Peer Reviewed and Referred Journal

# Application of Neem Leaf Powder (Bio-waste) For Removal of Cd(II) ions From Aqueous Solution.

**Meena Kunwar Rathore, Poonam Sharma, Pushplata Salvi, Varsha Dayma, Prabhat k. Baroliya and Ajay K. Goswami***

**Department of Chemistry**

**Mohanlal Sukhadia University**

**Udaipur Rajasthan**

**India**

Emails: rathoremeena1107@gmail.com, poonamsharma128@gmail.com, pushplataudr@gmail.com, varshadayma12@gmail.com ,

email: akumargoswami@rediffmail.com

## Abstract

This paper presents adsorption capacity of bio adsorbent. Many adsorbents were used for removal of heavy toxic metals but use of bio- adsorbent for removal of toxic heavy metals from aqueous solution investigated. Neem leaf powder used as a bio- waste for removal of Cd(II) ions. For this adsorption process some parameters were tested such as concentration of Cd(II) ions, quantity of adsorbent, pH,stirring time of solution and effect of temperature at optimum conditions. Langmuir and Freundlich adsorption isothermsmodels are best fitted. The maximum Cd(II) removal was 502.20 mg. FTIR,SEM,XRD technique were used to study adsorption process.Thermodynamic parameters such as entropy, enthalpyand Gibbs free energy calculated. The results show that neem leaf has good capacity for removal of Cd ions (97-98%).

**Keywords:** Neem leaf; Cd(II); Langmuir isotherm; Freundlich isotherm.

## Introduction

In the present time we are facing so many problems but the major problem is environment pollution. Environment pollution occur due to discharge of heavy toxic metals from industries and any other reason.Due to the accumulation and persistent nature of these heavy metals there is a serious damage occur and these heavy metals cause serious problems to humans,animals and plants.

There are so many toxic metals such as Hg, Cr, As, Zn and Cd is one of them which cause adverse effect. Cadmium is toxic heavy metals which causes adverse effects on human health. Exposure of cadmium causes lung cancer, and also kidney problems. After long time in environment this metal contaminated environment and harm animals and plant also.In present situation there is a need of some techniques to removal of these toxic metals. There are so many techniques and methods are available like precipitation, filtration, coagulation and many more but these methods are not sufficient because the results are not good and methods are time consuming, costly process. So we have to use adsorption process for removal of toxic metals because adsorption process gives better results and this is reliable process. For this adsorption process different adsorbent were used such as marble slurry. Fly ash, clay and many other bio- waste (1-6) and they give good results but problem was that these adsorbent were non degradable so we need to again disposal of them and again problem arises the same that again they create pollution, so this time we need to use some better ideas for this purpose and this is the new thing that we work on it.

We used bio- waste neem leaf powder(7-8)) which is very easily available, cheap, environment friendly, low cost adsorbent and the adsorption results are so good ( 97-98%) and the best thing is bio- waste is degradable so there is no need to disposal and the best part of these study is that neem leaf is reusable. Therefore, we use neem leaf powder as bio adsorbent for removal of Cd (II) ions from aqueous solution.

## Materials and Methods

## Apparatus

To investigate the adsorption process of toxic metal onto the surface of bio- waste AAS (Atomic Absorption Spectrophotometer) (Elico SL168), XRD, SEM technique were used.

Presence of functional group were detected by FTIR. PH meter and auto magnetic stirrer also used for the study.

## Materials

For these study we used powder of mature neem leaves as a bio-waste. These neem leaves were collected from nearby regions of Udaipur, Rajasthan and washed so many times to remove some soluble impurities, with double distilled water and dried them in oven for 48 hr. When neem leaves became dried and then crushed into a fine powder with the help of grinder to get fine powder of neem leaves.

These Neem leaf powderwithout colour and turbidity was used as an adsorbent. The wet powder of neem leaves kept in desiccator to dry and then NLP was stored in glass bottles for further use. Cadmium was used as $Cd(NO_3).4H_2O$ solution (stock solution).

Neem plant is easily available and this plant have medicinal property. Each part of neem plant has good adsorption capacity like its bark, fruit, roots and leaves. But in this chapter we use neem leaves as bio-adsorbent.

We get the results with different different neem leaves such as- neem leaves collected in summer, winter and in rainy seasons. we used these neem leaves in various types like new fresh neem leaves, mature neem leaves and we get good results.

## Methods

## Characterization

Characterization of adsorbent (neem leaf powder) was done with the help of FTIR and XRD technique and also SEM (scanning electron microscopic) was used for the surface study of adsorbent.

1. The particle size of neem leaf powder was determined by sieving process and these process was done in geology department, Udaipur.
2. Scanning electron microscopic (SEM) was taken by using (SEM; JEOL, JSM-6100, JAPAN, SAIF) Chandigarh. ( Fig 1 )

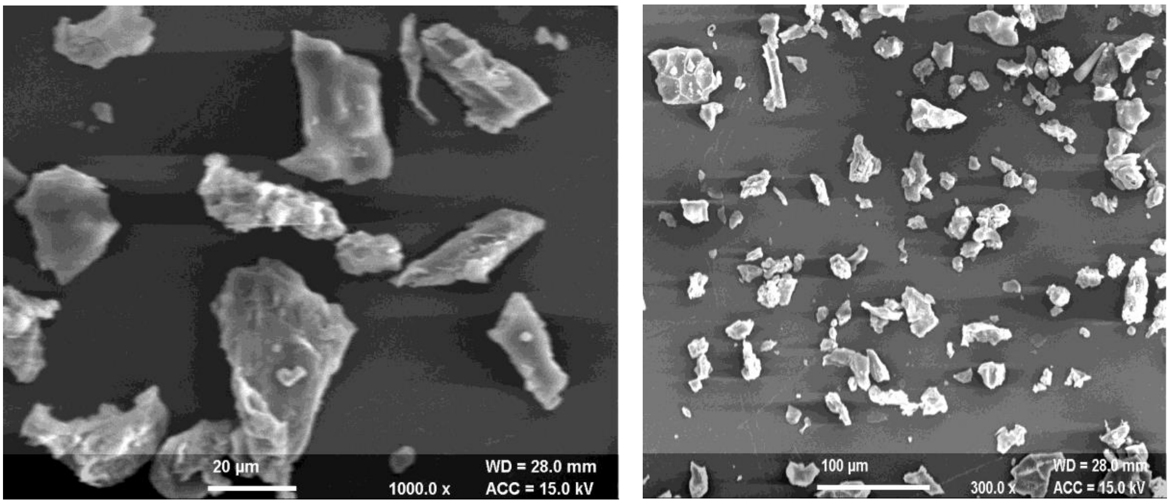



**Figure 1 (a) and (b)- (SEM) of neem leaf powder ( before adsorption process).**

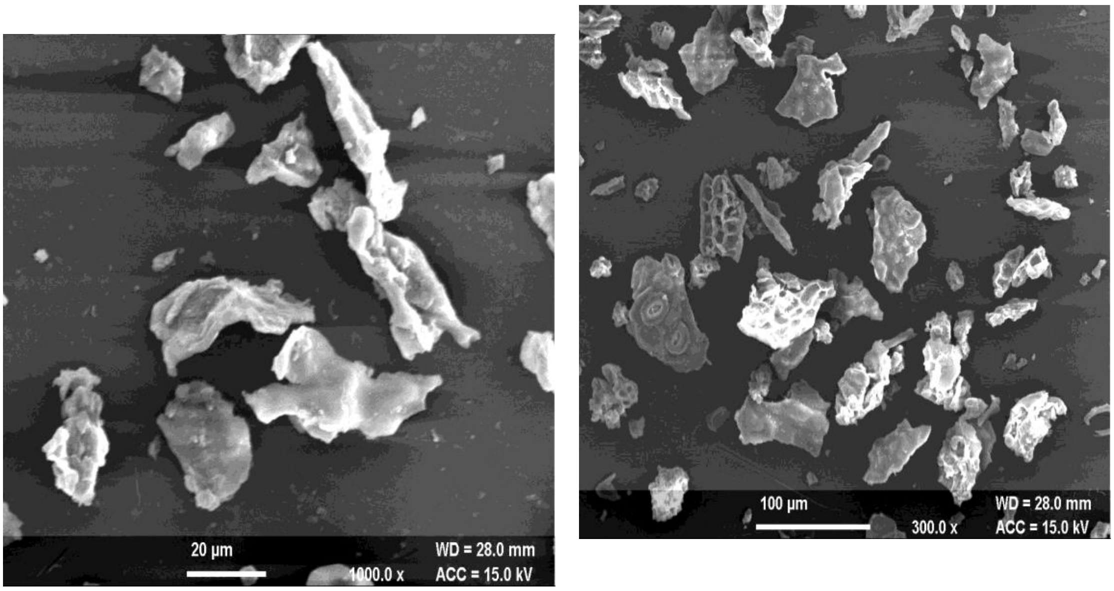



**Figure 1 (c) and (d). (SEM) of neem leaf powder (after adsorption).**

Figure 1(a ,b and c,d) representing the adsorption between neem leaves and metal Cd (II) ions. From this fig. we can say that at the surface of neem leaf some weak interactions ( bonding ) occur between neem leaves and Cd ions because Cd ions has positive charge in form of ( $Cd^{+2}$) . From figure 1 we can say that adsorbent have porous structure so it can adsorb metals.

## XRD Spectrum

To know more about the structure of neem leaf powder and adsorption process we also studied using X-ray diffractograms (XRDs) which obtained from an X-ray diffracto-meter, (Physics lab, MLSU) Udaipur. For the X-ray diffraction study Cu was used as a source, Ni as a filter media and K radiation maintained at 1.52 A˚, (2y) was kept at 10– $90^0$. The intensity of peak shows the value of 2y, where Bragg's law is used.

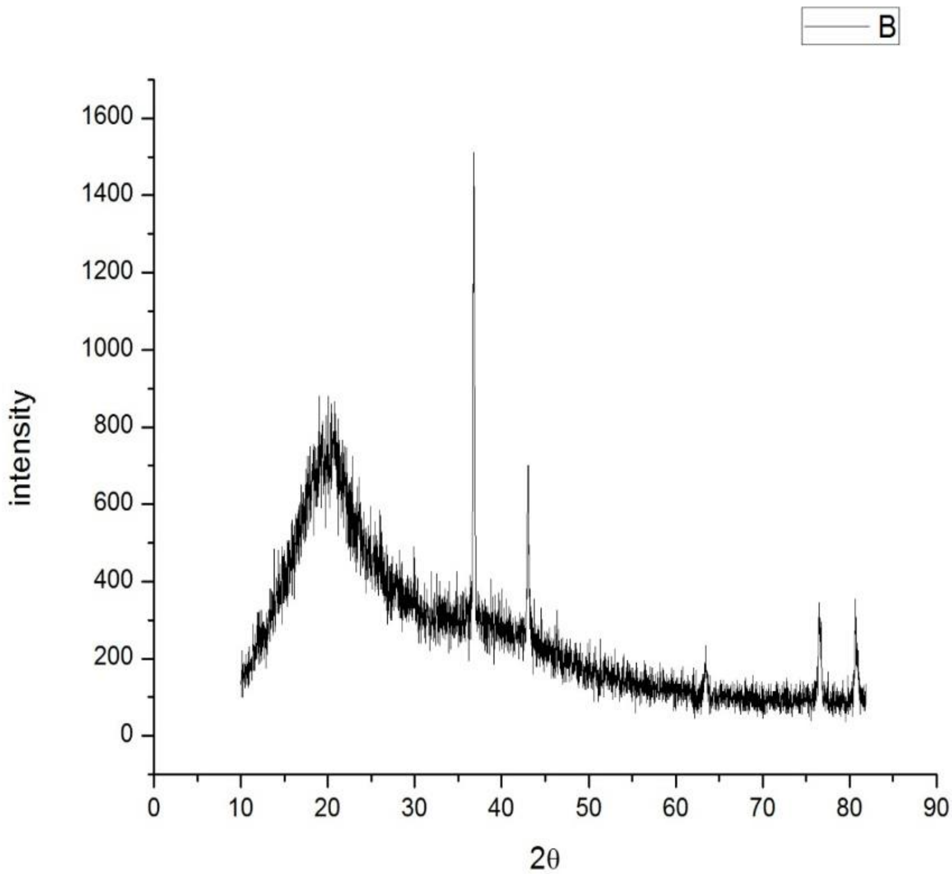



**Figure 2 (a) . XRD study of neem leaf powder (before adsorption).**

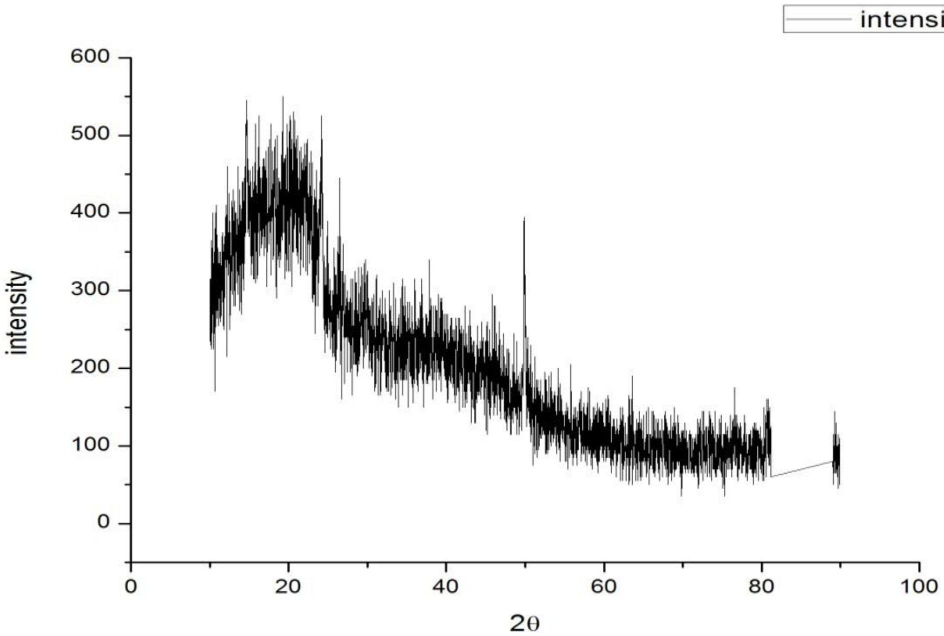


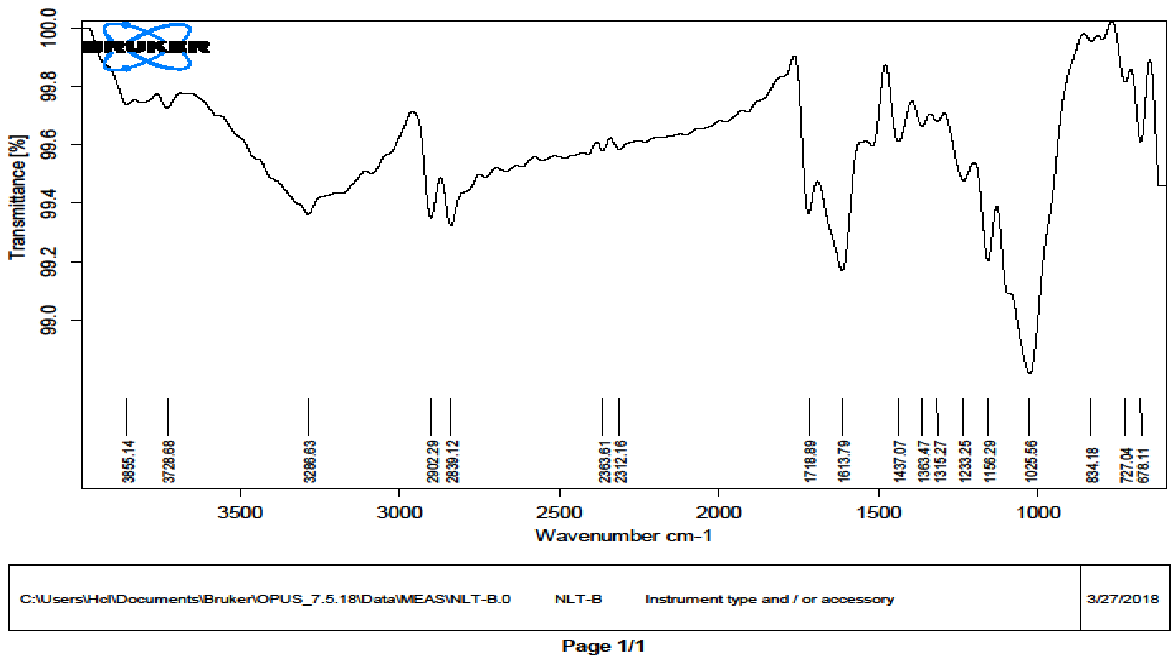

**Figure 2 (b). XRD study of neem leaf powder (after adsorption)**

Figure 2 show XRD spectrum of adsorption.

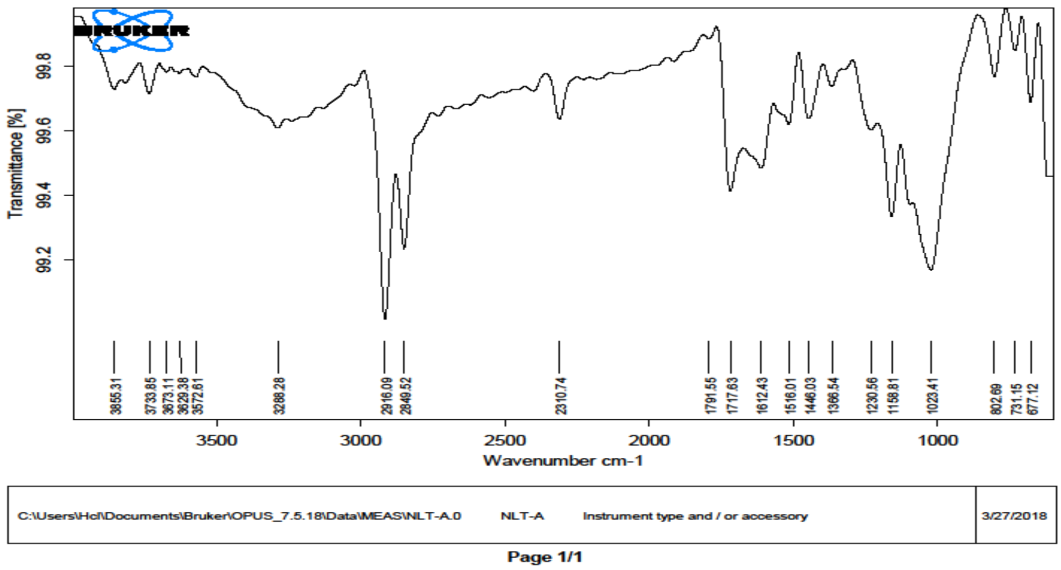
In (fig 2a ) the intense peak at $35^0$show the presence of metal in solution and in fig ( 2b ) the dis - appearance of peak show that adsorption process occur and metal are bound on adsorbent surface so free metals are not available in solution therefore peak were disappeared.

## FTIR

**Figure 3** shows FTIR spectra of adsorption process.




## 3(a) - FTIR SPECTRA OF NLP ( before adsorption)




## 3 (b) - FTIR Spectra of NLP ( after adsorption)

Fig ( 3a) shows some adsorption peaks which shows that in neem leaf some function groups are present. Peak around 3500-3600 shows the presence of –OH group, carbonyl group peak at 1690-1700 and also some aliphatic and aromatic group containing C-C and C-H and C=C bonding, as we know that plant contain cellulose, hemicellulose, lignin as plant material so these groups shows their peaks.

In fig ( 3b) some peaks shifted slightly so we can say that adsorption occur.

## Experimental Process

In the process of adsorption, we use Cd ion solution and for that we use cadmium nitrate. The concentration range of solution were 200-2000 mg/ liter. For each experiments we use some parameters and optimize every solution at each parameter and then filtered it and filtrate was analyzed by AAS.

The percent adsorption of Cd(II) on neem leaf powder has been calculated using Eq. (1) and (q) was calculated by Eq. (2).

$$\text{Adsorption (\%)} = C_i - C_r/C_i \times 100 \qquad (1)$$

$$q_e = [(C_i - C_r)/m]V \qquad (2)$$

where-
$C_i$ is initial concentration of Cd(II),
$C_r$ is residual concentration of Cd(II).
V is volume of suspension and m is weight of the adsorbent.

## Results And Discussion

## Effect of quantity of Neem Leaf Powder (Bio-waste)

Quantity of bio-waste plays an important role in adsorption process. Fig 1 clearly shows that as well as quantity of adsorbent increases adsorption also increases because surface area increases. we use different quantity of adsorbent and check the results. As we can say that there is maximum adsorption reached when quantity of adsorbent was 1200mg, here the adsorption of metal was 97-98%. So, 1200 mg adsorbent quantity use for further parameters.

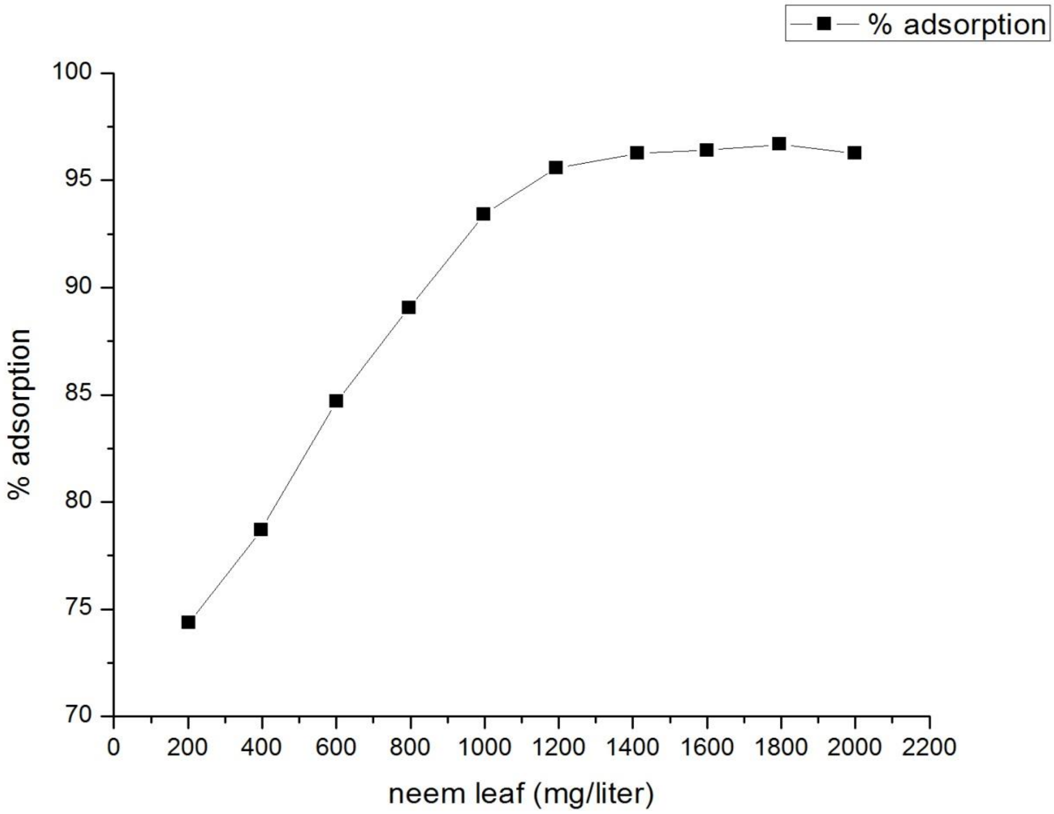



**Fig. 1. Effect of quantity of neem leaf powder on adsorption of Cd(II)ions.**

## Effect of Metal (Cd) ion concentration-

We prepare different -different concentration solution of metal Cd from 100 mg/liter to 1200 mg/liter). Fig. 2, shows thatmaximum adsorption done at 100-200 mg/liter and after that adsorption rate decreases. these happens due to minimum bonding site availability on the surface of adsorbent.

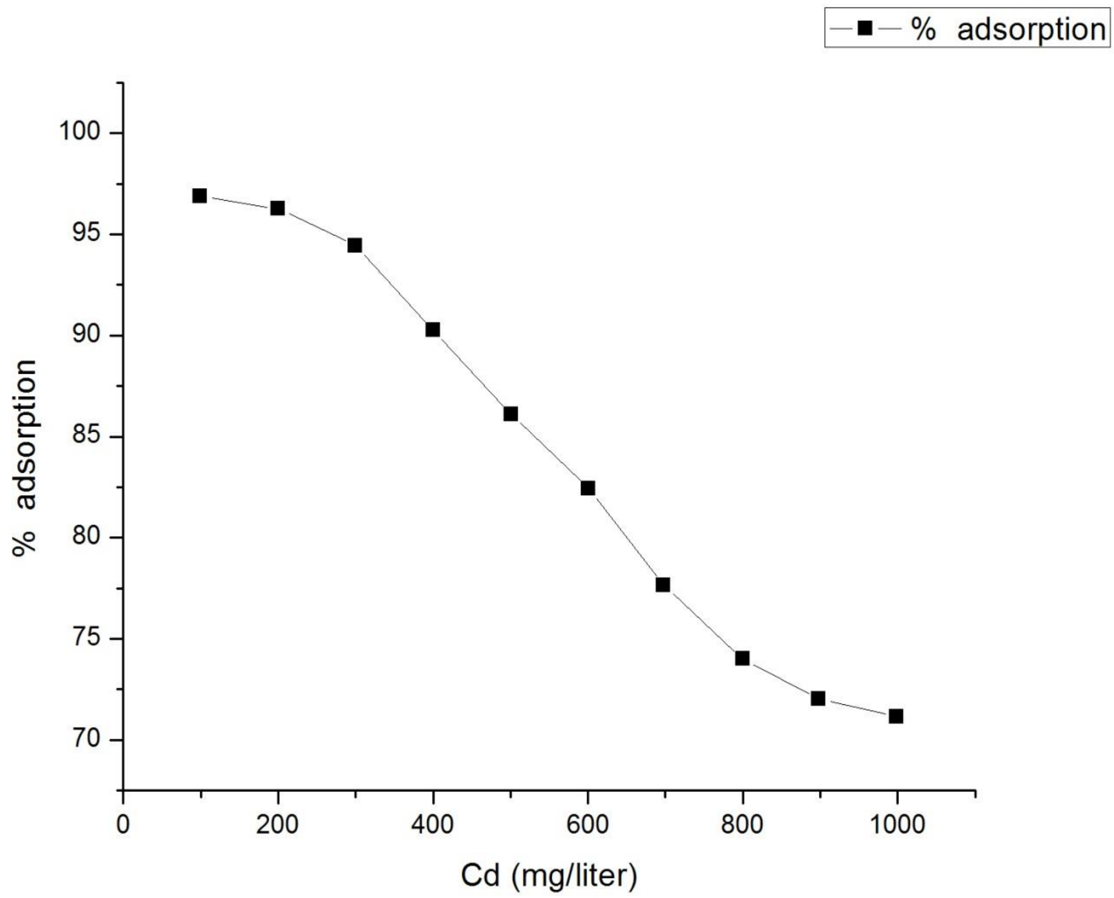



**Fig. 2. Effect of Cd(II) concentration on adsorption**

## Effect of pH

The pH value of solution plays very important role. At lower and high pH adsorption decreases but when we adjust pH at 7 then we get better results, Therefore for further experiment process PH value fix at the 7.

## Effect of Stirring Time On Adsorption.

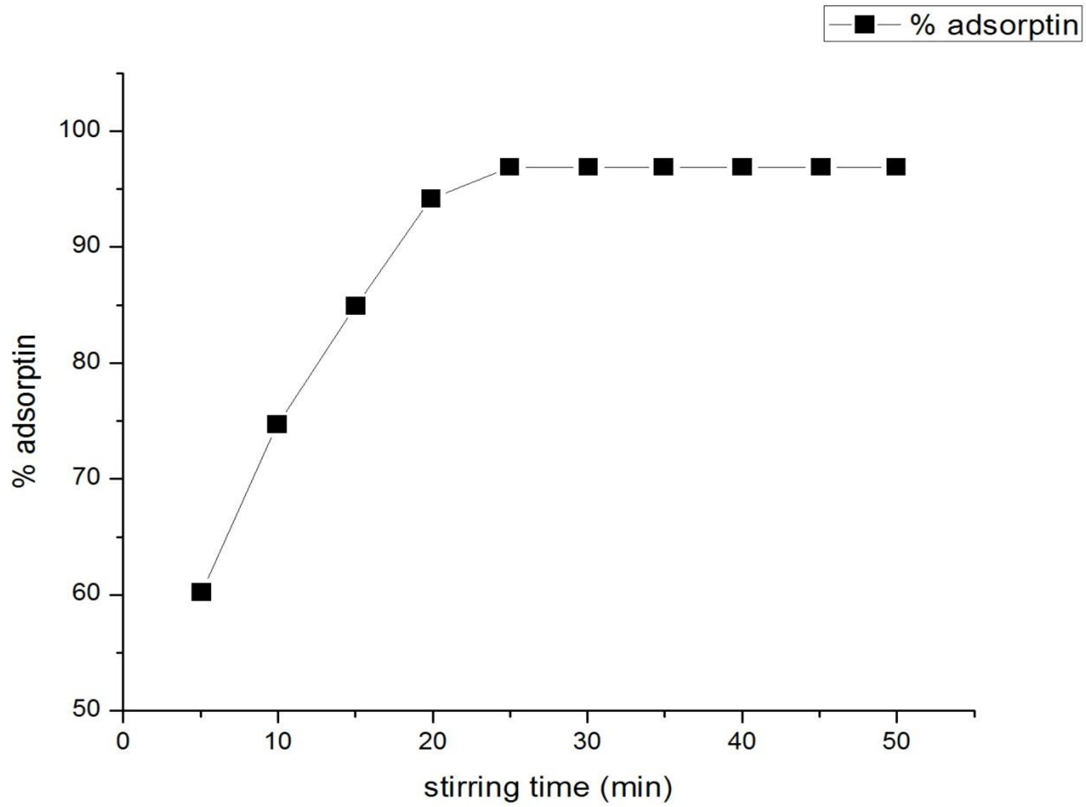



**Fig. 3. Effect of stirring time on adsorption process.**

Fig 3 shows that we get different results when we change the stirring time from 10 min to 2hr. Initially adsorption increases and after that it becomes constant. Maximum adsorption occurs when contact time is 30 min. So, this is the optimum stirring time where we get maximum adoption.

## Kinetics of the adsorption process

Kinetics of adsorption of metal ion onto bio – waste surface was investigated by Morris–Weber equation.

The equation may be written as:

$$qt = Kd(t)^{1/2} \qquad (3)$$

where -

qt is amount of Cd(II) ions adsorbed (mg/g) at time t,

$t^{1/2}$ is square root of different stirring time and

Kd is rate constant.

Two distinct regions were observed when qt was plotted against $t^{1/2}$.

As shown in Fig. 4,

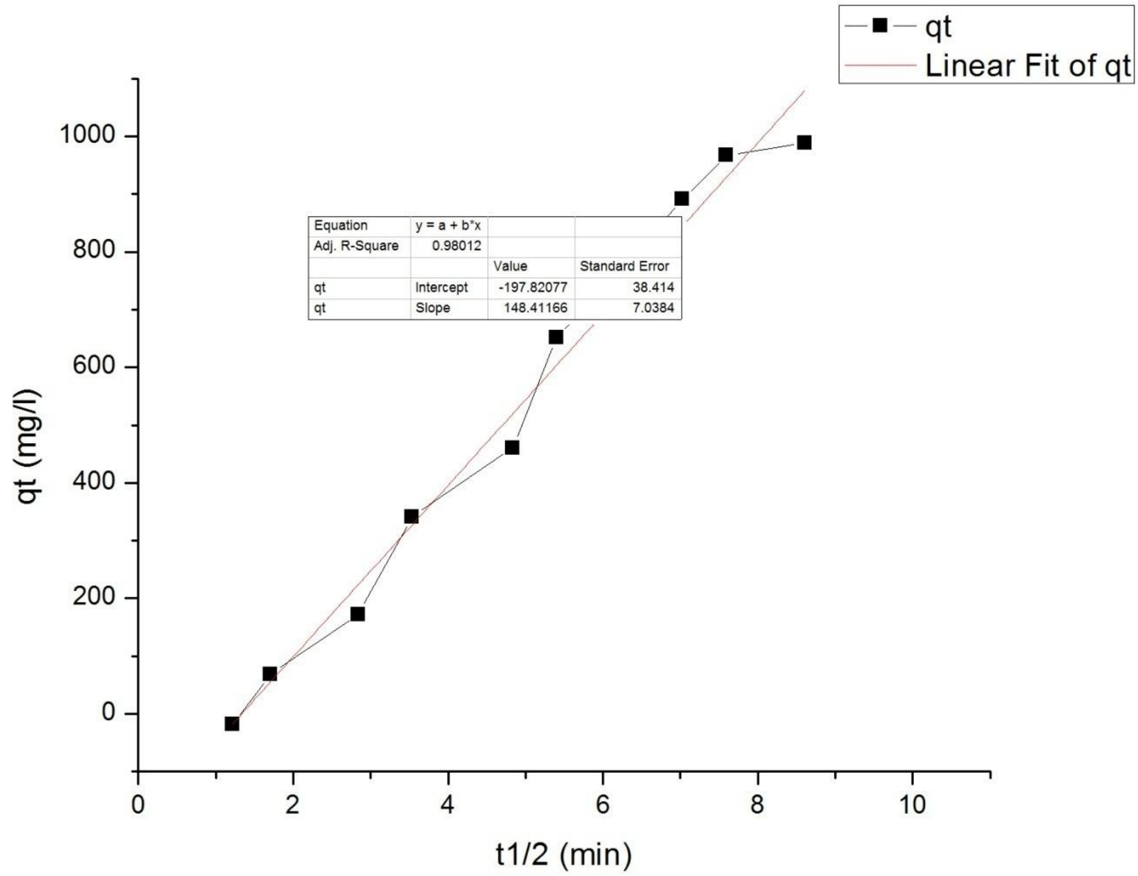



**Fig. 4. Plot of the quantity of Cd(II) ions (qt) adsorbed against square root of time**

The linearity of graph shows the effect of distribution.firstpart shows line diffusion effect and second part occur because of the intraparticle circulation. Rate constant Kdshow motility of Cd(II) ionsconcentration towards the neem leaf powder surface area.

## Isotherms-

Here we apply both adsorption isotherms on metal ion solution. We prepared different concentration solution of metal and investigate these process and we found that Langmuir and Freundlich isotherms followed at room temperature.

## Freundlich Isotherm-

The Freundlich equation -

$$\log qe = \log Kf + 1/n \log Ce \qquad (4)$$

Where –

qe (mg/g) quantity of Cd(II) ions adsorbed,

Kf isthe indicator of adsorption capacity,

1/n is intensity ofthe adsorption and

Ce is equilibrium concentration of Cd(II) ion in mg/L.

In fig (5) we get a linier graph. When we plotted graph between log Ce and log qe. Here we calculate the value of n and Kf by slope and intercept. We can say that Freundlich graph is best fitted to adsorption because we get n is greater than 1 which means adsorption process is supportive.

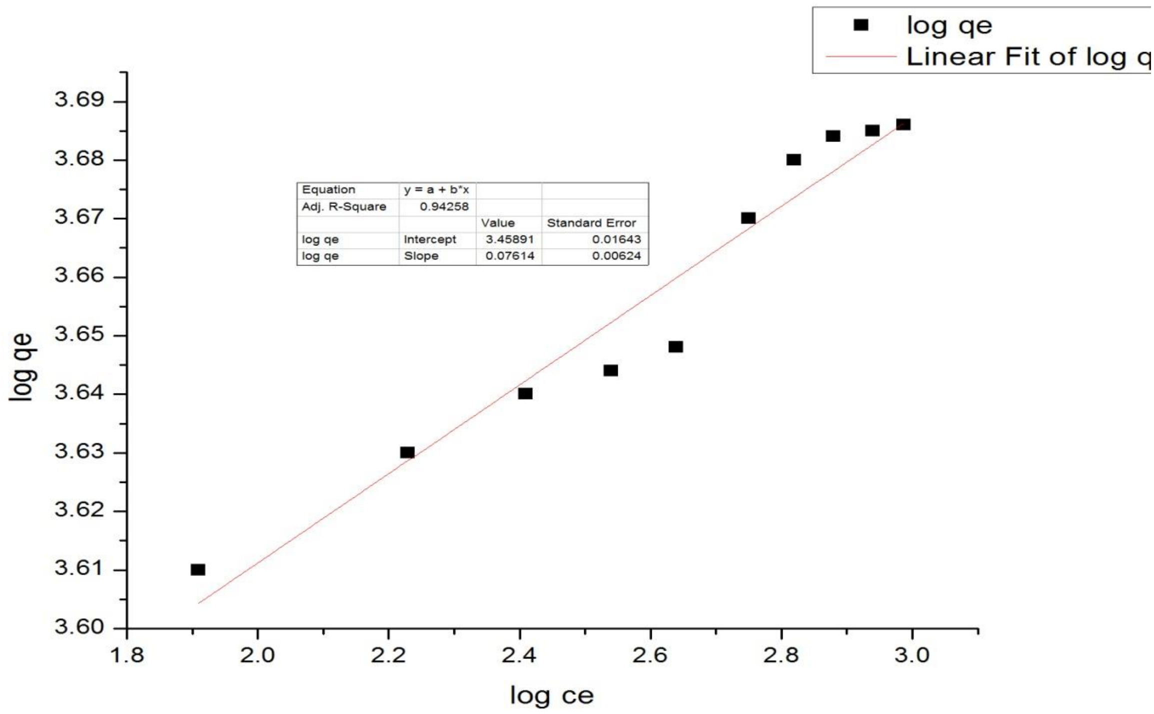



**Fig. 5. Freundlich graph for Cd(II) ions adsorption by neem leaf powder (adsorbent).**

## Langmuir Isotherm-

To know more about adsorption Langmuir adsorption isotherm also applied and we get results. Langmuir isotherm -

$$Ce/qe = Ce/qm + 1/qm\ b \qquad (5)$$

where -

Ce is equilibrium concentration of adsorbent in (mg/L),

qm is adsorption capacity in (mg/g),

1/b is free energy of adsorption,

qe is amount of Cd(II) ion adsorbed at equilibrium time.

In fig (6) we obtain a linier line when we plotted graph between ce and ce/qe which indicates the application of Langmuir isotherm. This adsorption isotherm indicates the adsorption process occur. Cd (II) ion adsorb on the neem leaf surface. Here qm and b calculated with the help of intercept and by the slope.

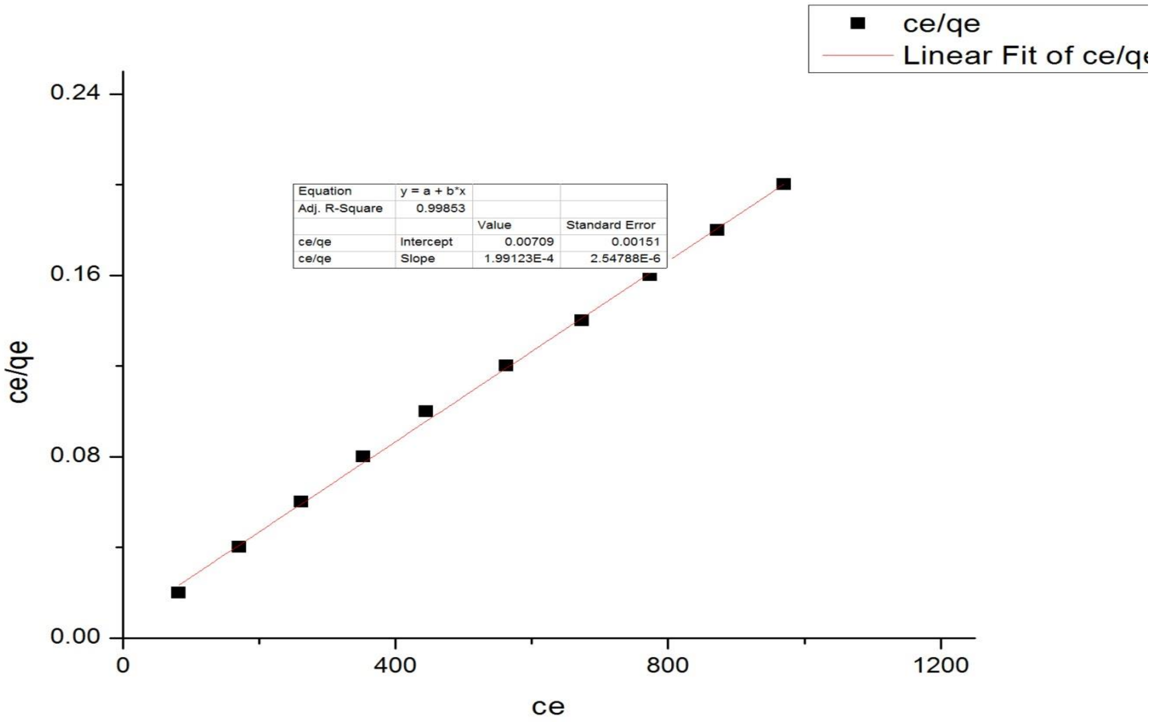



**Fig. 6. Langmuir plot for Cd(II) ions adsorption by neem leaf powder.**

## Thermodynamics Of Adsorption Process-

For calculating purpose, we have to use some formula.

Gibbs free energy calculated by-

$$\Delta G = RT \ln K_D \qquad (6)$$

Where-

$K_D$ is equilibrium constant. we get value of this by-

$$K_D = qe/Ce \qquad (7)$$

where qe and Ce are concentrations of cadmium.

$$\Delta G = \Delta H - T\Delta S \qquad (8)$$

$$\ln K_D = -\Delta H/RT + \Delta S/R \qquad (9)$$

Where

T is temperature,

H is enthalpy

S is entropy

R is gas constant

We get value of $-\Delta H/RT$ and $\Delta S/R$ were $-27.3$ and 3.953, respectively. $\Delta H$ = 226...97 kJ/mole $\Delta S$ = 32.86 J/(Mole-K) $\Delta G$ = $-9.74$ kJ/mole. Here, positive value of enthalpy indicates that process is endothermic and positive entropy shows that adsorption is irreversible and negative value of Gibbs free energy shows that adsorption is spontaneous process.

## Conclusion-

From the present study we can concluded that-

1. Bio waste is better option that we have to handle all the problems that created by heavy toxic metals.
2. Bio – waste is easily available and eco- friendly.
3. We get better results with neem leaf powder (97-98%) adsorption.
4. For this study we used Langmuir and Freundlich isotherms which are best fitted.
5. This process is endothermic, spontaneous in nature.
6. The best part of this study iswe used bio-waste neem leaf powder as adsorbent which is bio-degradable and reusable so there is no necessary to degrade it.

   So. We can say that neem leaf powder as adsorbent have good adsorption capacity and it used as bio-waste for heavy toxic metals.

## Acknowledgement

Author Acknowledge Prof. A. K. Goswami and the staff of coordination chemistry lab, Chemistry department, MLSU, Udaipur. (Rajasthan) and thanks for SEM (Chandigarh), XRD (Physics lab), FTIR (chemistry lab, Udaipur).

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