.3	95.4
7	100	0.047	1.67	96.6
8	120	0.023	0.82	98.36

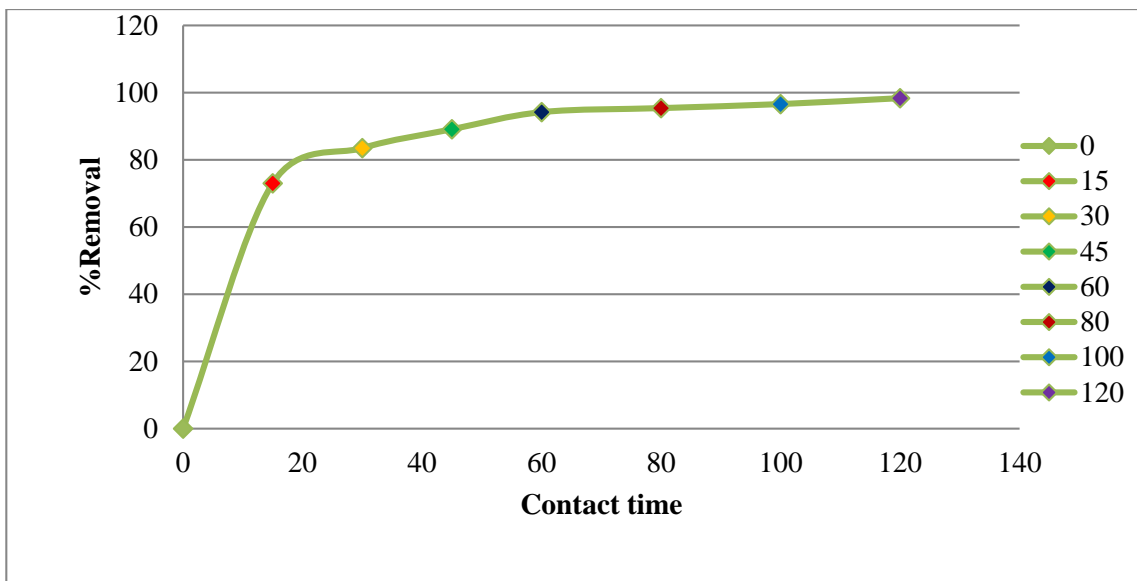


Fig.3. 2 Effect of contact time of Fe(II) at different time intervals (initial concentration 50 mg/L, adsorbent dose 2 g, initial pH 4.5).

Table 3.3. Effect of contact time of Cr (III) at different time intervals (initial concentration 50 mg/L, adsorbent dose 2 g, initial pH 4.5).

Experiment no.	Contact time (min)	Absorbance	Final conc.(mg/L)	% Removal
1	0	0	0	0
2	15	0.2653	5.7	88.6
3	30	0.2072	4.47	91
4	45	0.1670	3.6	92.8
5	60	0.0842	1.8	96.4
6	80	0.0691	1.49	97
7	100	0.0270	0.58	98.8
8	120	0.0206	0.4	99.2

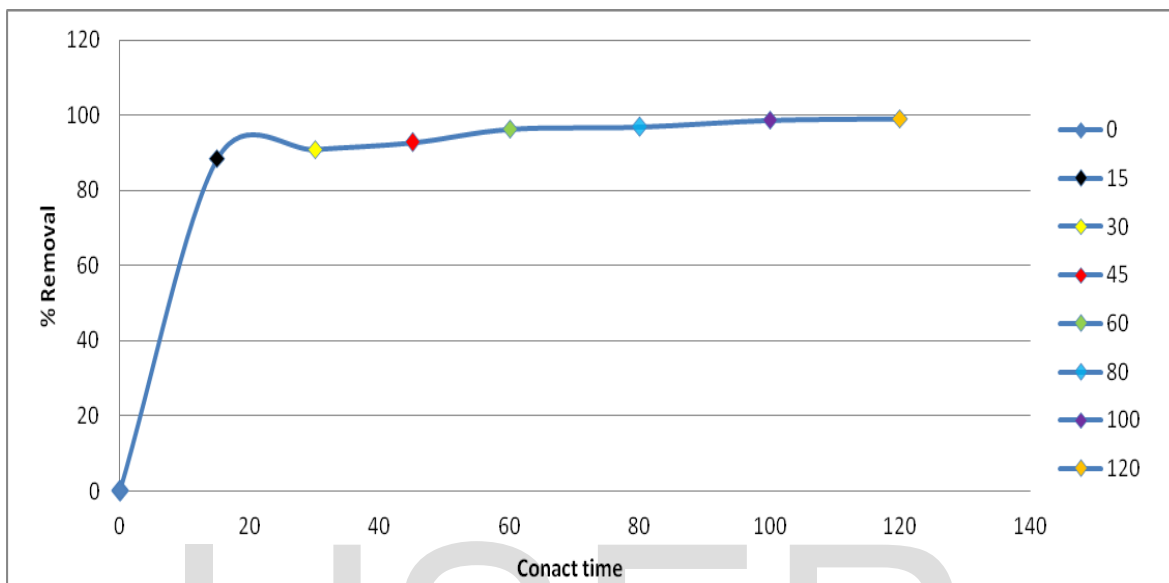


Fig .3.3 Effect of contact time of Cr (III) at different time intervals (initial concentration 50 mg/L, adsorbent dose 2 g, initial pH 4.5).

Table 3.4. Effect of contact time of Cd (II) at different time intervals (initial concentration 50 mg/L, adsorbent dose 2 g, initial pH 4.5).

Experiment no.	Contact time(min)	Absorbance	Final conc.(mg/L)	% Removal
1	0	0	0	0
2	15	0.3120	11.68	76.64
3	30	0.2651	9.9	80.2
4	45	0.2010	7.5	85
5	60	0.1520	5.6	88.8
6	80	0.1056	3.9	92.2
7	100	0.0543	2	96
8	120	0.0271	1	98

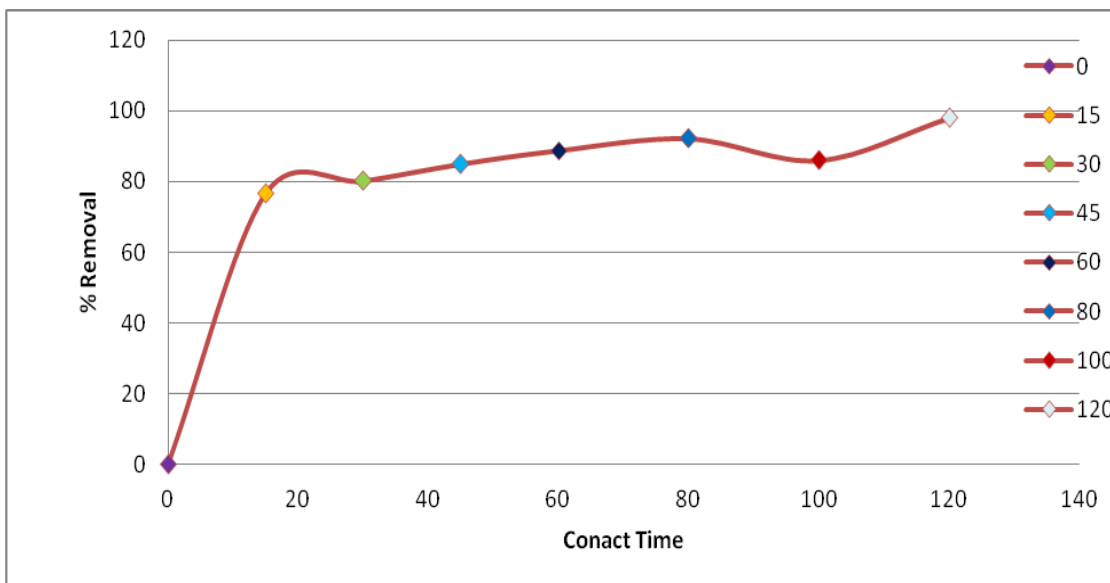


Fig. 3.4 Effect of contact time of Cd (II) at different time intervals (initial concentration 50 mg/L, adsorbent dose 2 g, initial pH 4.5).

Measurement for removal of all metals ions as a function of time indicates that the percentage adsorption increased with an increase in contact time and attained equilibrium after 15 min irrespective of the concentration of Cu(II), Fe (II), Cr (III) and Cd(II). But, the time taken to reach apparent equilibrium was increased at higher initial concentrations.

3.1.2 Effect of pH on the adsorption ions on MLP

pH is one of the most important controlling parameters in all adsorption processes. The pH of the solution affects the extent of adsorption because the distribution of surface charge of the adsorbent can change (because of the composition of raw materials and the technique of activation) thus varying the extent of adsorption according to the adsorbate functional groups [46, 47]. To Study the effect of pH on adsorption process for the removal of metal ions on MLP adsorption at different pH (2-10) were carried out at optimum amount of 0.4g, 100mg/L and contact time 60 minute for all metal ions. The results are presented in tables 3.5 to 3.8 and in figures 3.5 to 3.8.

Table 3.5 Effect of initial pH of Cu (II) at different initial pH (initial concentration 100mg/L, contact time 60 min, adsorbent dose 0.4 g/L).

Exp.No	Initial pH	Final conc.(mg/L)	% Removal	Equilibrium pH
1	0	0	0	0
2	2	18	82	4.63
3	3	10	90	5.46
4	4	7.8	92.2	5.70
5	5	5.9	94.1	5.82
6	6	4.9	95.1	5.94
7	7	13.24	86.76	6.30
8	8	1.9	98.1	6.01
9	9	2.4	97.6	6.12
10	10	2.82	97.71	6.13

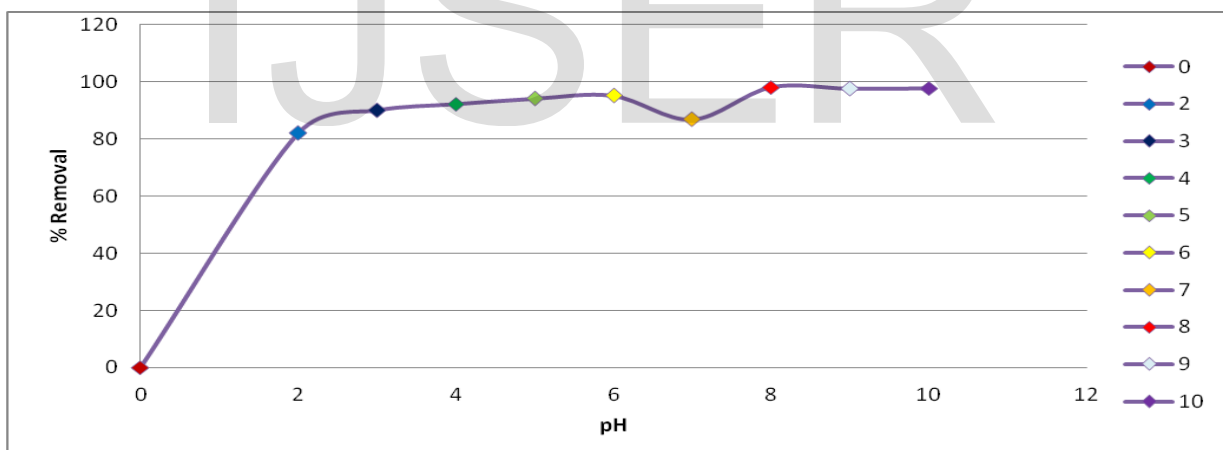


Fig.3.5 Effect of initial pH of Cu (II) at different initial pH (initial concentration 100mg/L, contact time 60 min, adsorbent dose 0.4 g/L).

Table 3.6. Effect of initial pH of Fe (II) at different initial pH (initial concentration 100mg/L, contact time 60 min, adsorbent dose 0.4 g/L).

Exp.No	Initial pH	Final conc.(mg/L)	% Removal	Equilibrium pH
1	0	0	0	0
2	2	29.3	70.7	4.26
3	3	16.1	83.9	5.18
4	4	8.3	91.7	5.50
5	5	2.8	97.2	5.70
6	6	1.9	98.1	5.74
7	7	15.4	84.6	6.30
8	8	0.75	99.25	6.00
9	9	1.1	98.9	6.15
10	10	0.82	99.2	6.18

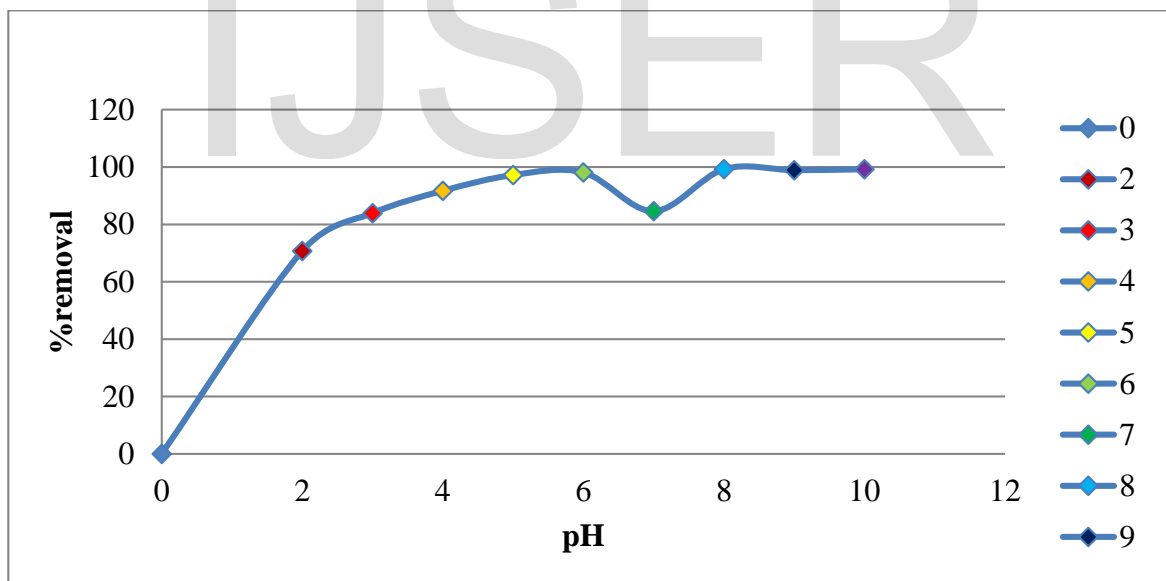


Fig 3.6 Effect of initial pH of Fe (II) at different initial pH (initial concentration 100mg/L, contact time 60 min, adsorbent dose 0.4 g/L).

Table 3.7 Effect of initial pH of Cr (III) at different initial pH (initial concentration 100mg/L, contact time 60 min, adsorbent dose 0.4 g/L).

Exp.No	Initial pH	Final conc.(mg/L)	% Removal	Equilibrium pH
1	0	0	0	0
2	2	19.47	80.53	4.56
3	3	7.94	92	5.28
4	4	3.26	96.75	5.57
5	5	1.56	98.44	5.68
6	6	0.96	99.04	5.80
7	7	10	90	6.30
8	8	0.45	99.55	6.00
9	9	0.73	99.27	6.10
10	10	0.63	99.37	6.12

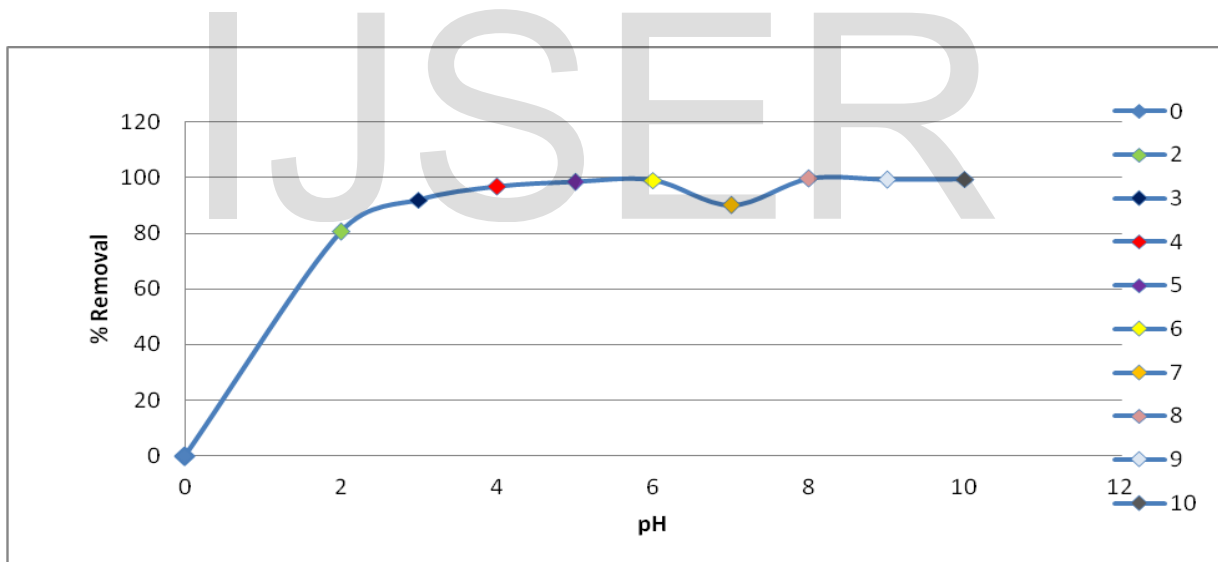


Fig.3.7 Effect of initial pH of Cr (III) at different initial pH (initial concentration 100mg/L, contact time 60 min, adsorbent dose 0.4 g/L).

Table 3.8 Effect of initial pH of Cd (II) at different initial pH (initial concentration 100mg/L, contact time 60 min, adsorbent dose 0.4 g/L).

Exp.No.	Initial pH	Final conc.(mg/L)	% Removal	Equilibrium pH
1	0	0	0	0
2	2	21.8	78.2	4.60
3	3	9	91	5.17
4	4	3.6	96	5.58
5	5	2.8	97.2	5.74
6	6	2	98	5.82
7	7	14.8	85.2	6.30
8	8	1	99	6.00
9	9	1.49	98.51	6.08
10	10	1.29	98.71	6.11

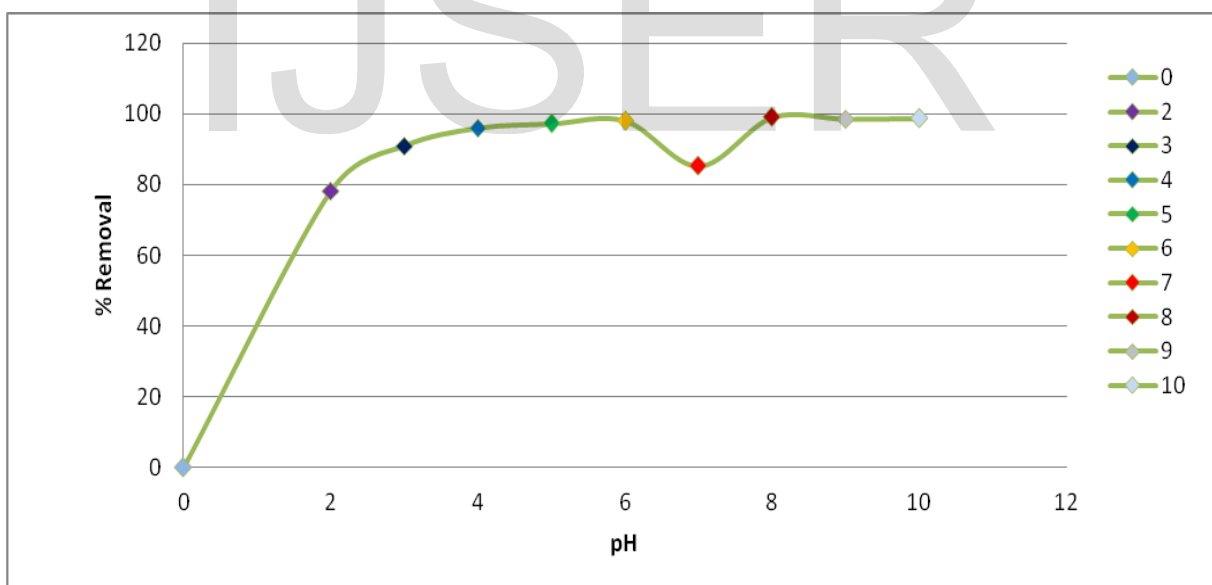


Fig.3.8 Effect of initial pH of Cd (II) at different initial pH (initial concentration 100mg/L, contact time 60 min, adsorbent dose 0.4 g/L).

In the present study, Fig.3.5, 3. 6, 3. 7 and 3.8 shows the adsorption capacity of Cu (II), Fe (II), Cr (III) and Cd (II) as a function of pH of the adsorbate at fixed adsorbent dose, fixed agitation time, fixed adsorbate concentration at room temperature.

It is clearly shows that Copper, Iron, Chromium and Cadmium adsorption of metals ions was increase with increasing pH of the solution within the range studied. In strong acidic pH (pH < 2.0), the overall surface charge on the active sites of adsorbent became positive, so Cu(II),Fe(II) ,Cr(III) and Cd(II) ions and protons compete for binding in the active sites on the biosorbent surfaces, which results in a lower uptake of the metal ions. The biosorbent surfaces became more negatively charged as the pH solution increased from 2.0 to 10 and the functional groups became more deprotonated and thus availability of the studied metal ions get adsorbed is increases [48].It is observed from Fig. 3.5, 3.6, 3.7 and 3.8 thus the amount of metal ion adsorption increases rapidly as the pH increased from 2 to 10 and the optimum pH was observed at six upon MLP used as adsorbent.

3.1.3 Effect of adsorbent dose

The effect of the adsorbent dose was studied at 30°C by varying the amount of adsorbent, MLP. The initial concentration for metal ions was fixed and the adsorption of metal ion get increases as the adsorbent dosage increases due to the limited availability of the number of adsorbing species for a relatively larger number of surface sites on the adsorbent at higher dosage of adsorbent. It is plausible that with higher dosage of adsorbent there would be greater availability of exchangeable sites from metals ions [49]. The significant increase in uptake was observed when the dose was increased. Any further addition of the adsorbent beyond this did not cause any significant change in the adsorption. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles [50].

The percentage adsorption of Cu (II), Fe (II), Cr (III) and Cd (II) was studied by increasing the dose of adsorbent (0.4 g/L to 1 g/L). It was introduced into the 100 mg/L initial concentration of Cu (II), Fe (II), Cr (III) and Cd (II) solutions in separate reaction vessel. After the adsorption was undergone at a given contact time, concentration of metal ions were determined by AAS. The results are shown in table 3.9-3.12 and figure 3.9-3.12.

Table 3.9. Effect of adsorbent dose of Cu (II) at different adsorbent dose (initial concentration 100 mg/L, contact time 120 min, initial pH 4.5).

Exp.No.	Adsorbent dose (g/L)	Final conc.(mg/L)	% Removal	Removal capacity
1	0	0	0	0
2	0.4	14.56	85.4	213.6
3	0.6	7	92.64	155
4	0.8	2.8	97.2	121.5
5	1	0.90	99.1	99.1

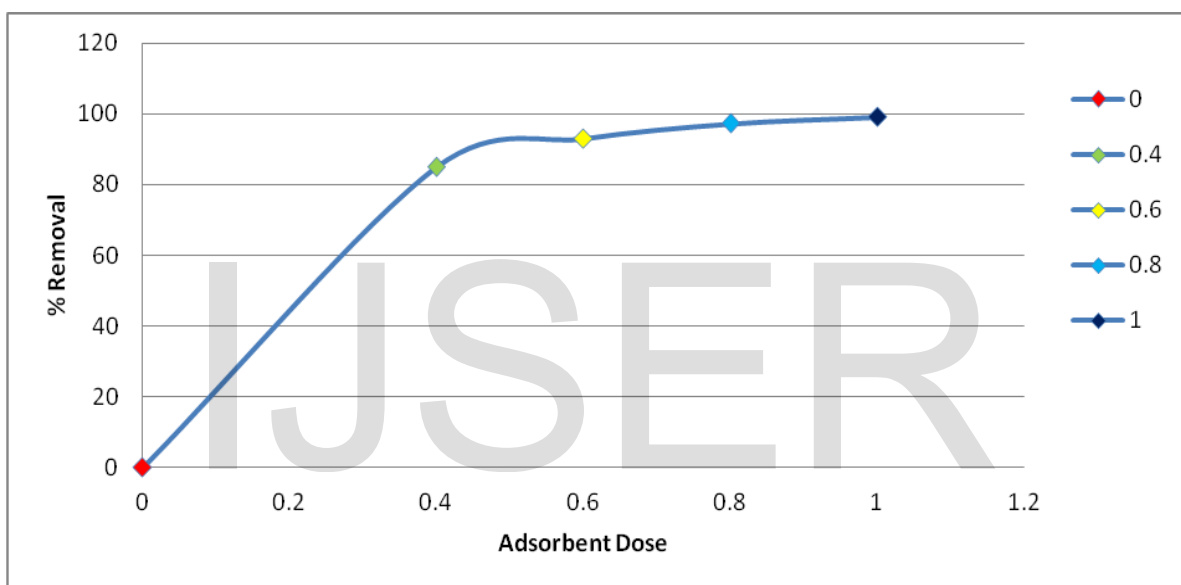


Fig.3.9 Effect of adsorbent dose of Cu (II) at different adsorbent dose (initial concentration 100 mg/L, contact time 120 min, initial pH 4.5).

Table 3.10. Effect of adsorbent dose of Fe (II) at different adsorbent dose (initial concentration 100 mg/L, contact time 120 min, initial pH 4.5).

Exp.No.	Adsorbent dose (g/L)	Final conc.(mg/L)	% Removal	Removal capacity
1	0	0	0	0
2	0.4	3.5	96.5	241.25
3	0.6	2.25	97.75	162.91
4	0.8	1.64	98.36	122.95
5	1	0.86	99.14	99.14

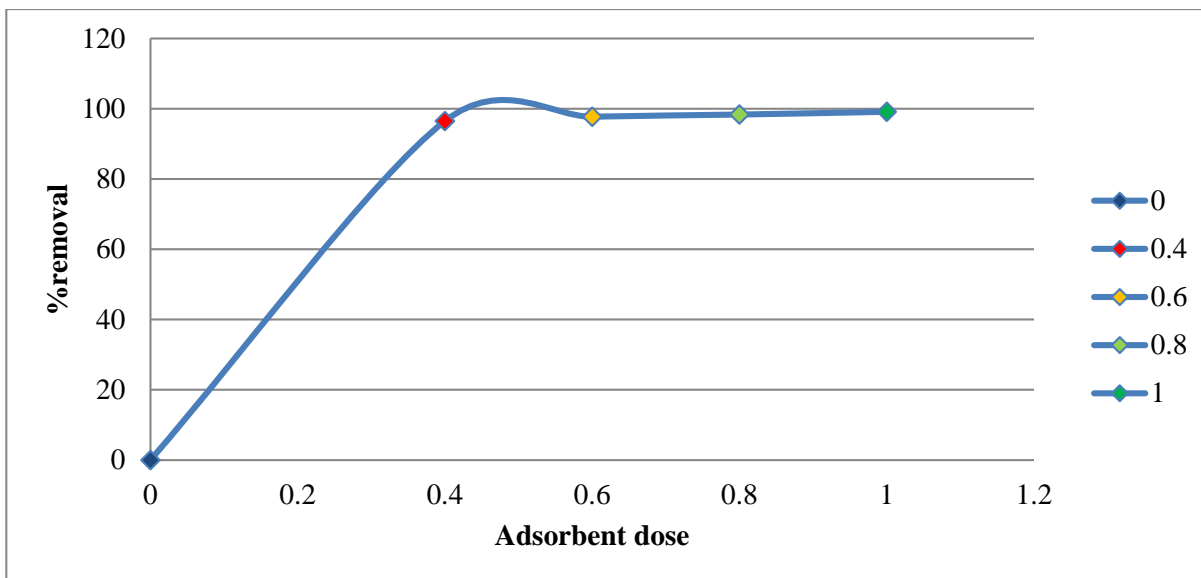


Fig.3.10 Effect of adsorbent dose of Fe (II) at different adsorbent dose (initial concentration 100 mg/L, contact time 120 min, initial pH 4.5).

Table 3.11. Effect of adsorbent dose of Cr (III) at different adsorbent dose (initial concentration 100 mg/L, contact time 120 min, initial pH 4.5).

Exp.No	Adsorbent dose (g/L)	Final conc.(mg/L)	% Removal	Removal capacity
1	0	0	0	0
2	0.4	5	95	237.5
3	0.6	4.42	95.58	159.3
4	0.8	1.2	98.8	123.5
5	1	0.41	99.59	99.59

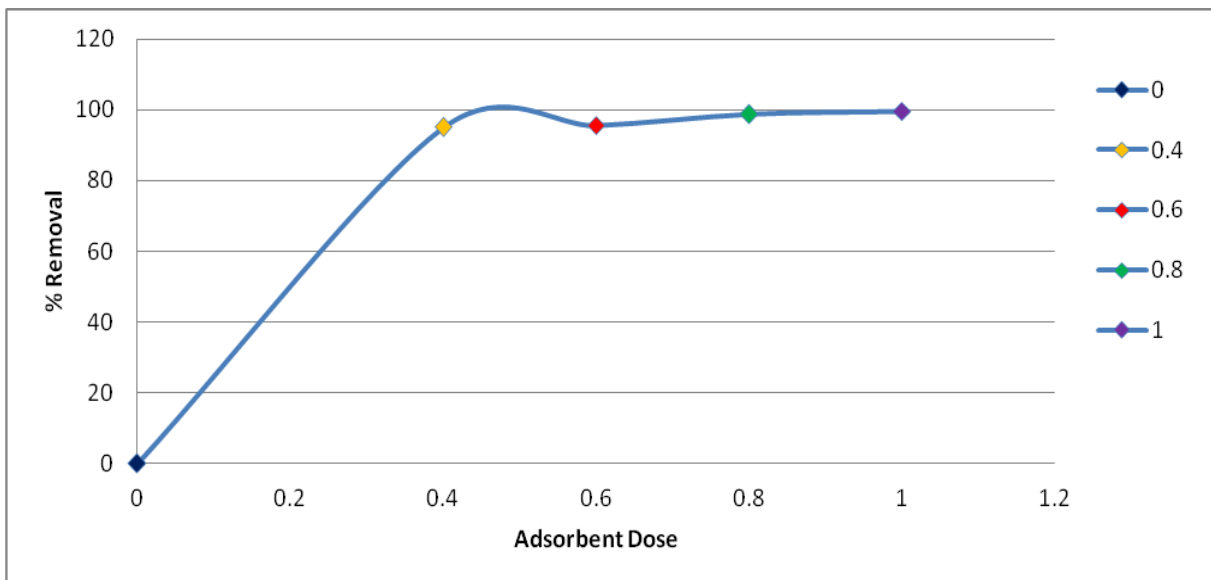


Fig 3.11. Effect of adsorbent dose of Cr (III) at different adsorbent dose (initial concentration 100 mg/L, contact time 120 min, initial pH 4.5).

Table 3.12 Effect of adsorbent dose of Cd (II) at different adsorbent dose (initial concentration 100 mg/L, contact time 120 min, initial pH 4.5).

Exp.No	Adsorbent dose (g/L)	Final conc.(mg/L)	% Removal	Removal capacity
1	0	0	0	0
2	0.4	8.85	91.15	227.5
3	0.6	6.7	93.3	155.5
4	0.8	1.87	98.13	122.6
5	1	0.67	99.36	99.36

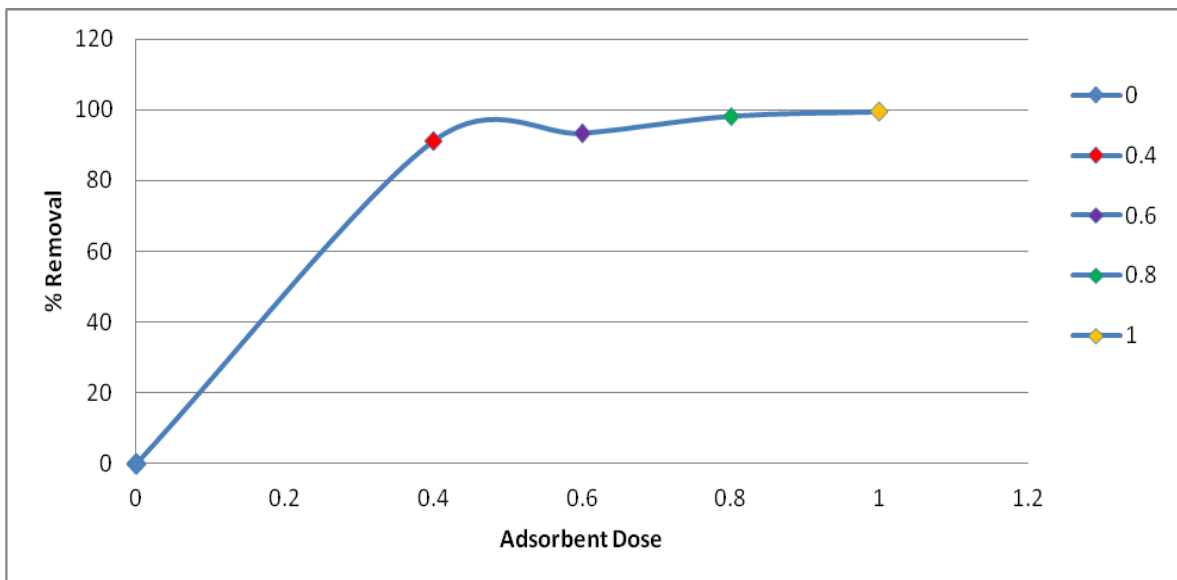


Fig 3.12. Effect of adsorbent dose of Cd (II) at different adsorbent dose (initial concentration 100 mg/L, contact time 120 min, initial pH 4.5).

Fig. (3.9-3.12) shows the relationship of metal Cu^{2+} , Fe^{+2} , Cr^{+3} and Cd^{+2} up take with the biosorbent dosage upon 120 minutes of contact time. The results were revealed that the increase in the biosorbent beyond the optimum dosage of adsorbent cause to decrease the metal uptake. This may be due to at high sorbent dosages the available metal ions are insufficient to cover all the exchangeable sites on the biosorbent, usually resulting in a low metal up take. Besides, it might due to the formation of aggregation during biosorption causing a decrease in the effective adsorption area when the biomass concentration increases. Thus, it could be concluded that the highest metal uptake occurs at the biosorbent (MLP) dosage about 0.4 g/L.

3.1.4 Effect of initial concentration

The initial metal ion concentration plays an important role towards the performance of a batch biosorption. The effect can be studied from the results of experiments at constant dosages of MLP. The adsorption was carried out using a concentration range of 50mg/L, 75mg/L and 100mg/L. This was carried out by contacting 0.4g/L of Mango leaf powder with 100mL of each metal ion solutions at optimal pH in 250mL of Erlenmeyer flasks. The flasks were then agitated at 180 rpm using rotary shaker about 2 hours at room temperature. The samples were filtered and the concentration of residual metal ions in each solution was determined by AAS. The data are presented in tables 3.13 – 3.16 and figures 3.13 – 3.16 respectively.

Table.3.13 Effect of initial concentration of Cu (II) at different initial concentration (Adsorbent dose 0.4g/L, contact time 120 min, initial pH 4.5).

Exp.No.	Initial conc.(mg/L)	Final conc.(mg/L)	% Removal
1	0	0	0
2	50	0.58	98.88
3	75	1.87	97.5
4	100	2.57	97

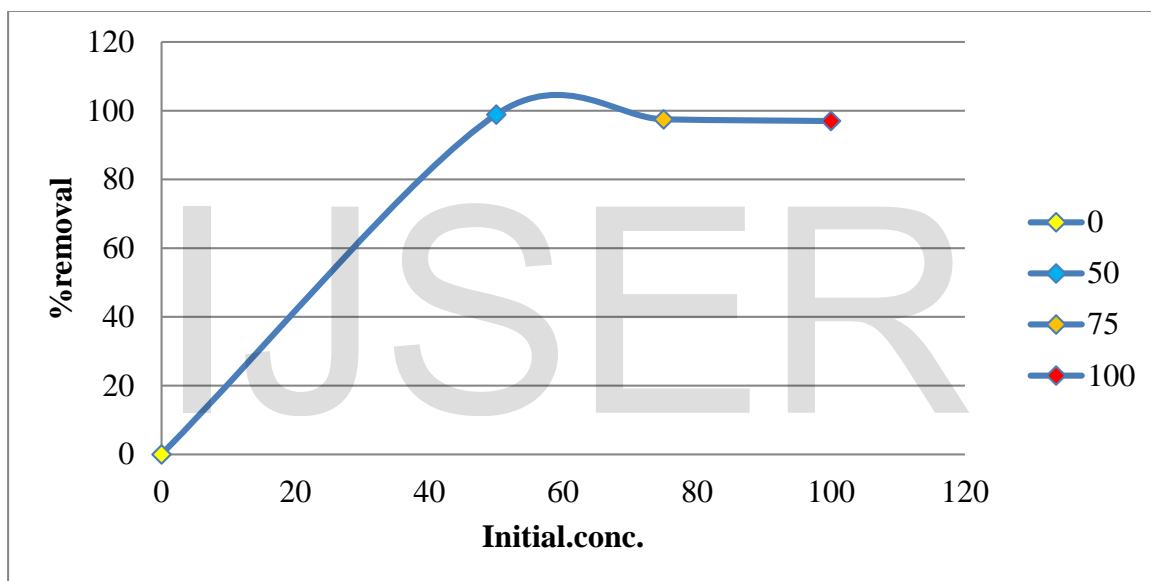


Fig .3.13. Effect of initial concentration of Cu (II) at different initial concentration (Adsorbent dose 0.4g/L, contact time 120 min, initial pH 4.5).

Table3.14 Effect of initial concentration of Fe (II) at different initial concentration (Adsorbent dose 0.4g/L, contact time 120 min, initial pH 4.5).

Exp.No.	Initial conc.(mg/L)	Final conc.(mg/L)	% Removal
1	0	0	0
2	50	0.835	98.33
3	75	2.7	96.4
4	100	6.6	93.4

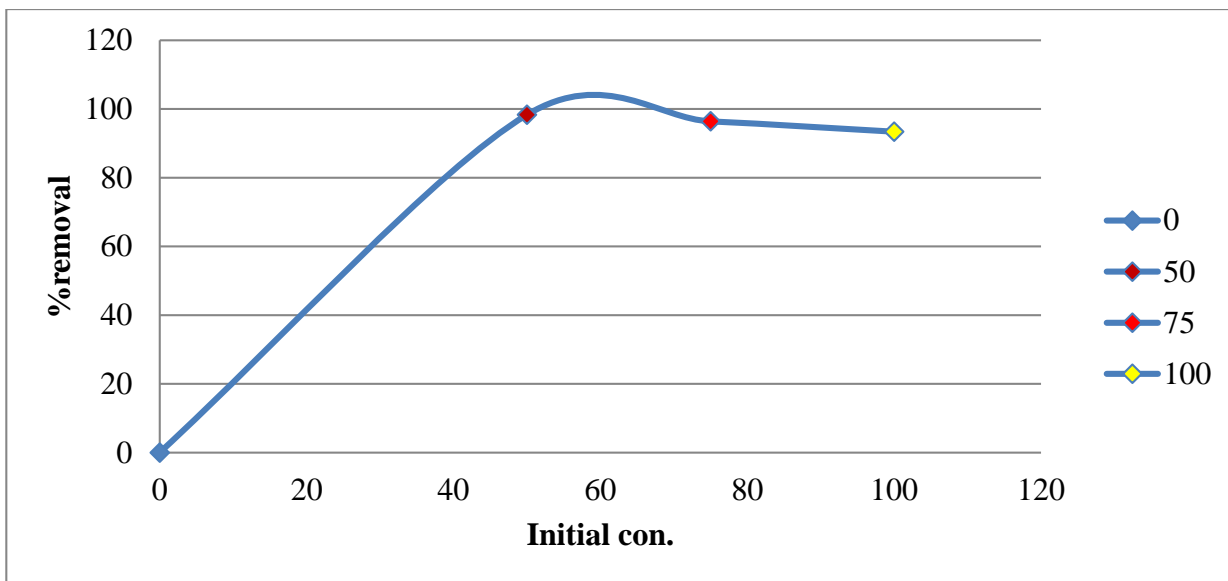


Fig .3.14. Effect of initial concentration of Fe (II) at different initial concentration (Adsorbent dose 0.4g/L, contact time 120 min, initial pH 4.5).

Table 3.15. Effect of initial concentration of Cr (III) at different initial concentration (Adsorbent dose 0.4g/L, contact time 120 min, initial pH 4.5).

Exp.No.	Initial conc.(mg/L)	Final conc.(mg/L)	% Removal
1	0	0	0
2	50	0.43	99.14
3	75	1.1	98.5
4	100	2.7	97.3

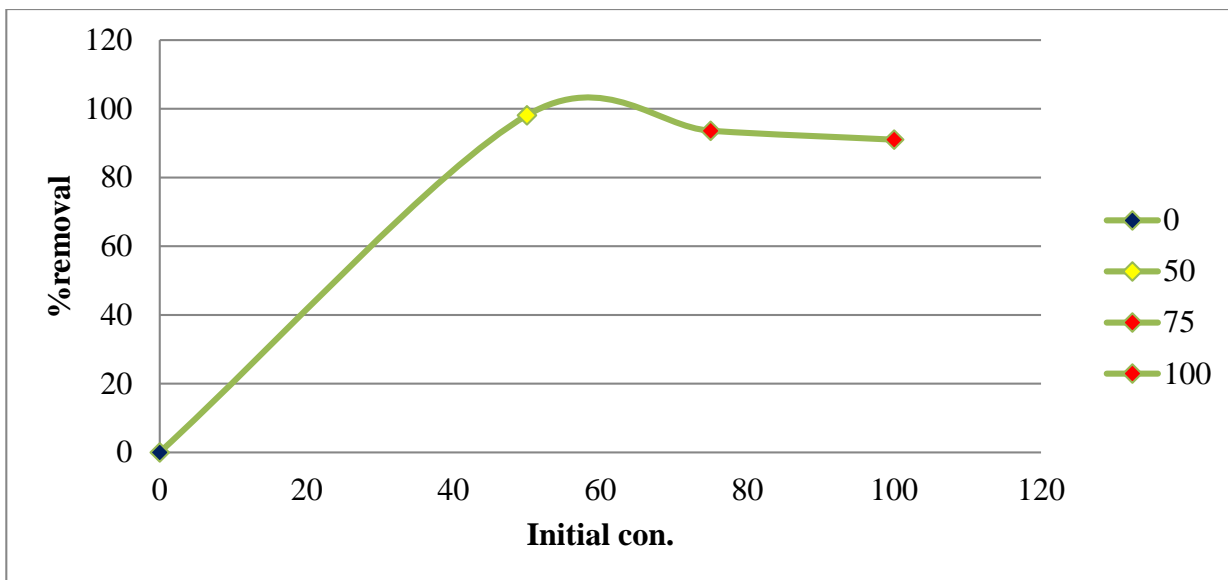


Fig.3.15. Effect of initial concentration of Cr (III) at different initial concentration (Adsorbent dose 0.4g/L, contact time 120 min, initial pH 4.5).

Table 3.16. Effect of initial concentration of Cd (II) at different initial concentration (Adsorbent dose 0.4g/L, contact time 120 min, initial pH 4.5).

Exp.No.	Initial conc.(mg/L)	Final conc.(mg/L)	% Removal
1	0	0	0
2	50	0.95	98.1
3	75	4.8	93.6
4	100	9	91

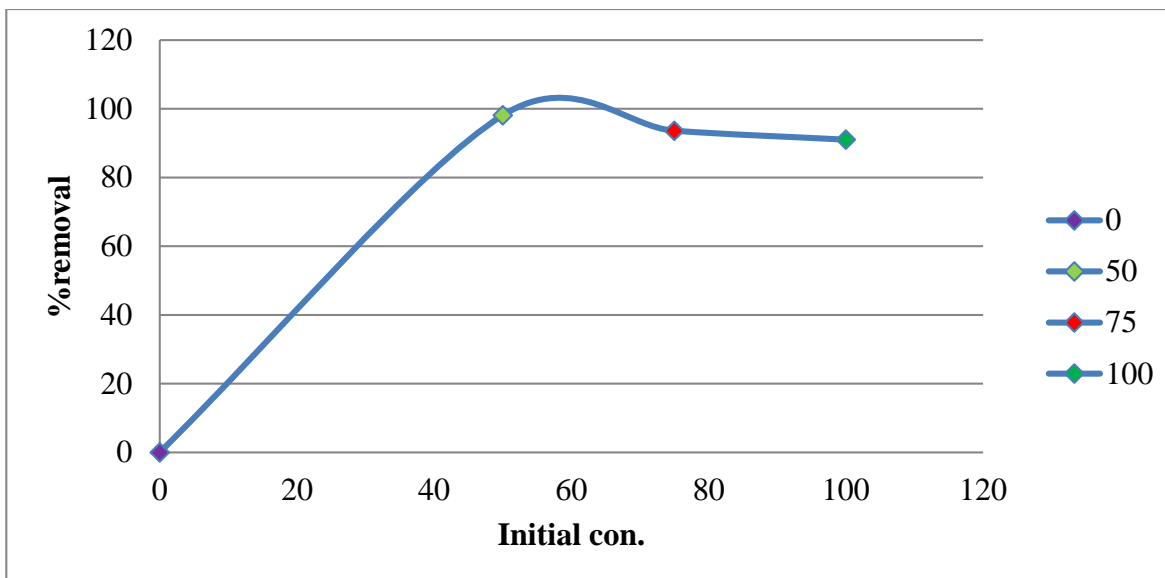


Fig .3.16. Effect of initial concentration of Cd (II) at different initial concentration (Adsorbent dose 0.4g/L, contact time 120 min, initial pH 4.5).

Adsorption experiments at varying initial Cu (II), concentrations from 50, 75 and 100 mg/L were performed with fixed doses (0.4 g/L) of adsorbent. The results were indicates that percentage removal of Cu(II),Fe(II) Cr (III) and Cd(II) decreases as the initial concentration of metal ions increased. The percent removal efficiency of Cu(II), Fe(II) Cr(III) and Cd(II) ions ranged from 98% to 97% ,98.33% to 93.4%, 99.14% to 97.3% and 98.1% to 91% respectively (shown in tables and Figures 3.13 - 3.16. This can be explained by the fact that all the adsorbents had a limited number of active sites, which would have become saturated above a certain concentration.

The initial metal ion concentration functions as the driving force to overcome mass transfer resistances between the aqueous and solid phases [52, 53]. In addition, greater the initial concentration of metal ion may cause greater metal uptake due to increase the number of collisions between the metal ion and the biosorbent, if its have enough amount [54-60]. Thus, it could be concluded that the highest metal uptake would occur at the optimum metal ion concentration, which is 50 mg/L, (shown in tables and Figures 3.13 - 3.16).

3.1.5 Effect of Temperature

The effect of temperature on metal ions by biosorption was examined by the initial concentration, contact time and adsorption dosage are kept constant with different temperatures. The metal ion removal was recognized as slowly increased by increasing temperature [61]. This was established at higher temperature, chemical interaction between adsorbates and adsorbent, creation of some new adsorption sites or the increased rate of intra-particle diffusion of adsorbate molecules into the pores of the adsorbent at higher temperatures [62].

The experiments were employed at 30°C, 45°C and 60°C for the initial Copper, Iron, Chromium and Cadmium concentrations of 50mg/L at constant adsorbent dose of 0.6 g/L. The results were presented in tables and figures are 3.17 – 3.20 for Cu (II), Fe (II), Cr (III) and Cd (II) respectively

Table3. 17. Effect of Temperature of Cu (II) at different Temperature (Initial con.50mg/L, Adsorbent dose 0.6g/L, contact time 60 min, initial pH 4.5).

Exp.No	Temp. (K)	Final conc.(mg/L)	% Removal
1	0	0	0
2	30	9.5	81
3	45	4.35	91.3
4	60	1.9	96.2

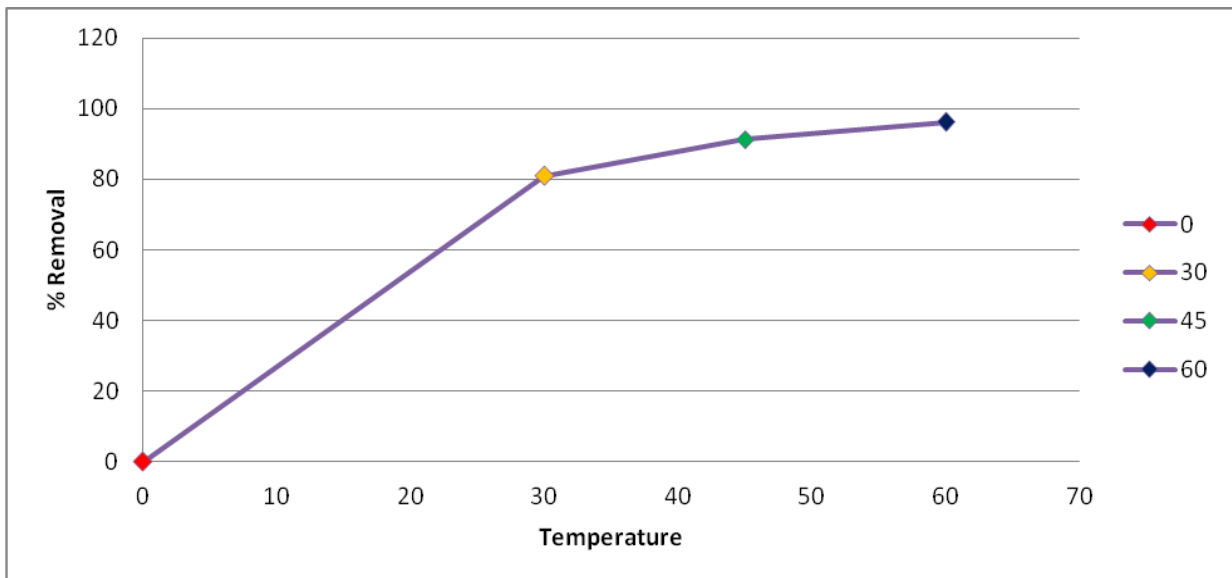


Fig.3.17. Effect Temperature of Cu Removal onto Mango leaf Powder (Cu Concentration=50 mg/L, Adsorbent Dose=0.6g/L and contact Time=1 h)

Table3. 18. Effect of Temperature of Fe (II) at different Temperature (Initial con.50mg/L, Adsorbent dose 0.6g/L, contact time 60 min, initial pH 4.5).

Exp.No	Temp. (K)	Final conc.(mg/L)	% Removal
1	0	0	0
2	30	9.27	81.46
3	45	3.01	93.98
4	60	2	96

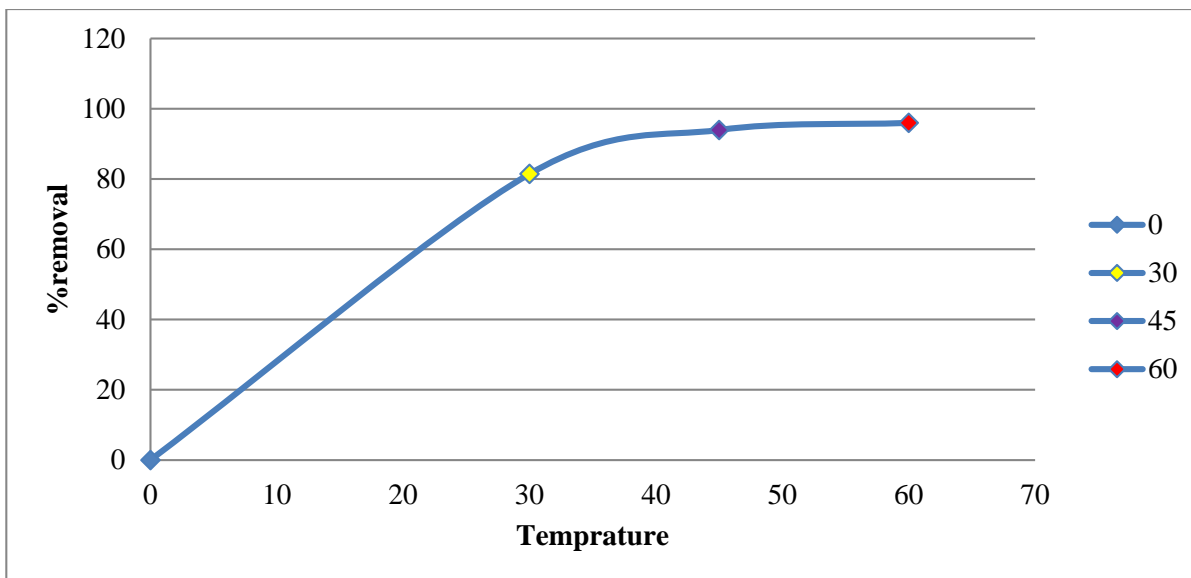


Fig.3.18. Effect Temperature of Fe Removal onto Mango leaf Powder (Cu Concentration=50 mg/L, Adsorbent Dose=0.6g/L and contact Time=1 h)

Table 3.19. Effect of Temperature of Cr (III) at different Temperature (Initial con.50mg/L, Adsorbent dose 0.6g/L, contact time 60 min, initial pH 4.5).

Exp.No	Temp.	Final conc.(mg/L)	% Removal
1	0	0	0
2	30	7.65	84.7
3	45	3.85	92.3
4	60	0.46	99.08

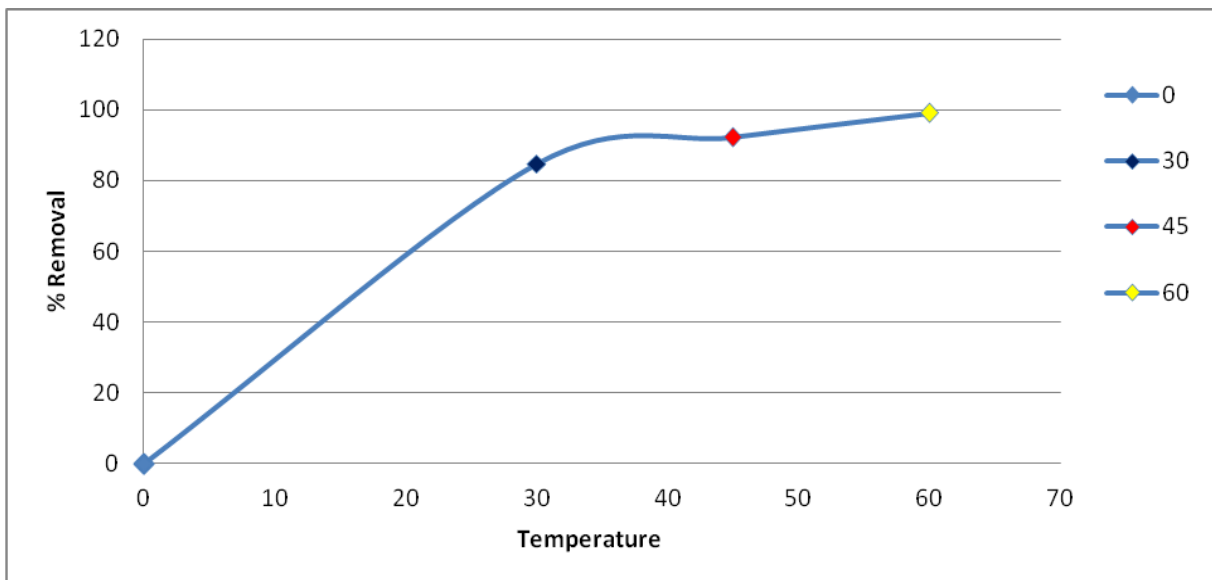


Fig.3.19. Effect Temperature of Cr Removal onto Mango leaf Powder (Cr Concentration=50 mg/L, Adsorbent Dose=0.6g/L and contact Time=1 h).

Table 3.20. Effect of Temperature of Cd (II) at different Temperature (Initial con.50mg/L, Adsorbent dose 0.6g/L, contact time 60 min, initial pH 4.5).

Exp.No.	Temp.	Final conc.(mg/L)	% Removal
1	0	0	0
2	30	8.65	82.7
3	45	2.85	94.3
4	60	1.08	97.84

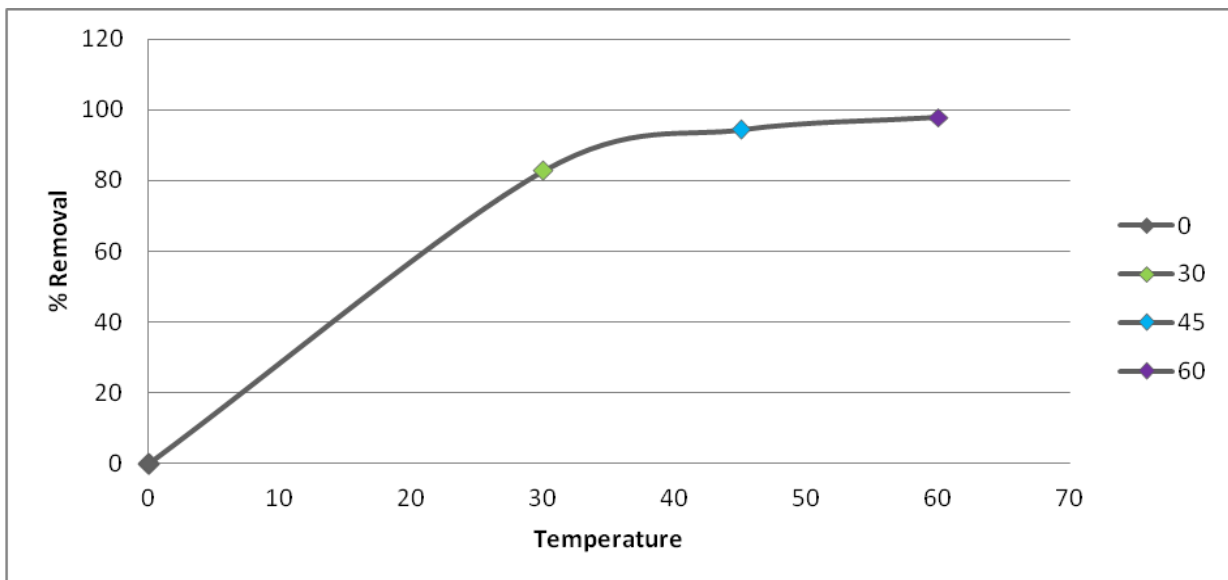


Fig.3.20. Effect Temperature of Cd Removal onto Mango leaf Powder (Cd Concentration=50 mg/L, Adsorbent Dose=0.6g/L and contact Time=1 h).

The results (shown in tables 3.17-3.20 and figures.3.17-3.20) indicates that the clear trend could observe. So, temperature variation plays an important role on metal ion biosorption. The percentage adsorption of metal ions increases when the temperature gets increased. This is more significant at low concentration of metal ions (50 mg/L) with the highest increase in adsorption efficiency. Increase the percentage of adsorption with temperature signifies the endothermic nature of the adsorption process. Thus, increasing the temperature, the rate of diffusion will also increase and this leads to the diffusion of adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution.

3.2 Adsorption isotherms

Many models have been proposed to explain adsorption equilibrium, but the most important factor is to have applicability over the entire range of process conditions. The most widely used isotherms for solid-liquid adsorption are the Langmuir and Freundlich isotherms. Both of these isotherms relate the adsorption density, q_e (metal uptake per unit weight of adsorbent) to equilibrium adsorbate concentration in the bulk fluid phase, C_e [63].

3.2.1 Langmuir isotherm

Langmuir isotherm model [64, 65] generally demonstrates the equilibrium distribution of ions between solids and liquid phases. This isotherm is derived from the assumption that a maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with constant energy of adsorption, and no transmigration of adsorbate in the plane of the surface [66]. The correlation coefficient that was obtained from the Langmuir plot as shown in Figure 3.21-3.24, which is ≥ 0.828 indicates the data are well fitted in Langmuir. Thus, values obtained by linear regression correlation coefficient (R^2) for Langmuir suggest that monolayer sorption may exist under that experimental condition as well.

The adsorption equilibrium data obtained at a fixed initial concentration and varying adsorbent dose have been fitted into the linearized Langmuir adsorption isotherms. The simplest adsorption isotherm, Langmuir isotherm, is based on the assumptions that every adsorption site is equivalent and that the ability of a particle to bind there is independent of whether or not adjacent sites are occupied. The essential characteristic of the Langmuir isotherm [67] can be expressed by the dimensionless constant called equilibrium parameter, R_L , calculated as;

$$R_L = \frac{1}{1 + K_L C_i}$$

Where K_L is the Langmuir constant and C_i is the initial concentration of sorbate (mol L^{-1}), the R_L values indicate the type of isotherm [50]. $R_L = 0$: irreversible isotherm $0 < R_L < 1$: favorable isotherm $R_L = 1$: linear isotherm $R_L > 1$: unfavorable isotherm. The values R_L in this study was between 0 and 1 it shows the Langmuir isotherm was favorable.

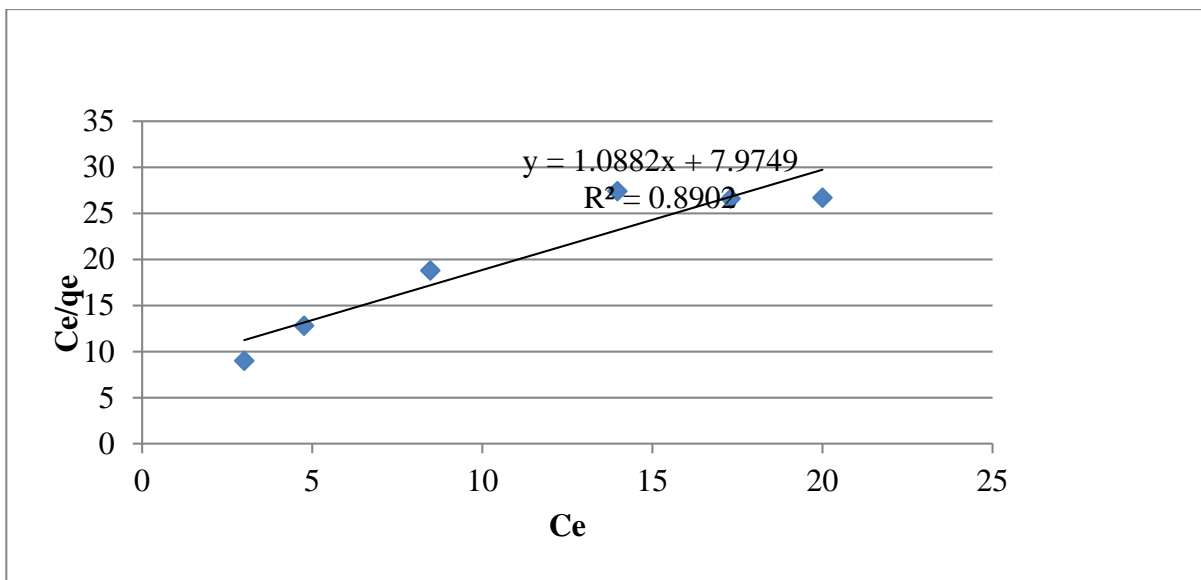


Fig .3.21 Langmuir adsorption isotherm for adsorption of Cu (II) onto mango leaf powder (initial concentration 50 mg/L, contact time 60 min, initial pH 4.5).

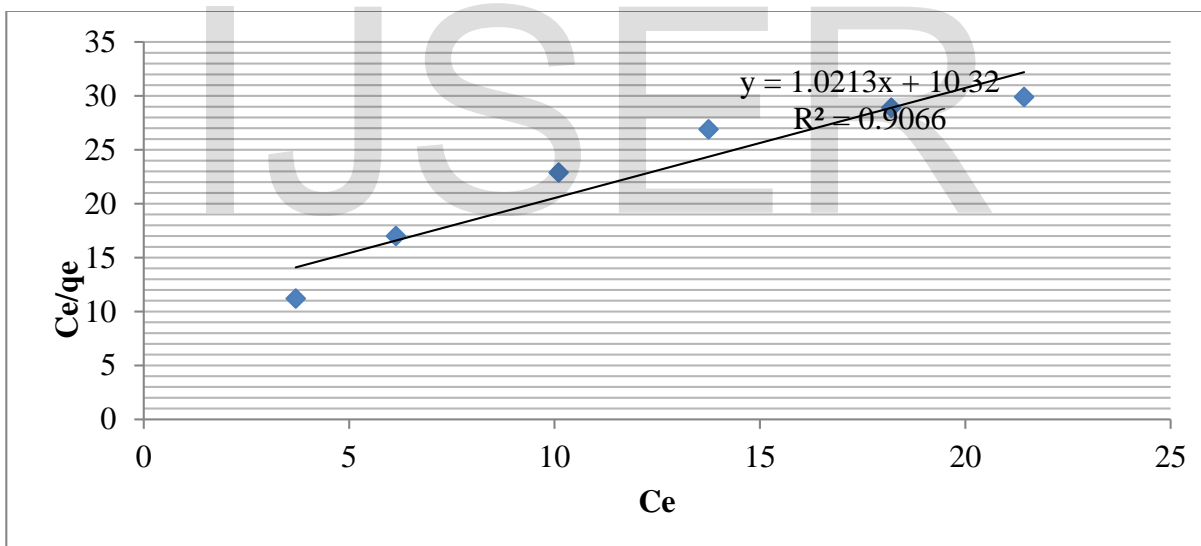


Fig .3.22. Langmuir adsorption isotherm for adsorption of Fe (II) onto mango leaf powder (initial concentration 50 mg/L, contact time 60 min, initial pH 4.5).

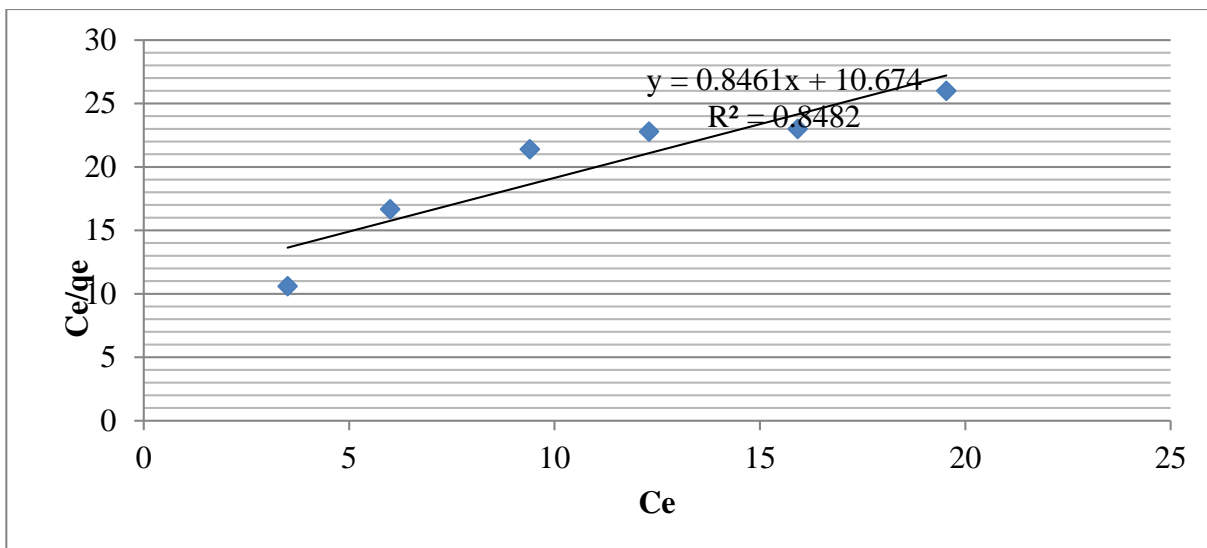


Fig. 3.23. Langmuir adsorption isotherm for adsorption of Cr (III) onto mango leaf powder (initial concentration 50 mg/L, contact time 60 min, initial pH 4.5).

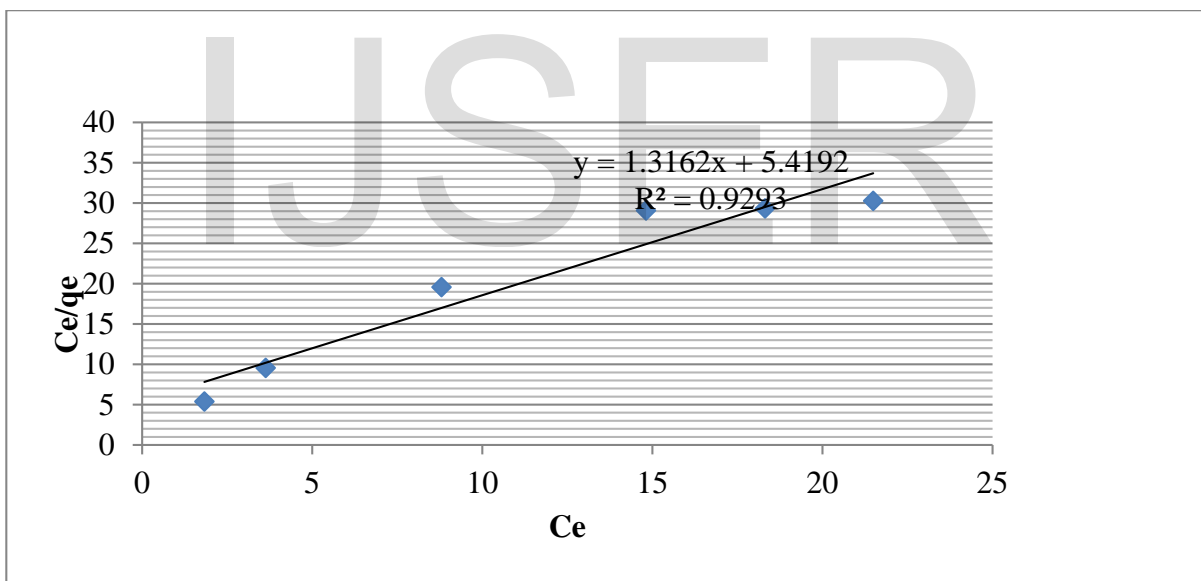


Fig. 3.24 Langmuir adsorption isotherm for adsorption of Cd (II) onto mango leaf powder (initial concentration 50 mg/L, contact time 60 min, initial pH 4.5).

Table 3.21 Langmuir isotherm models of cu (II), Fe (II), Cr (III) and Cd (II) MLP systems

Langmuir isotherm				
Metal ion	R ²	q _m (mg g ⁻¹)	K _L (L ml ⁻¹)	Parameters
Cu(II)	0.890	0.92	0.14	Contact time
Fe(II)	0.906	0.98	0.099	Contact time
Cr(III)	0.848	1.18	0.079	Contact time
Cd(II)	0.929	0.76	0.24	Contact time

3.2.2 Freundlich isotherms

Freundlich isotherm gives the relationship between the equilibrium liquid and solid phase capacity based on multilayer adsorption (heterogeneous surface). The Freundlich isotherm is based on the assumption that the adsorption sites are distributed exponentially with respect to the heat of [66]. Based on Figure. 3.25-3.28, the correlation coefficient that was found from the Freundlich plot is ≥ 0.8775 . This greater value of R² indicates the adsorption is favorable for a Freundlich isotherm. In addition, (n) should have value lying in the range of 1 to 10 for classification as favorable adsorption the adsorption intensity, n, values for this study was found to be Copper 0.659, Iron 0.72, Chromium 0.304 and Cadmium 1.06. This values value is smaller than one, indicates adsorption in unfavorable adsorption in Cu, Fe and Cr ions. But the value of Cadmium is grater than 1 it shows the favorable adsorption. Meanwhile, the Freundlich constant, K_F was found to be Copper 0.87, Iron 1.096, Chromium 0.774 and Cadmium 0.776. These results also indicate that the MLP surface is heterogeneous in the long range, but may have short range of uniformity [68].

The Freundlich isotherm plots for Copper, Iron, Chromium and Cadmium ions are presented in figures 3.25 - 3.28:

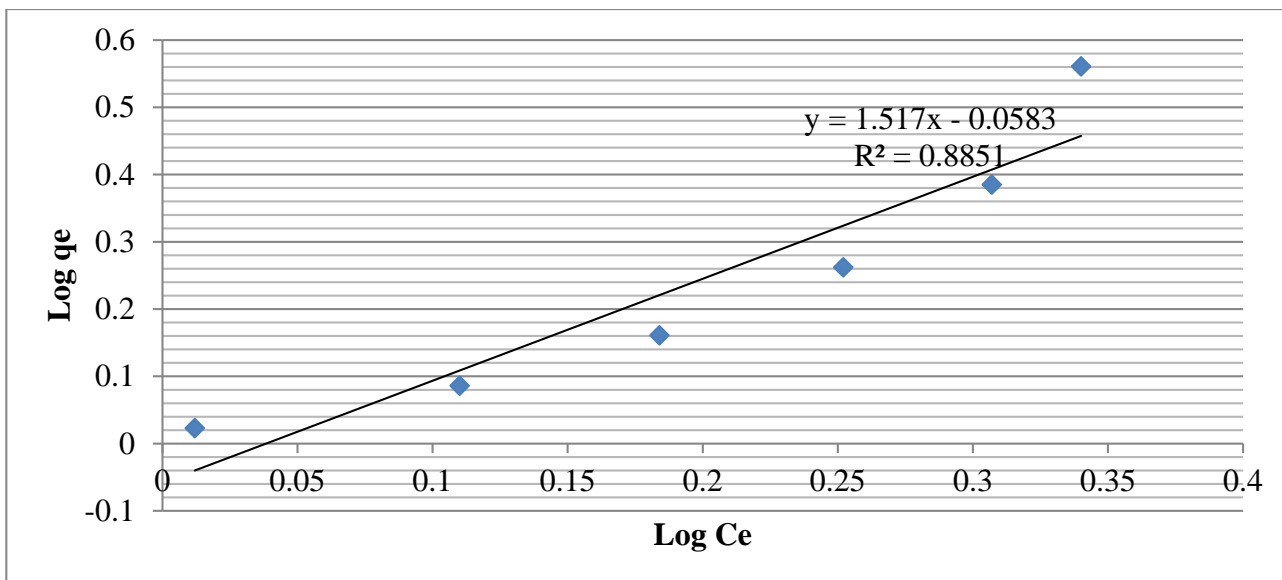


Fig.3.25. Freundlich adsorption isotherm for adsorption of Cu (II) on mango leaf powder (initial concentration 75 mg/L, contact time 60 min, initial pH 4.5).

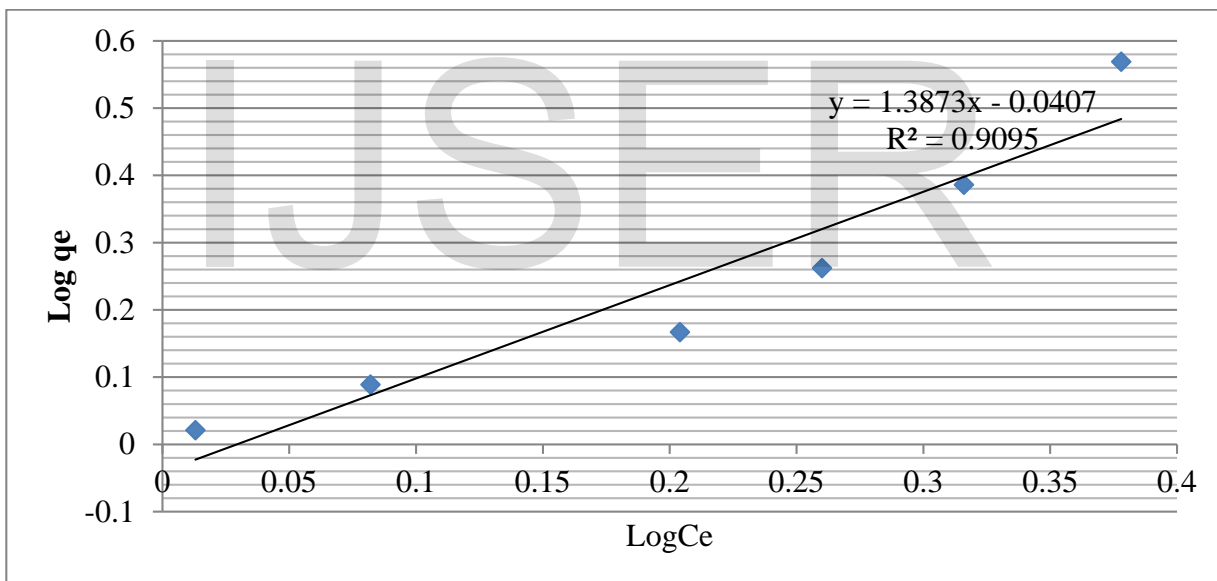


Fig.3.26. Freundlich adsorption isotherm for adsorption of Fe (II) on mango leaf powder (initial concentration 75 mg/L, contact time 60 min, initial pH 4.5).

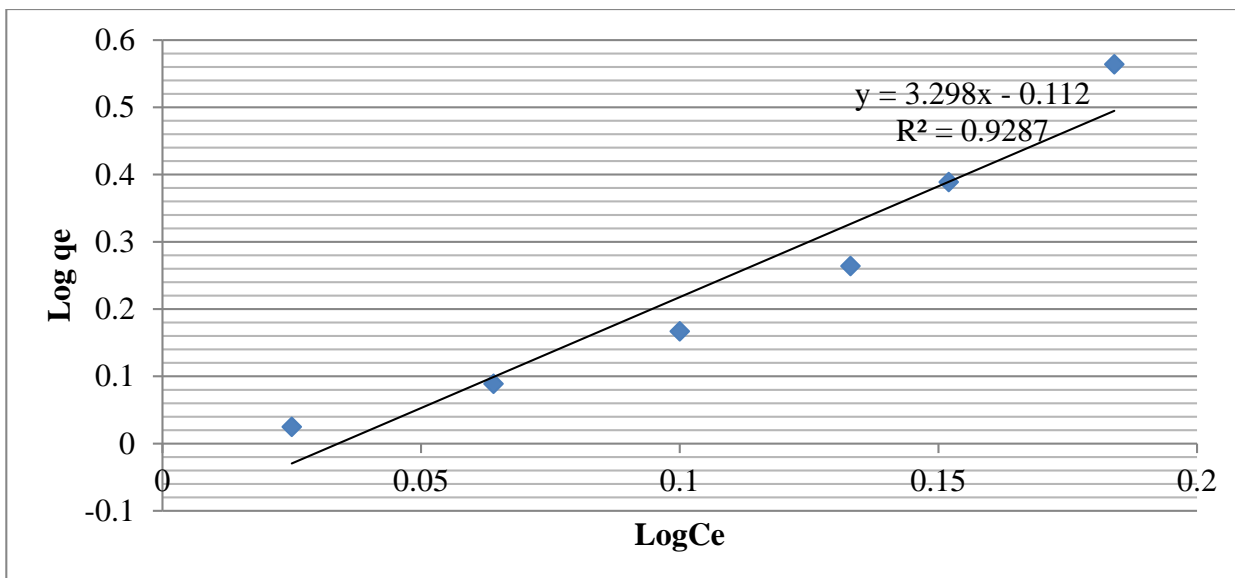


Fig.3.27. Freundlich adsorption isotherm for adsorption of Cr (III) on mango leaf powder (initial concentration 75 mg/L, contact time 60 min, initial pH 4.5).

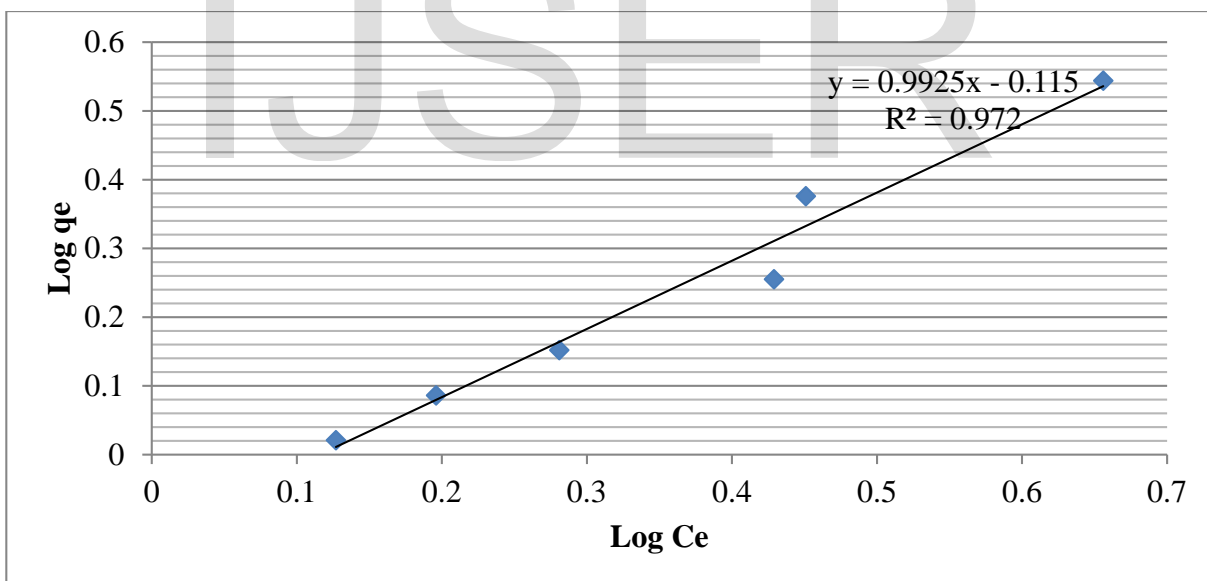


Fig.3.28. Freundlich adsorption isotherm for adsorption of Cd (II) on mango leaf powder (initial concentration 75 mg/L, contact time 60 min, initial pH 4.5).

Table 3.22 Freundlich isotherm model of the Cu (II),Fe(II),Cr(III) and Cd(II) in Mango leaf powder

Freundlich System				
Metal ion	R ²	K _f (mg g ⁻¹)	n (L g ⁻¹)	Parameters
Cu (II)	0.885	0.875	0.659	Contact time
Fe(II)	0.909	0.912	0.720	Contact time
Cr(III)	0.928	0.773	0.303	Contact time
Cd(II)	0.992	0.767	1.00	Contact time

The comparison of two isotherm regression co-efficients (R²) is shown in Table 3.21 and 3.22. The order of favorability on the basis of R² is as: Langmuir copper ion (0.89), Freundlich of copper (0.885), respectively. From both isotherm observation may concluded that the higher adsorption capacity showing agreement with the Langmuir isotherm model. The R² values in Freundlich isotherm for Iron ion(0.909),Chromium ion (0.928) and Cadmium ion(0.992) respectively.R² values in Langmuir isotherm for Iron ion(0.906),Chromium ion(0.848) and Cadmium ion(0.929) respectively. Therefore, each isotherm has appropriate merits in describing the potential of mango leaf powder for the adsorption of metals ions. From these observations it may be concluded that the higher adsorption capacity was showing agreement with the Freundlich isotherm model.

3.3 .Thermodynamic study

Thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) and change of adsorption can be evaluated. The values of ΔH° and ΔS° are determined from the slope and the intercept of the plots of plots of $\log K_c$ versus $1/T$, shown in Figure. 3.29-3.30. The ΔG° values were calculated using Eq. (2.6). The plots were used to compute the values of thermodynamic parameters (shown in table 3.23). The negative ΔG° value indicates the feasibility and spontaneous nature of the adsorption process; positive ΔH° value suggests the endothermic nature of adsorption and the ΔS° can be used to describe the randomness at the Mango leaf powder-solution interface during the sorption. To calculate the ΔH° and ΔS° plot the following graph.

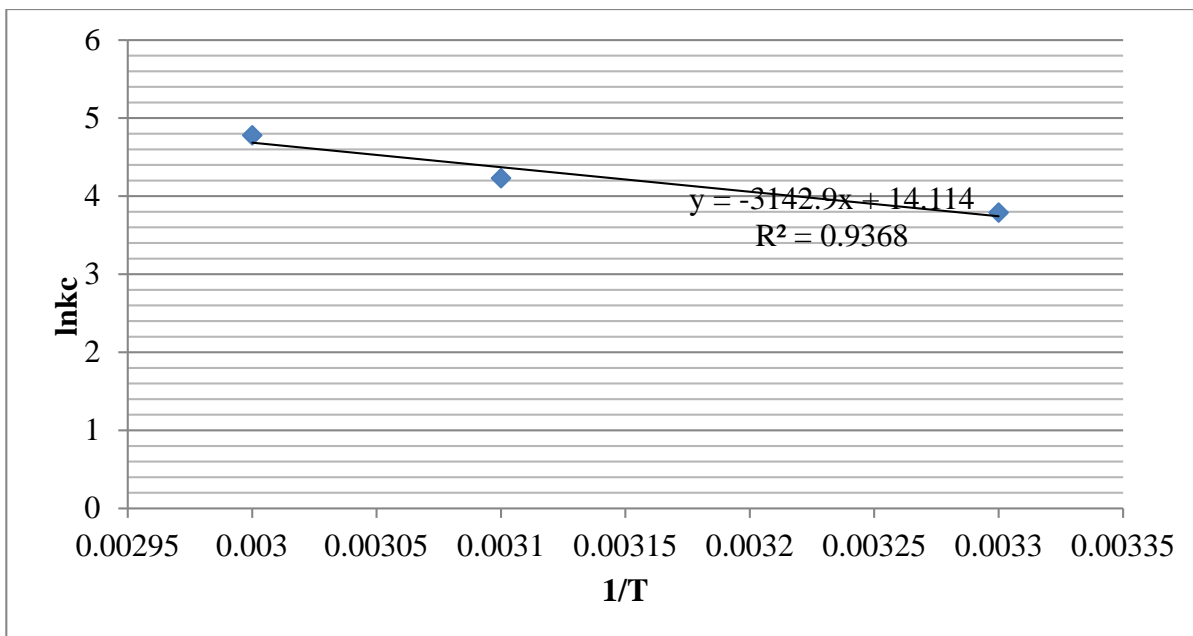


Fig .3.29 Plot of thermodynamic Study of Cu (II).

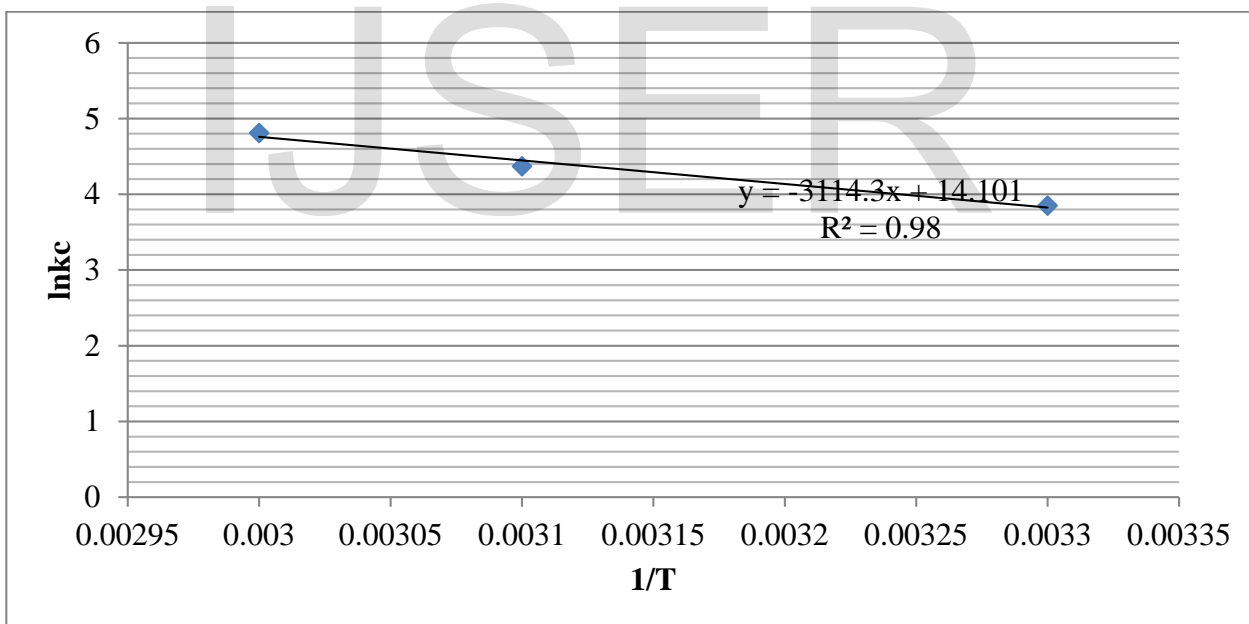


Fig .3.30 Plot of Thermodynamic Study of Fe (II).

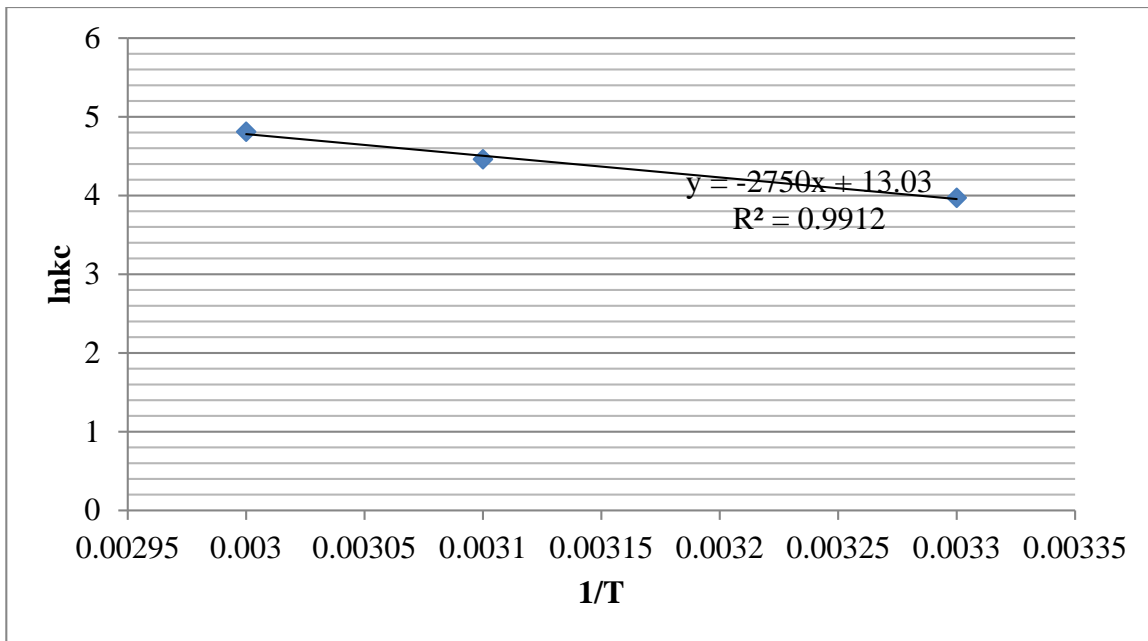


Fig.3.31.Plot of thermodynamic Study of Cr (III).

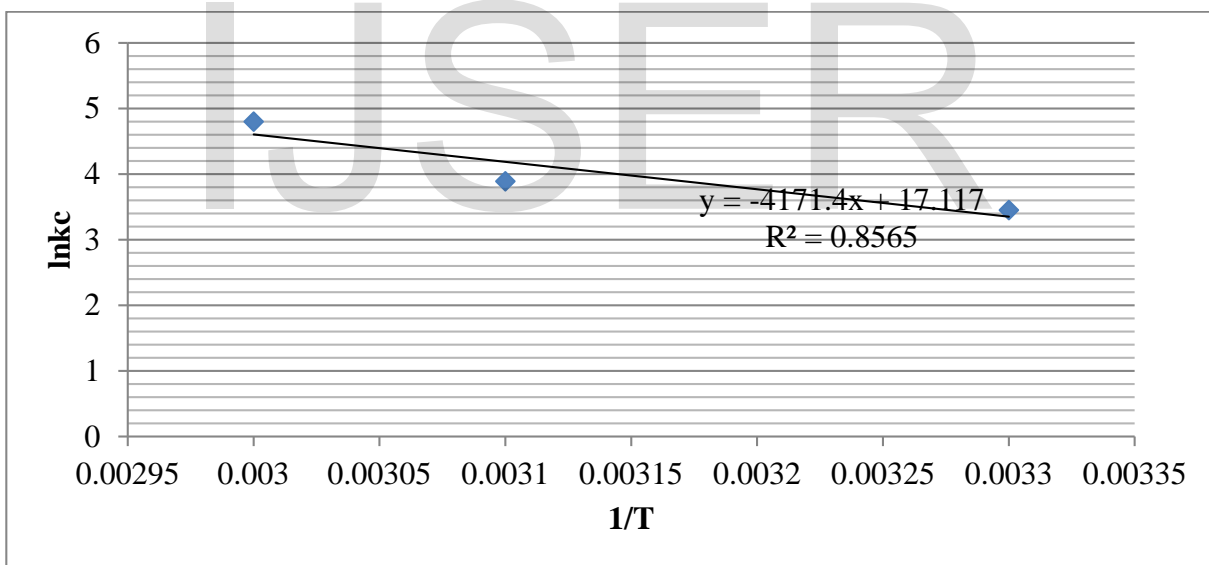


Fig.3.32 Plot of thermodynamic Study of Cd (II).

Table 3.23 Thermodynamic Parameters for the Adsorption of Cu (II), Fe (II), Cr (III) and Cd(II)Ions onto Mango Leaf Powder.

Metal ion	Initial ion con.(mg/L)	ΔH° (KJ/Mol)	ΔS° (J/Mol/K)	ΔG° KJ/Mol		
				30 ⁰ c	45 ⁰ c	60 ⁰ c
Cu(II)	50	26.122	117.31	-9.548	-11.183	-13.233
Fe(II)	50	25.889	117.234	-9.698	-11.553	-12.929
Cr(III)	50	22.863	3108.33	-10.00	-11.791	-13.316
Cd(II)	50	34.677	142.25	-8.691	-10.284	-13.239

In an earlier literature[69] was reported that ΔG° up to -20 kJ/mol are consistent with electrostatic interaction between sorption sites and the metal ion (physical adsorption), while ΔG° values more negative than -40 kJ/mol involve charge sharing or transfer from the biomass surface to the metal ion to form a coordinate bond (chemical adsorption) [69]. The ΔG° values obtained in this study for the Cu^{2+} , Fe^{2+} , Cr^{3+} and Cd^{2+} ions are <-15 kJ/mol, spontaneous in nature which indicates that physical adsorption was the predominant mechanism in the sorption process [70]. In the present study, the positive values of ΔH were confirmed that the nature of adsorption takes place as endothermic, while in adsorption of metal ions on MLP. Furthermore, the value of $\ln K_c$ was also increased by increasing the temperature, and slightly positive value of entropy (ΔS) suggests the increased randomness at the solid/solution interface during the adsorption of metal ion onto the mango leaf powder.

3.4. Adsorption kinetic modeling

The models of adsorption kinetics were correlated with the solute uptake rate, hence these models are important in water treatment process design. In this study, for a batch reaction, the adsorption dynamics was followed by conducting the adsorption of Cu (II) Fe (II), Cr (III) and Cd (II) on Mango leaf powder at optimized pH and adsorbent dosage. Chemical kinetics explain how fast the rate of chemical reaction occurs and also on the factors affecting the reaction rate. The nature of sorption process will depend on physical or chemical characteristics of the adsorbent systems and also on the system conditions. The most

commonly used kinetic expressions to explain the solid/liquid adsorption processes are the pseudo first order kinetics and pseudo second-order kinetic model [71, 72, and 73]. External mass transfer and Intraparticle diffusion model were also used to predict the sorption kinetics [72, 74 and 75]

Experiments were performed in order to understand the kinetics of copper, Iron, Chromium and Cadmium ion absorption on mango leaf powder in aqueous solution. Adsorption kinetics experiments were carried out 50mg/L known initial concentration of ionic solutions were agitated with 0.06 g of mango leaf powder at 32 °C with a pH of 4.5 and at a constant agitation speed of 800rpm upon 120minute. After shaking in deferent time interval the sample was filtered by using filter paper. The concentration in the supernatant solution was analyzed using AAS.

3.4.1. Pseudo first-order adsorption kinetics model

The sorption kinetics may be described by a pseudo first order equation (2.10). The equation applicable to experimental results generally differs from a true first-order equation in two ways: the parameter $k_1(q_e - q_t)$ does not represent the number of available sites, and the parameter $\log q_e$ is an adjustable parameter which is often not found equal to the intercept of a plot of $\log (q_e - q_t)$ against t , whereas in a true first-order sorption reaction, $\log q_e$ should be equal to the intercept of $\log(q_e - q_t)$ against t . In order to fit Equation 2.10 to the experimental data, the equilibrium sorption capacity q_e must be known. In many cases, q_e is unknown and as chemisorption tends to become un-measurably slow, the amount sorbed is still significantly smaller than the equilibrium amount.

In most cases in the literature, the pseudo-first-order equation of Lagergren does not fit well for the whole range of contact time and is generally applicable over the initial 20 to 60 min of the sorption process. Furthermore, one has to find some means of extrapolating the experimental data to infinite of time, on treating q_e as an adjustable parameter to be determined by trial and error. For this reason, it is therefore necessary to use trial and error to obtain the equilibrium sorption capacity, in order to analyze the pseudo-first-order model kinetics [76]. The best and worse fit of experimental kinetic data in pseudo first-order kinetics by non-linear and linear method suggests the kinetics is transforming to the worse while linearizing the non-linear pseudo first-order kinetics expression.

Thus it is inappropriate to use the Lagergren pseudo first-order kinetic expression to check whether the experimental kinetic is following a first-order kinetics.

The pseudo-first-order rate constant can be obtained from the slope of plot between $\log(q_e - q_t)$ against time, t . Figure 3.33-3.36 shows the Lagergren pseudo-first-order kinetic plot for the absorption of Cu(II), Fe(II), Cr(III) and Cd(II) ions on Mango leaf powder. The pseudo-first-order rate constant values were calculated from the slope of the plots.

Table 3.24. Pseudo first-order of Cu (II) at different time intervals (initial concentration 50 mg/L, adsorbent dose 0.6g/L, initial pH 4.5).

Exp.No..	Log($q_e - q_t$)	Time (minute)
1	0.16	15
2	0.12	30
3	0.04	45
4	0	60
5	-0.01	80
6	-0.04	100
7	-0.06	120

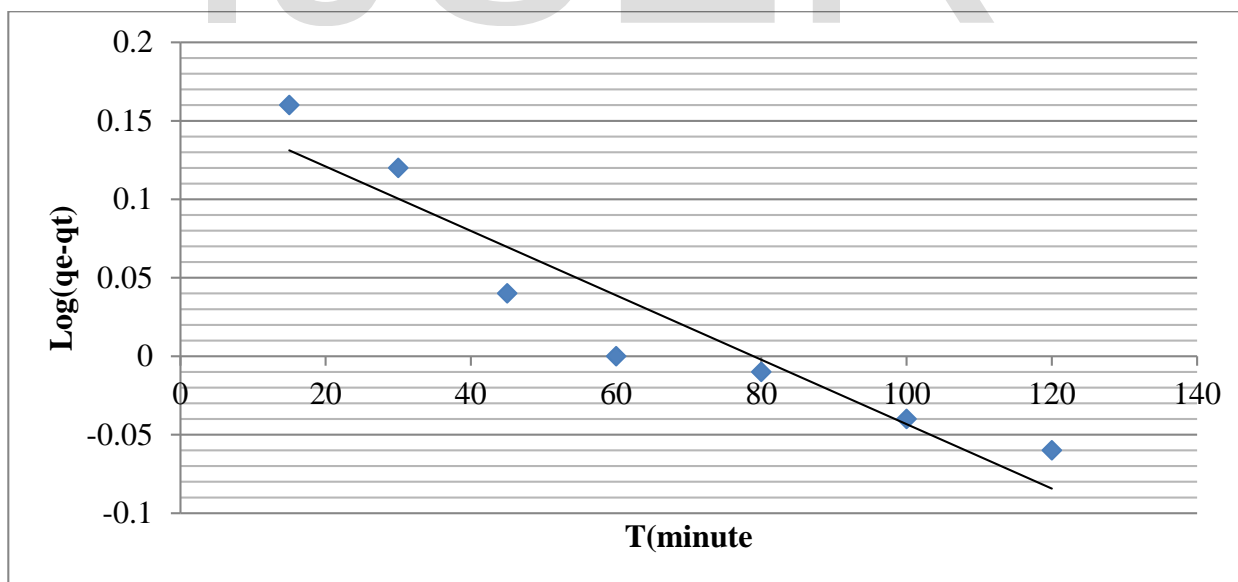


Fig.3.33 Pseudo first-order of Cu (II) at different time intervals (initial concentration 50 mg/L, adsorbent dose 0.6g/L, initial pH 4.5).

Table 3.25 Pseudo first-order of Fe (II) at different time intervals (initial concentration 50 mg/L, adsorbent dose 0.6g/L, initial pH 4.5).

Exp.No.	Log(qe-qt)	Time (minute)
1	0.16	15
2	0.07	30
3	0.03	45
4	0	60
5	-0.01	80
6	-0.05	100
7	-0.07	120

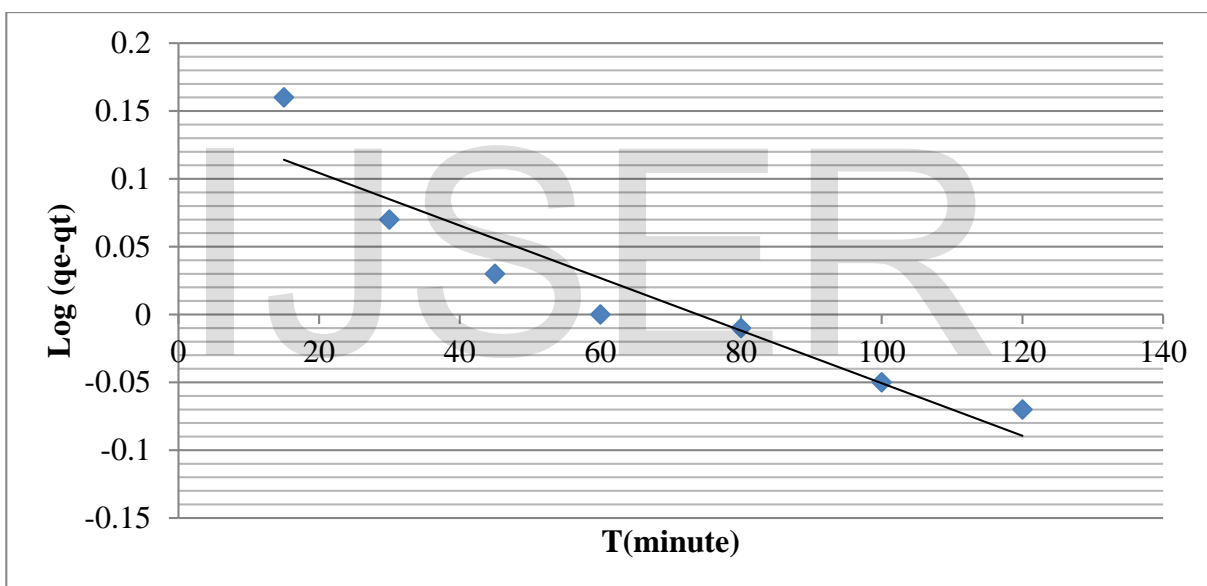


Fig .3.34 Pseudo first-order of Fe (II) at different time intervals (initial concentration 50 mg/L, adsorbent dose 0.6g/L, initial pH 4.5).

Table 3.26. Pseudo first-order of Cr (III) at different time intervals (initial concentration 50 mg/L, adsorbent dose 0.6g/L, initial pH 4.5).

Exp.No.	Log(q _e -q _t)	Time (minute)
1	0.17	15
2	0.08	30
3	0.03	45
4	0	60
5	-0.01	80
6	-0.02	100
7	-0.04	120

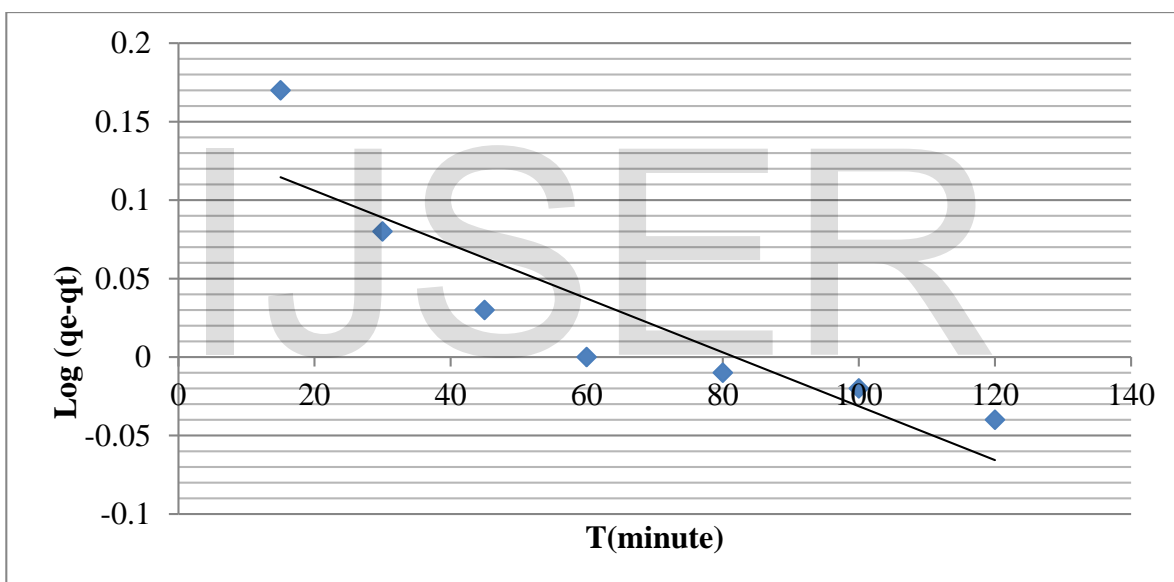


Fig.3.35. Pseudo first-order of Cr (III) at different time intervals (initial concentration 50 mg/L, adsorbent dose 0.6g/L, initial pH 4.5).

Table 3.27 Pseudo first-order of Cd (II) at different time intervals (initial concentration 50 mg/L, adsorbent dose 0.6g/L, initial pH 4.5).

Exp.No.	Log(qe-qt)	Time (minute)
1	0.17	15
2	0.14	30
3	0.04	45
4	0	60
5	-0.01	80
6	-0.03	100
7	-0.05	120

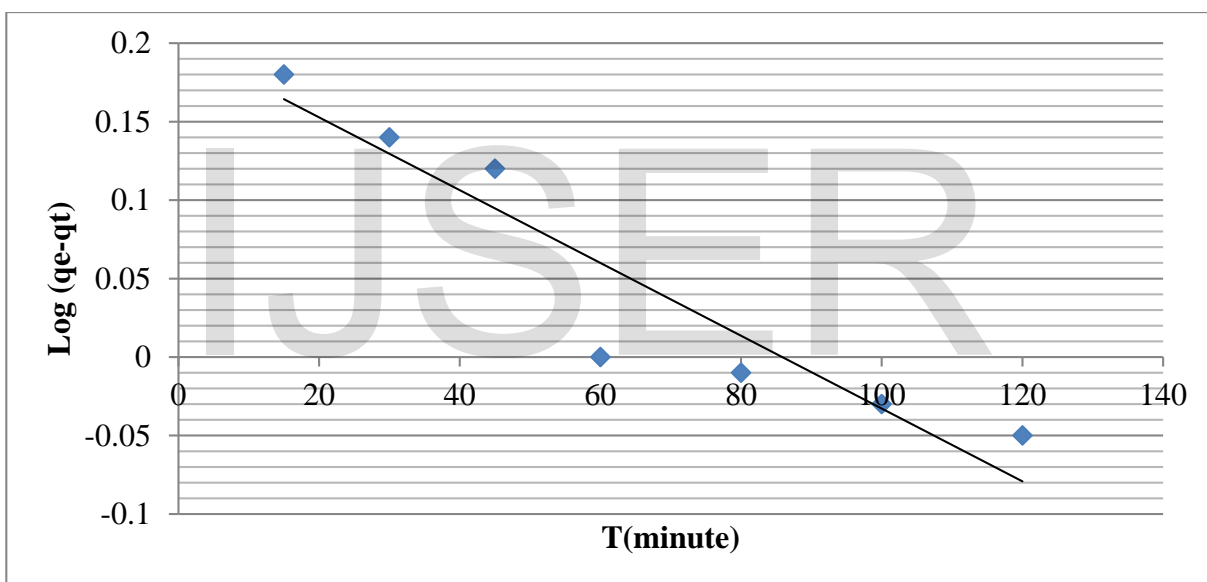


Fig.3.36. Pseudo first-order of Cd (II) at different time intervals (initial concentration 50 mg/L, adsorbent dose 0.6g/L, initial pH 4.5).

Table.3.28 Comparison of pseudo first-order adsorption, rate constants, calculated experimental q_e and correlation coefficients values for initial concentrations.

Pseudo first –order				
Metal ion	Initial con.(mg/L)	k_1 (1/minute)	q_e (mg/g)	R^2
Cu(II)	50	0.0460	1.85	0.895
Fe(II)	50	0.0230	1.84	0.887
Cr(III)	50	0.0230	1.88	0.794
Cd(II)	50	0.0460	1.86	0.885

Figure 3.33-3.36 shows a plot of linearization form of pseudo first-order model at all concentrations studied. The slopes and intercepts of plots $\text{Log}(q_e - q_t)$ of versus t were used to determine the pseudo first-order constant k_1 and equilibrium adsorption density q_e . However, the experimental data deviated considerably from the theoretical data. A comparison of the results with the correlation coefficients is shown in table 3.28. The correlation coefficients for the pseudo first order kinetic model obtained at all the studies concentrations was low. Also the theoretical q_e values found from the pseudo first-order kinetic model did not give reasonable values. This suggests that this adsorption system is not a pseudo first-order reaction

3.4.2 Pseudo second order

The adsorption kinetics may also be described by a pseudo-second-order [77-83]. By linear method, a theoretical pseudo second-order model found to well represent the experimental kinetic data. If pseudo-second-order kinetics is applicable, the plot of t/q_t versus t should give a linear relationship, from which q_e and k can be determined from the slope and intercept of the plot. The linear regression correlation coefficient R^2 values are high. The higher values confirm that the adsorption data are well represented by pseudo-second-order kinetics [84, 85 and 77]. The pseudo second order kinetic data of all metal ion adsorption on MLP is presented in tables 3.29 – 3.32 and in figures 3.37. – 3.40.

Table 3.29 Pseudo second-order of Cu (II) at different time intervals (initial concentration 50 mg/L, adsorbent dose 0.6g/L, initial pH 4.5).

Exp.No	Time(minute)	q _t (mg/g)	t/q _t (min/mg g ⁻¹)
1	15	49.91	0.30
2	30	56.73	0.53
3	45	64.33	0.69
4	60	70.51	0.85
5	80	72.95	1.16
6	100	79.15	1.26
7	120	81.87	1.46

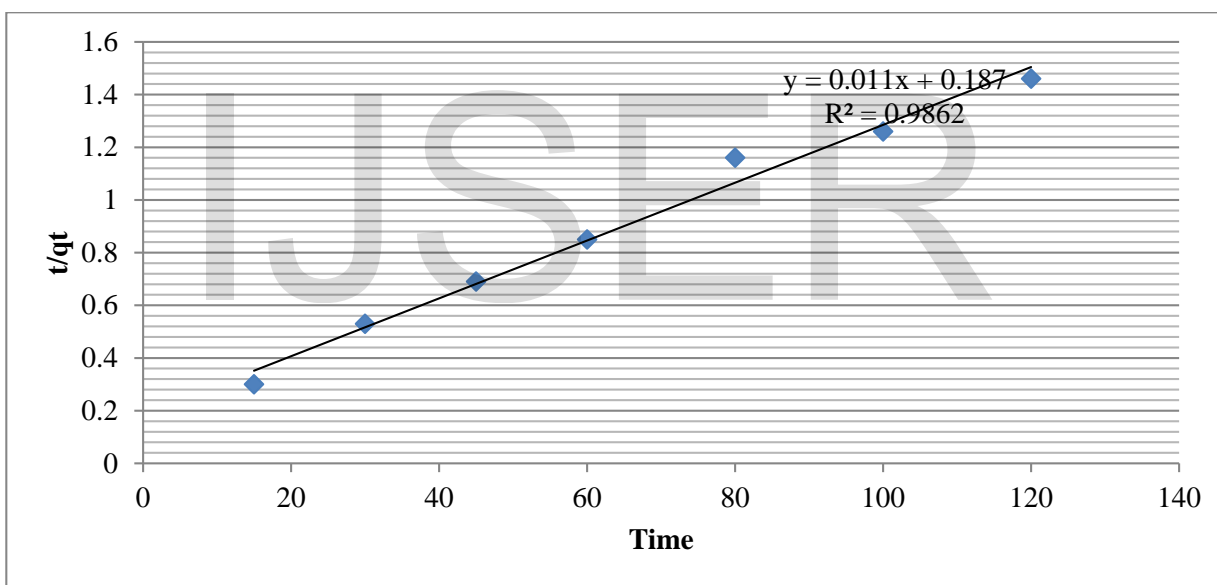


Fig.3.37. Pseudo second-order of Cu (II) at different time intervals (initial concentration 50 mg/L, adsorbent dose 0.6g/L, initial pH 4.5).

Table 3.30 Pseudo second-order of Fe (II) at different time intervals (initial concentration 50 mg/L, adsorbent dose 0.6g/L, initial pH 4.5).

Exp.No	Time(minute)	q_t (mg/g)	t/q_t (min/mg g ⁻¹)
1	15	48.13	0.31
2	30	58.93	0.51
3	45	64.77	0.69
4	60	69.93	0.86
5	80	71.6	1.12
6	100	78.5	1.27
7	120	81.96	1.46

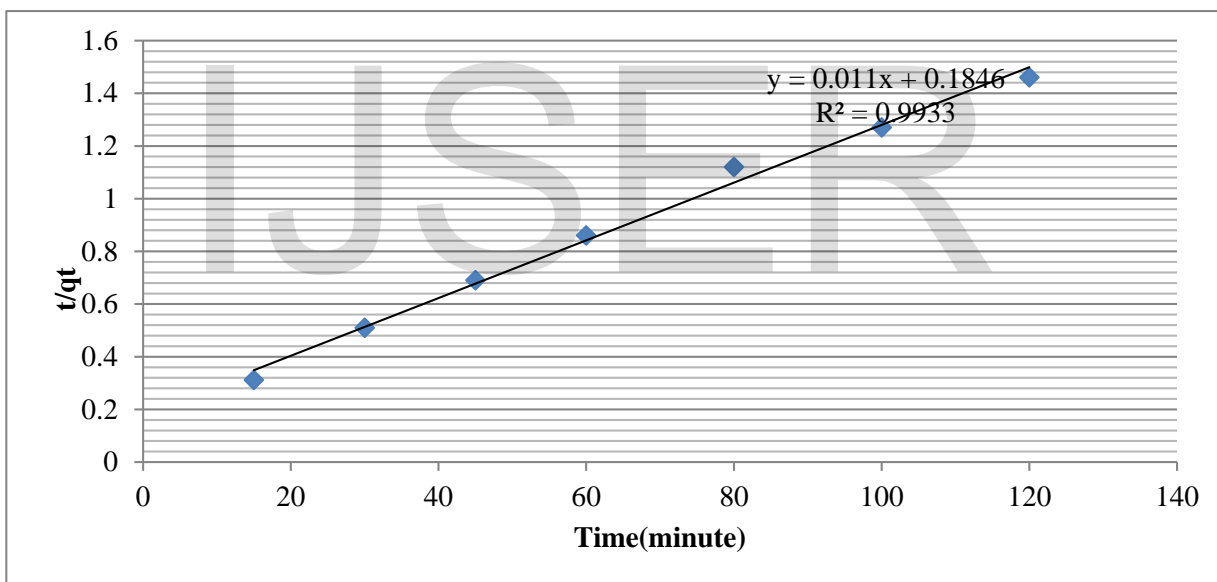


Fig.3.38. Pseudo second-order of Fe (II) at different time intervals (initial concentration 50 mg/L, adsorbent dose 0.6g/L, initial pH 4.5).

Table 3.31. Pseudo second-order of Cr (III) at different time intervals (initial concentration 50 mg/L, adsorbent dose 0.6g/L, initial pH 4.5).

Exp.No	Time(minute)	q _t (mg/g)	t/q _t (min/mg g ⁻¹)
1	15	51.93	0.289
2	30	63.93	0.469
3	45	70.55	0.638
4	60	75.67	0.793
5	80	78.21	1.023
6	100	81.10	1.233
7	120	82.57	1.453

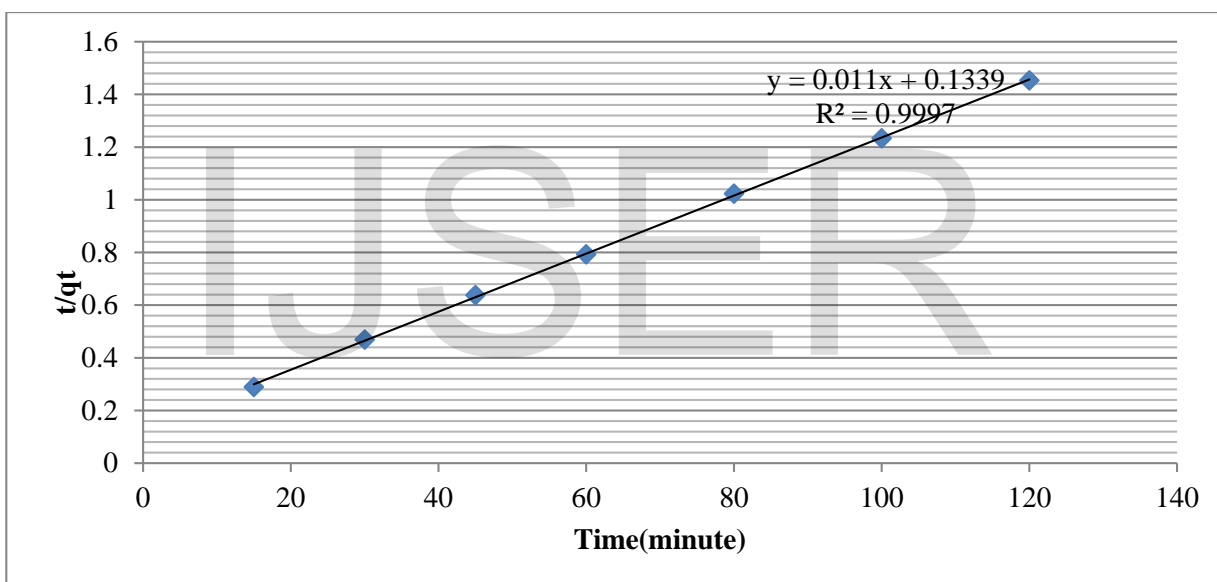


Fig.3.39. Pseudo second-order of Cr (III) at different time intervals (initial concentration 50 mg/L, adsorbent dose 0.6g/L, initial pH 4.5).

Table 3.32. Pseudo second-order of Cd (II) at different time intervals (initial concentration 50 mg/L, adsorbent dose 0.6g/L, initial pH 4.5).

Exp.No	Time(minute)	q _t (mg/g)	t/q _t (min/mg g ⁻¹)
1	15	47.81	0.313
2	30	59.23	0.506
3	45	67.15	0.670
4	60	72.47	0.827
5	80	74.80	1.069
6	100	79.13	1.264
7	120	81.70	1.477

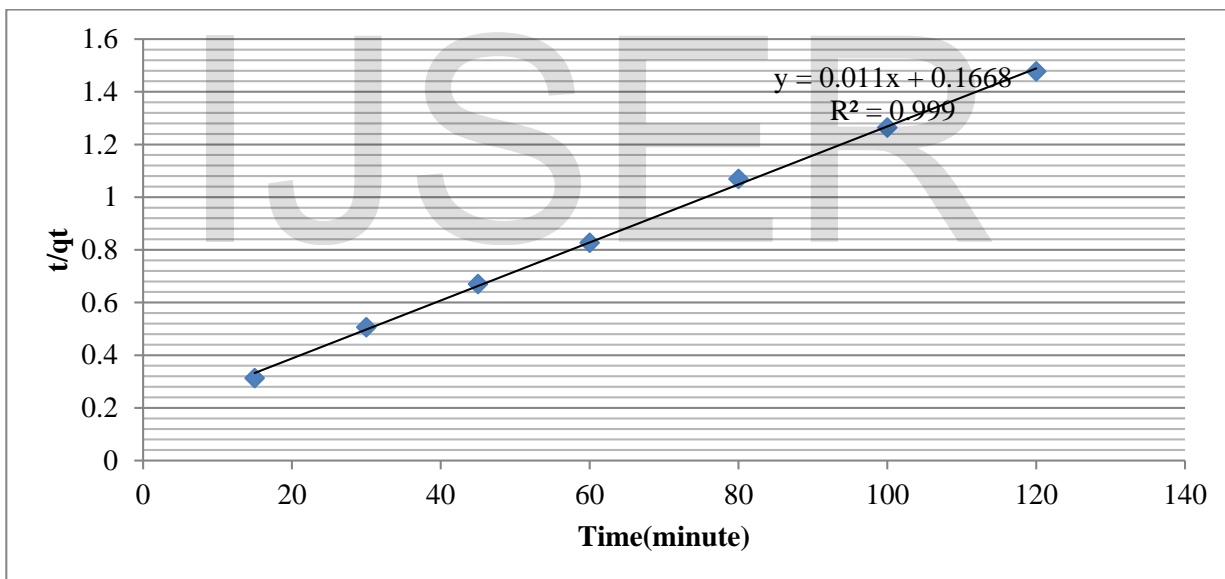


Fig. 3.40. Pseudo second-order of Cd (II) at different time intervals (initial concentration 50 mg/L, adsorbent dose 0.6g/L, initial pH 4.5).

Table 3.33. Comparison of pseudo second-order adsorption, rate constants, and calculated experimental q_e values for initial concentrations.

Pseudo second –order				
Metal ion	Initial con.(mg/L)	K_2 (g/mg min)	q_e .cal (mg/g)	R^2
Cu(II)	50	0.0650	90.90	0.986
Fe(II)	50	0.0657	90.90	0.993
Cr(III)	50	0.091	90.90	0.999
Cd(II)	50	0.0720	90.90	0.999

From above figures and tables the data of the present study is concluded that slopes and intercepts of plots t / q_t versus t were used to calculate the pseudo second-order rate constants k_2 and q_e . The straight lines in plot of t / q_t versus t Figure 3.37-3.40 show good agreement of experimental data with the pseudo second-order kinetic model. Table 3.33 lists the computed results obtained from the pseudo second-order kinetic model. The correlation coefficients for pseudo second-order kinetic model obtained were greater than 0.986 for all metals ion concentrations. The calculated q_e values also agree very well with the experimental data. These indicate that the adsorption system studied belongs to the second order kinetic model.

3.4.3 The Intra-particle Diffusion Model

The intra-particle diffusion model is expressed as equation 2.10 and 2.11. Intra-particle diffusion model indicating that two or more steps take place. The first, sharper portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where Intraparticle diffusion is rate controlled. The third portion is the final equilibrium stage where Intraparticle diffusion starts to slow down due to extremely low adsorbate (metal ions) concentrations in the solution. In general, the slope of the line in stage two is called as intra-particle diffusion rate constant, K_p . Studies were undergone, calculated the intra-particle diffusion constants for adsorption of metal ions on MLP and presented in tables 3.34-3.37 and figures 3.41-3.44:

Table 3.34 Intraparticle diffusion of Cu (II) at different time intervals (initial concentration 50 mg/L, adsorbent dose 0.6g/L, initial pH 4.5).

Exp.No.	q_t (mg/g)	$t^{(1/2)}$
1	49.91	3.87
2	56.73	5.47
3	64.33	6.70
4	70.51	7.74
5	72.95	8.94
6	79.15	10.00
7	81.87	10.95

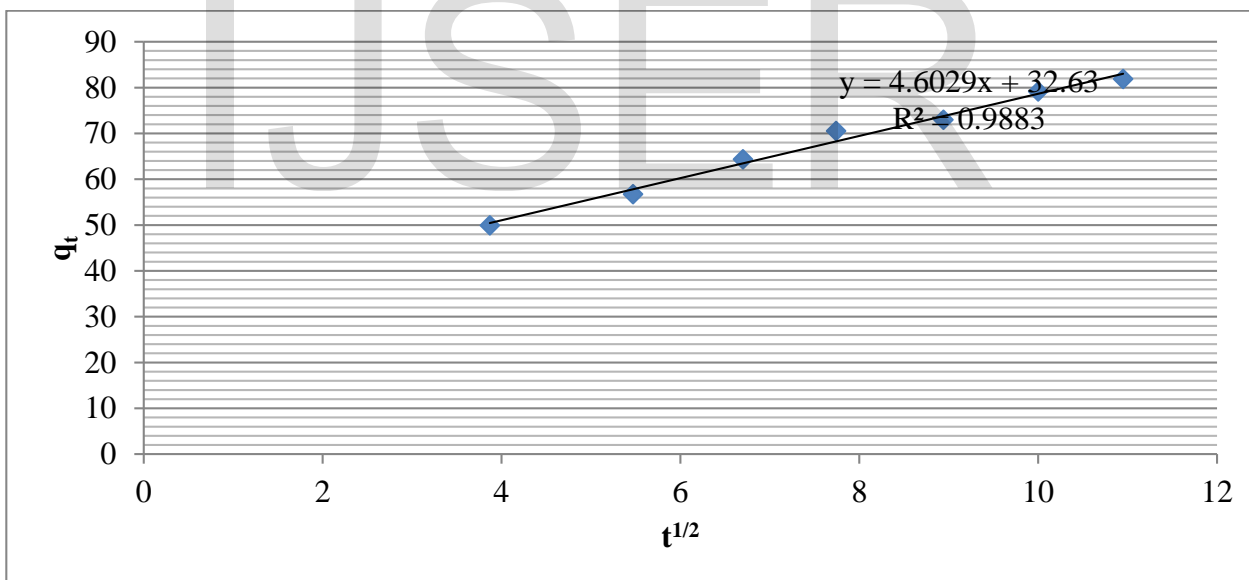


Fig .3.41. Intraparticle diffusion of Cu (II) at different time intervals (initial concentration 50 mg/L, adsorbent dose 0.6g/L, initial pH 4.5).

Table 3.35. Intraparticle diffusion of Fe (II) at different time intervals (initial concentration 50 mg/L, adsorbent dose 0.6g/L, initial pH 4.5).

Exp.No.	q_t (mg/g)	$t^{(1/2)}$
1	48.13	3.87
2	58.93	5.47
3	64.77	6.70
4	69.93	7.74
5	71.60	8.94
6	78.50	10.00
7	81.96	10.95

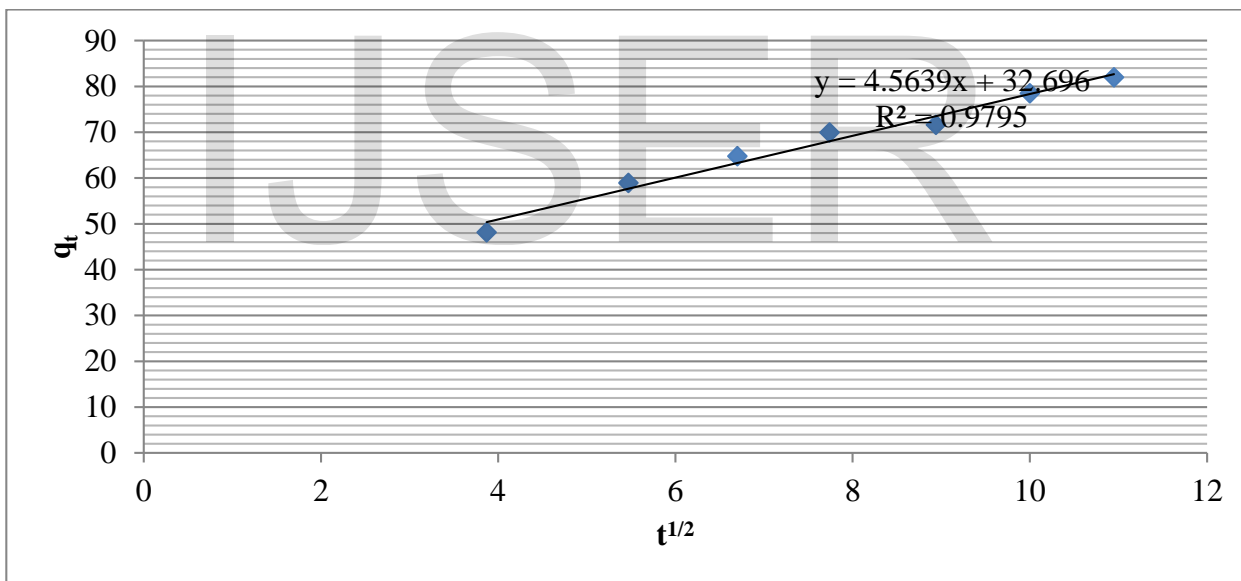


Fig. 3.42. Intraparticle diffusion of Fe (II) at different time intervals (initial concentration 50 mg/L, adsorbent dose 0.6g/L, initial pH 4.5).

Table 3.36 Intraparticle diffusion of Cr (III) at different time intervals (initial concentration 50 mg/L, adsorbent dose 0.6g/L, initial pH 4.5).

Exp.No.	q_t (mg/g)	$t^{(1/2)}$
1	51.93	3.87
2	63.93	5.47
3	70.55	6.70
4	75.67	7.74
5	78.21	8.94
6	81.10	10.00
7	82.57	10.95

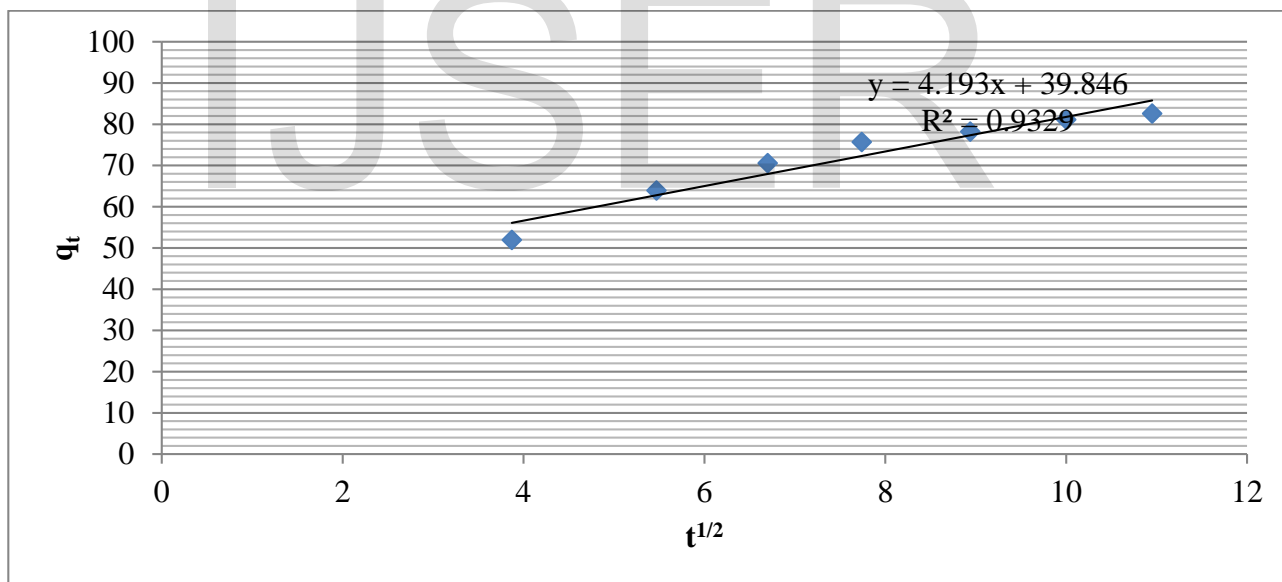


Fig.3.43. Intraparticle diffusion of Cr (III) at different time intervals (initial concentration 50 mg/L, adsorbent dose 0.6g/L, initial pH 4.5).

Table 3.37. Intraparticle diffusion of Cd (II) at different time intervals (initial concentration 50 mg/L, adsorbent dose 0.6g/L, initial pH 4.5).

Exp.No.	q_t (mg/g)	$t^{(1/2)}$
1	47.81	3.87
2	59.23	5.47
3	67.15	6.70
4	72.47	7.74
5	74.80	8.94
6	79.13	10.00
7	81.70	10.95

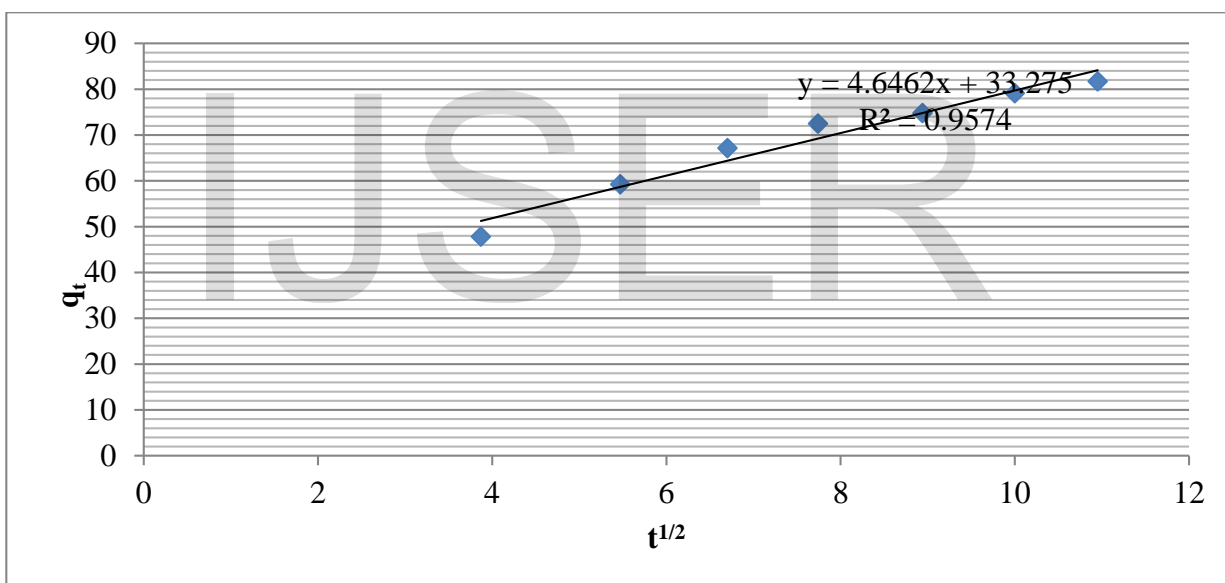


Fig.3.44. Intraparticle diffusion of Cd (II) at different time intervals (initial concentration 50 mg/L, adsorbent dose 0.6g/L, initial pH 4.5).

Table 3.38 Comparison of Intraparticle diffusion rate constants, and correlation coefficients for initial concentrations.

Intraparticle diffusion			
Metal ion	Initial con.(mg/L)	$k_p(\text{mg/g min}^{1/2})$	R^2
Cu(II)	50	4.602	0.988
Fe(II)	50	4.563	0.979
Cr(III)	50	4.193	0.932
Cd(II)	50	4.646	0.957

The Figure (3.41-3.44) show a plot of the linearized form of the intra-particle diffusion model at all metal ions concentrations were studied, indicates the external surface adsorption (stage 1) is completed before 15 min., and then the stage of intra-particle diffusion control (stage 2) is attained and continuous from 15 min to 60 min. Finally, equilibrium adsorption (stage 3) starts after 60 min. the Copper (II), Iron (II), chromium (III) and Cadmium (II) is slowly transported via intra-particle diffusion into the particles and is finally retained in the micropores. In general, the slope of the straight line for all metal ions intra-particles diffusion in stage 2 is called as intra-particle diffusion rate constant k_p .

4. CONCLUSION AND RECOMMENDATION

Adsorption of Cu (II) Fe (II), Cr (III) and Cd (II) ions on a non-conventional plant biosorbent mango leaf powder (MLP) was developed from mature leaves of mango and the adsorption characteristics were evaluated. The following conclusions were drawn based on the investigation of Cu(II) Fe(II),Cr(III) and Cd(II) adsorption by MLP: The optimum contact time for the maximum adsorption capacity of all metal ions are 120 minutes by using MLP as adsorbent. The metal uptake of Cu (II), Fe (II), Cr (III) and Cd (II) on MLP decreased with increasing MLP dosage.

The adsorption efficiency of metal ions on MLP increased with increasing metal ion concentration. The maximum adsorption capacity of Cu(II) Fe(II),Cr(III) and Cd(II) on MLP was 213.6, 241.25, 237.5 and 227.5 mg/g respectively which is obtained by 0.4 g/L MLP dosage, 100 mg/L Cu(II) Fe (II), Cr (III) and Cd (II) concentration and a pH of 4.5 Higher adsorption efficiency of Cu(II) Fe(II),Cr(III) and Cd(II) on MLP was observed at higher temperatures. The experimental data for the adsorption of Cu (II) Fe (II), Cr (III) and Cd (II) on MLP fits well for the Freundlich isotherm.

Adsorption is a strong choice for removal of heavy metals from synthetic water. The adsorption process of this study shows that that it is an exothermic and also follows a pseudo-second-order kinetic than a pseudo-first-order one. The adsorption of Copper, iron, Chromium and cadmium on mango leaf powder reached equilibrium in 60 minutes. Mango leaf powder showed high adsorption capacities and it can be successfully used for treatment of Copper, iron, Chromium and cadmium containing wastewater. Since this method involves cheapest (less capital cost) and highly efficient, also practically feasible for developing countries. The regeneration of mango leaf powder is not essential because it is an easily available material. The results of this investigation will be useful for the removal of metals from synthetic water contain heavy metal ions.

Further research work is recommended to identify and quantify the potential source of those major and heavy metals to the synthetic water and the same instruments are not functional. The present study strongly recommends the people by using mango leaf powder removing the metals ions drink the synthetic water. Continues monitoring is important to have up to dated information regarding metal concentration in water.

5. References

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Appendix 1 Absorbance of standard solution prepare for metals determination

Metal	concentration of standards (ppm)	absorbance
Cu	5	0.067
	10	0.073
	15	0.238
	20	0.534
	25	0.691
Fe	5	0.0214
	10	0.0632
	15	0.1450
	20	0.3240
	25	0.6021
Cr	5	0.0190
	10	0.215
	15	0.567
	20	0.745
	25	0.896
Cd	5	0.026
	10	0.054
	15	0.082
	20	0.270
	25	0.585

Appendix2 Langmuir isotherm of mass of powder, Absorbance, mass of adsorbent and q_e

Metal ion	mass of powder (mg)	Absorbance	mass of adsorbent (mg/L)	q_e (mg/mg)
Cu (II)	14	0.105	4.7	0.33
	12	0.163	4.5	0.37
	9	0.290	4.1	0.45
	7	0.478	3.6	0.51
	5	0.592	3.27	0.65
	4	0.684	3	0.75
Fe (II)	14	0.104	4.6	0.33
	12	0.172	4.38	0.36
	9	0.283	3.99	0.44
	7	0.385	3.60	0.51
	5	0.509	3.18	0.63
	4	0.600	2.86	0.72
Cr(III)	14	0.162	4.65	0.33
	12	0.273	4.4	0.36
	9	0.432	4	0.44
	7	0.562	3.77	0.54
	5	0.728	3.4	0.68
	4	0.893	3.0	0.75

	14	0.049	4.8	0.34
	12	0.097	4.6	0.38
	9	0.235	4	0.45
Cd (II)	7	0.396	3.5	0.51
	5	0.489	3.17	0.63
	4	0.574	2.85	0.71

Appendix3 Freundlich isotherm of mass of powder, Absorbance, mass of adsorbent and q_e Cu (II), Fe (II), Cr (III) and Cd (II)


Metal ion mass of powder (mg) Absorbance mass of adsorbent (mg/L) q_e
 (mg/mg)

	7	0.0352	7.39	1.056
	6	0.0441	7.37	1.22
	5	0.0524	7.34	1.45
Cu (II)	4	0.0613	7.32	1.83
	3	0.0694	7.29	2.43
	2	0.0752	7.28	3.64

	7	0.029	7.39	1.056
	6	0.034	7.38	1.23
	5	0.045	7.34	1.47
Fe (II)	4	0.051	7.32	1.83
	3	0.058	7.29	2.43
	2	0.067	7.26	3.63

	7	0.086	7.39	1.055
	6	0.0529	7.38	1.23
	5	0.0576	7.37	1.47
Cr(III)	4	0.0624	7.36	1.84
	3	0.0651	7.35	2.45
	2	0.0701	7.34	3.67

	7	0.036	7.36	1.05
	6	0.042	7.34	1.22
	5	0.051	7.31	1.42
Cd (II)	4	0.072	7.23	1.80
	3	0.093	7.15	2.38
	2	0.121	7.00	3.5



Appendix 4 Thermodynamics of Temperature, Absorbance, K_{ad} and C_e Cu (II), Fe (II), Cr (III) and Cd (II)

Metal ion	Temp.	Absorbance	K_{ad} (mg/g)	C_e (mg/L)
Cu (II)	30	0.091	118.3	2.66
	45	0.060	120.6	1.75
	60	0.035	122.45	1.02
Fe (II)	30	0.071	118.67	2.53
	45	0.043	121.2	1.53
	60	0.032	122.15	1.14
Cr (III)	30	0.103	119.3	2.25
	45	0.064	121.5	1.4
	60	0.046	122.5	1
Cd (II)	30	0.098	115.8	3.67
	45	0.065	118.9	2.43
	60	0.028	122.5	1

Appendix5 pseudo first-order of Absorbance and q_t Cu (II), Fe (II), Cr (III) and Cd (II)

Absorbance				q_t (mg/g)		
Cu (II)	Fe (II)	Cr (III)	Cd (II)	Cu (II)	Fe (II)	Cr (III)
0.686	0.591	0.861	0.569	49.91	48.13	51.93
47.81						
0.546	0.410	0.532	0.486	56.73	58.93	63.93
59.23						
0.390	0.312	0.350	0.259	64.33	64.77	70.55
67.15						
0.263	0.225	0.210	0.174	70.51	69.93	75.67
72.47						
0.214	0.197	0.140	0.138	72.95	71.6	78.21
74.8						
0.086	0.087	0.061	0.067	79.15	78.5	81.1
79.13						
0.031	0.023	0.021	0.026	81.87	81.96	82.57
81.7						