

# A COMPARATIVE STUDY OF ADSORPTION ISOTHERMS OF $Pb^{2+}$ & $Cd^{2+}$ FROM AQUEOUS SOLUTION USING BIOSORBENT PREPARED FROM SEEDS OF CASUARINAS EUISETIFOLIA.

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**ABSTRACT:** Society gets suffered by soil, water & air pollution because of only transformation, development & industrialization. Industries discharges their throw away into the nearby source of water without giving treatment, which include a lot of destructive harmful components such as heavy metal ions, carcinogenic dyes, chemicals & oily matters. This is responsible for water pollution which is dangerous for aquatic life as well as remaining living things. At present water pollution by heavy metals has been a major concern for harsh damage to the surrounding & atmosphere also a bad effect on the health of people. Heavy metals are non degradable & once they gather within the body stay there for an extensive period. As heavy metals are utilized in the industry for different reasons, therefore heavy metals are one of the main pollutants of the industrial waste water. A range of techniques are existing to get rid of heavy metal ions from industrial waste water however adsorption by using adsorbent is most commonly used technique. Carbonised material of seeds of Casuarinas Equisetifolia activated by using 30% phosphoric acid can be verified as an excellent adsorbent for removal of  $Pb^{2+}$  &  $Cd^{2+}$  from its aqueous solution. Different factors are studied such as effect of amount of adsorbent, pH, temperature & time. 0.7 gm & 0.6 gm of activated carbon of Casuarinas Equisetifolia at temperature 50°C & 35°C at pH 4 & 6 gives best results i.e. 90% removal of  $Pb^{2+}$  &  $Cd^{2+}$  90.77%.

**Keywords:** Casuarinas Equisetifolia, Adsorption, Equilibrium and kinetic, Langmuir, Freundlich and Temkin.

## I. INTRODUCTION

Industrial waste water is full of different forms of contaminant in the form of inorganic & organic. It is extremely challenging to eliminate this pollutant; if we use methods other than adsorption then it will be costlier & time consuming (11). Heavy metals are ecologically very essential because they are noxious in nature & having terrible effects on living organisms including human beings. In industry there are several operations or steps are carried out through which  $Pb^{2+}$  &  $Cd^{2+}$  discharges into the waste water. The toxicological information about  $Pb^{2+}$  &  $Cd^{2+}$  has been well filed in literature & its existence in industrial waste water is at an elevated menace for the surroundings, atmosphere & public health (6-9). Hence, it is essential to put up more appropriate, economically cheaper & less time consuming procedure to keep away from the pollution cause by  $Pb^{2+}$  &  $Cd^{2+}$  release & to ease the hazards correlated to its existence in the surroundings (9-10). As talk about earlier the techniques which are accessible for elimination of heavy metals from industrial waste water are exchange, solvent extraction, oxidation, biodegradation, & adsorption and so on (7). But, adsorption is the most efficient & economical technique (11), by using less adsorbent also there is a possibility for recovery of adsorbent all the way through process of desorption & renewal of adsorbent (8). Activated carbon get ready from Casuarinas Equisetifolia treated by using 30% phosphoric acid is used to eliminate the  $Pb^{2+}$  &  $Cd^{2+}$  from the aqueous solution. Experimental data is utilized for study

of adsorption isotherms such as Langmuir, Freundlich and Temkin. Seeds of casuarinas equisetifolia is an agricultural waste material, after separating the seeds from plant can used for preparation of bio adsorbent.

## II. EXPERIMENTATION

Adsorption of  $Pb^{2+}$  &  $Cd^{2+}$  is carried out by using Digital pH Meter (Make: Equiptronics) Model EQ-610.

### **Preparation of 30% phosphoric acid treated activated carbon of seeds of Casuarinas Equisetifolia.**

In case of Casuarinas Equisetifolia plant needle shaped leaves as well as seeds can be used for the preparation of activated carbon. Seeds of Casuarinas Equisetifolia are sun dried for 4-5 days. Then it is washed down with distilled water to eliminate sludge impurity from it. In the 30% solution of phosphoric acid all the cut material immersed for all night with stable stirring for the period of this operation all the impurity present on the surface of seeds get removed. After this it is washed constantly with distilled water till the water shows neutral pH with the help of pH paper. Then cut pieces are dried in oven at temperature  $120^{\circ}C$  then carbonization process is carried out in muffle furnace in presence of inert medium nitrogen gas at temperature  $500^{\circ}C$  to  $600^{\circ}C$  for 6 Hrs. Then material is pulverized to convert into a fine powder, using sieve of particle size 0.063 mesh adsorbent is divided. Then adsorbent is stored into polythene air tight container to avoid contact with moisture.

### **2.1 Preparation of Adsorbate**

Aqueous solutions of various concentrations of  $Pb^{2+}$  (100, 200, 300 & 400 ppm) &  $Cd^{2+}$  (50, 100, 150 & 200 ppm) are prepared with the help of stock solution (1000 ppm) by using distilled water. The pH of solution was adjusted using 0.1 N HCl or NaOH solutions.

### **2.2 Batch Adsorption Studies**

To investigate the equilibrium point for adsorption of  $Pb^{2+}$  &  $Cd^{2+}$  onto carbonized powder of Casuarinas Equisetifolia Seeds, originally the quantity of metal ions present in known solution is worked out by titrating 50 ml of solution of metal ion with 0.01M EDTA solution, then 700 mg & 600 mg of adsorbent prepared from seeds of Casuarinas Equisetifolia were added into 50 ml solution of  $Pb^{2+}$  &  $Cd^{2+}$  respectively with concentration 100 & 50 ppm at room temperature for different time intervals. Continuous stirring was carried out by using a magnetic stirrer. Later for given time interval equilibrium concentration ( $C_e$ ) of the heavy metal ion solution was found out by titrating with 0.01M EDTA solution. Similar experimental procedure was carried out for remaining concentration solutions.

## III. RESULTS AND DISCUSSION

### **A. Adsorption of $Pb^{2+}$ & $Cd^{2+}$**

#### **3.1.1 Effect of Contact Time**

Adsorption of  $Pb^{2+}$  &  $Cd^{2+}$  was carried out by using different concentration solutions (100, 200, 300 & 400 ppm) of  $Pb(NO_3)_2$  & (50, 100, 150 & 200 ppm) of  $3CdSO_4 \cdot 8H_2O$  solutions by means of 700 mg & 600 mg of carbonized powder of Casuarinas Equisetifolia seeds per 50 ml of solution for time 120 & 90 min at different pH (2 to 6) & consequences are exhibited in Figure. It designates that adsorption speed varies uniformly with reference to time. For less concentration solution of  $Pb^{2+}$  &  $Cd^{2+}$  it gives maximum adsorption due to availability of maximum surface area. The carbonized powder provides sufficient surface area for adsorption of  $Pb^{2+}$  with adsorption capacity (2.66 to 4.74 mg/gm) & % removal 80% at equilibrium time 120 min while to that of  $Cd^{2+}$  adsorption capacity (1.44 to 3.31 mg/gm) & percentage removal 81.54% at equilibrium time 90 min. If adsorption process is kept on following stability tip then repulsion among  $Pb^{2+}$  &  $Cd^{2+}$  takes place which causes desorption route.

### 3.1.2 Effect of pH

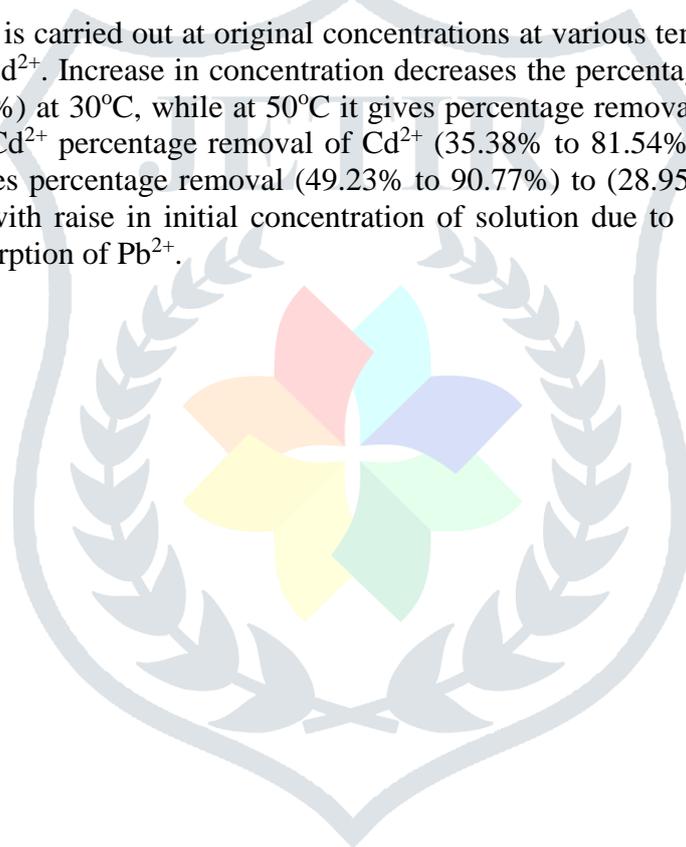
When the adsorption process is carried out in the pH range 2 to 6 for different concentration solution of  $Pb^{2+}$  &  $Cd^{2+}$  for given time interval it was found that at pH 6 & 4 the percentage adsorption of heavy metal ions is almost i.e. 90% for 100 ppm & 50 ppm solution of  $Pb^{2+}$  &  $Cd^{2+}$ .

### 3.1.3 Effect of Adsorbent Dose

By changing the amount of adsorbent & keeping time period constant about 60 minutes for  $Pb^{2+}$  &  $Cd^{2+}$  when adsorption process is carried out it was detected that removal boosts with increase in amount of adsorbent. 100 ppm solution of  $Pb^{2+}$  & 50 ppm solution of  $Cd^{2+}$  offers the highest percentage removal 75% & 77.25% for amount 700 mg & 600 mg per 50 ml of solution therefore it is chosen as optimized dose but at the same time adsorption capacity reduces (5.18 to 4.44 mg/gm) for  $Pb^{2+}$  & (4.50 to 3.19 mg/gm) for  $Cd^{2+}$ .

### 3.1.4 Effect of Initial Concentrations & Temperature

Adsorption of  $Pb^{2+}$  &  $Cd^{2+}$  is carried out at original concentrations at various temperatures (30° to 50°C) for  $Pb^{2+}$  & (25° to 35°C) for  $Cd^{2+}$ . Increase in concentration decreases the percentage removal of  $Pb^{2+}$  (45% to 80%) to (26.30% to 51.21%) at 30°C, while at 50°C it gives percentage removal (60% to 90%) to (29.41% to 57.44%), similarly for  $Cd^{2+}$  percentage removal of  $Cd^{2+}$  (35.38% to 81.54%) to (26.69% to 52.63%) at 25°C, while at 35°C it gives percentage removal (49.23% to 90.77%) to (28.95% to 54.89%). It illustrates that % adsorption lessen with raise in initial concentration of solution due to less availability of sites for adsorption, maximum adsorption of  $Pb^{2+}$ .



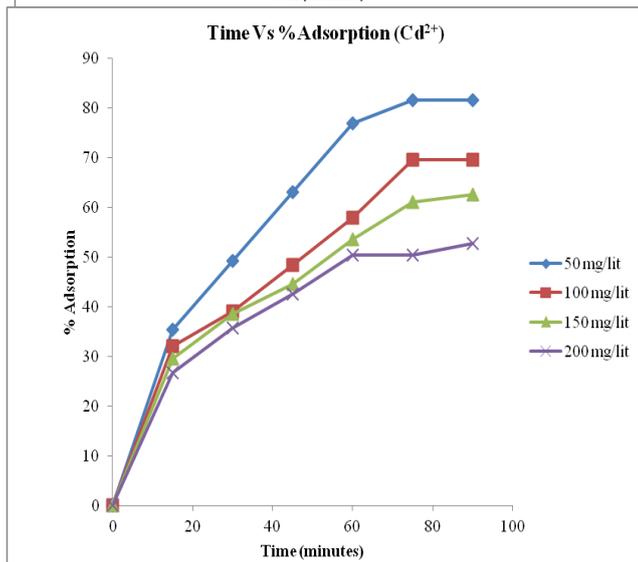
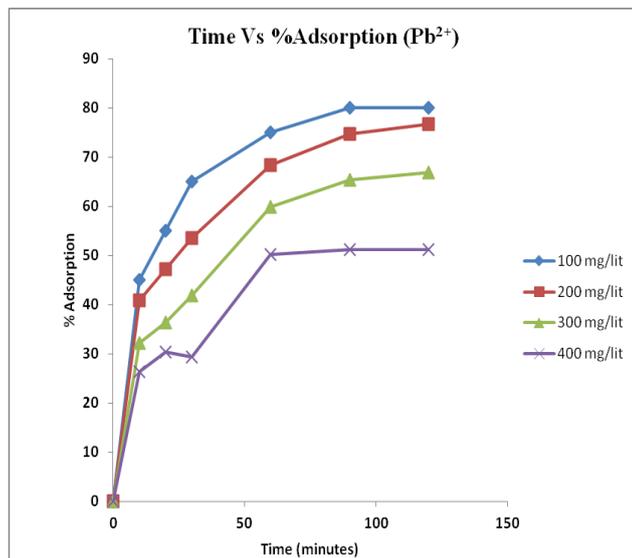


Figure 1. Contact time Vs % Adsorption of Pb<sup>2+</sup>

Figure 2. Contact time Vs % Adsorption of Cd<sup>2+</sup>

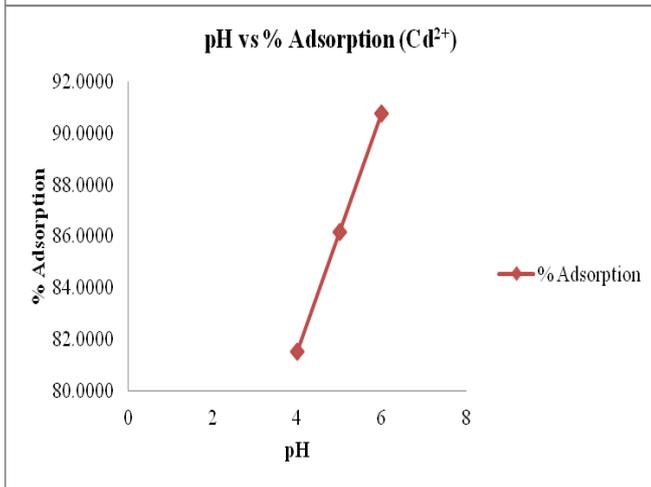
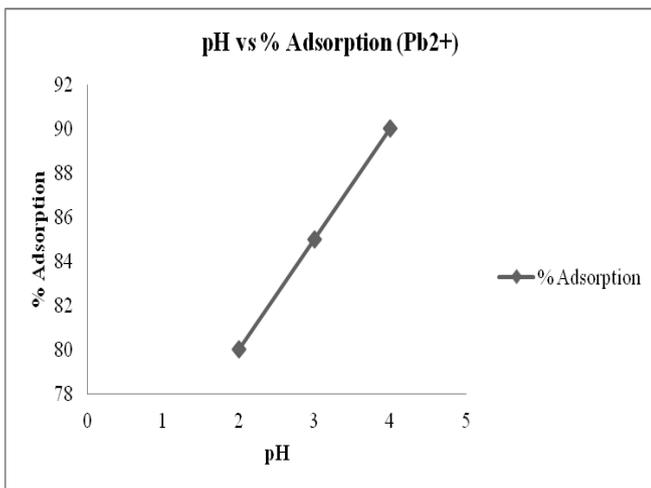


Figure 3. pH Vs % adsorption of Pb<sup>2+</sup>

Figure 4. pH Vs % adsorption of Cd<sup>2+</sup>

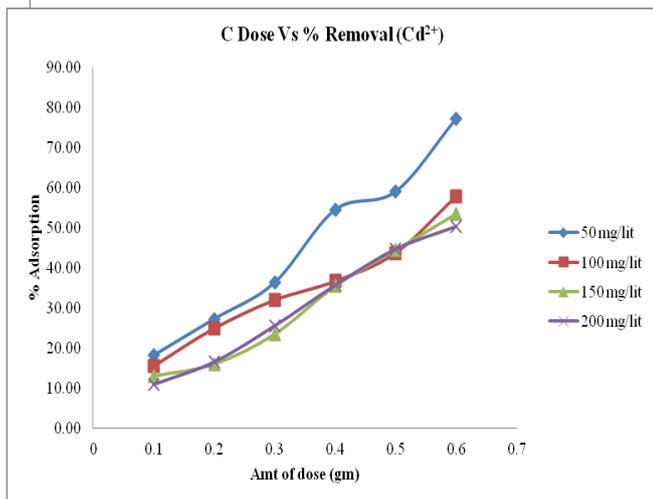
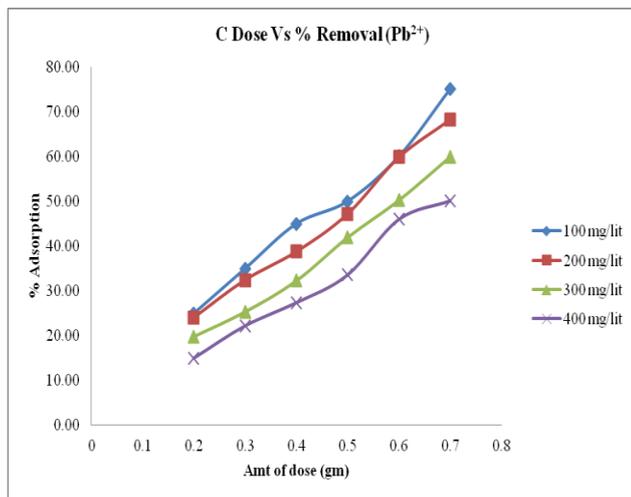


Figure 5. Amount of adsorbent Vs % Adsorption of Pb<sup>2+</sup>

Figure 6. Amount of adsorbent Vs % Adsorption of Cd<sup>2+</sup>

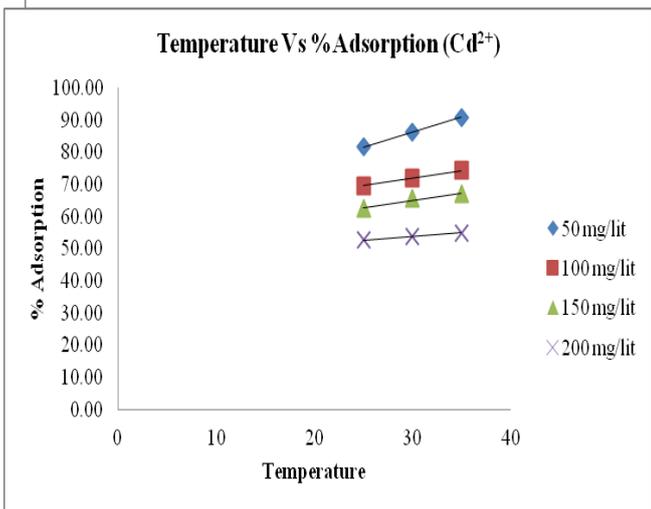
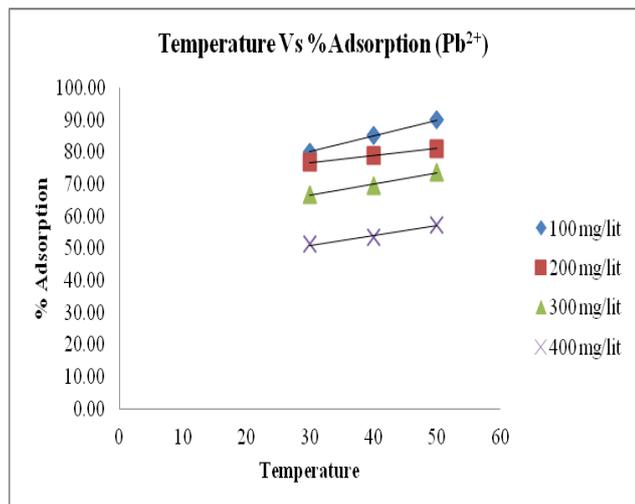


Figure 7. Temperature Vs %adsorption of Pb<sup>2+</sup>

Figure 8. Temperature Vs %adsorption of Cd<sup>2+</sup>

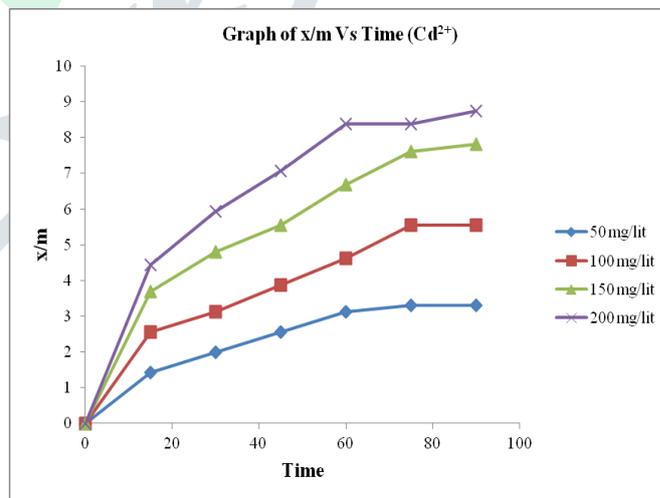
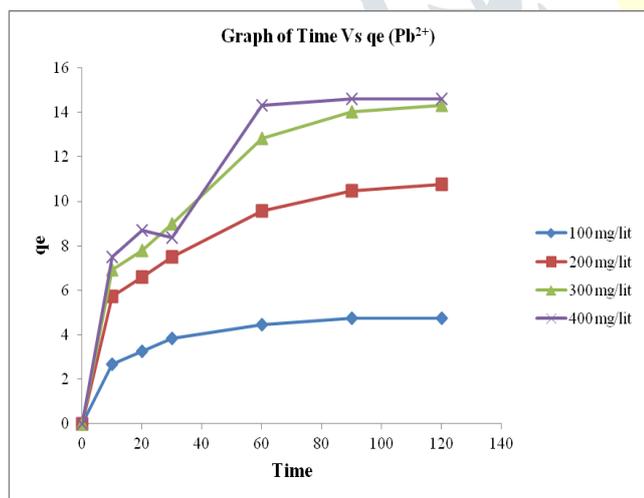


Figure 9. Contact time Vs Adsorption Capacity of Pb<sup>2+</sup>

Figure 10. Contact time Vs Adsorption Capacity of Cd<sup>2+</sup>

**B. Adsorption Isotherms**

The facts which were achieved by performing experimentation at different temperatures for Pb<sup>2+</sup> & Cd<sup>2+</sup> were tested by means of Langmuir, Freundlich & Temkin isotherm models. The isotherm factors obtained from the graph are symbolized in table. As the value of R<sup>2</sup> > 0.9 for Langmuir, freundlich and Temkin

isotherm fitted in experimental data. By evaluating these three isotherms & the  $R^2$  value it was concluded that value of  $R^2$  for Langmuir isotherm is greater therefore it is fitted in Langmuir isotherm

### 3.2 Langmuir Isotherm

The connection among the number of vigorous sites of the exterior go through adsorption & pressure is given by Langmuir Equation. Langmuir isotherm believes monolayer adsorption & the opportunity of configuration of monolayer is barely at low down pressure situation<sup>8</sup>. At elevated pressure the postulation smash down as gas molecule is a magnet for more and more molecules on the way to each other. For the study of maximum adsorption of  $Pb^{2+}$  &  $Cd^{2+}$  linearized form Langmuir isotherm equation was used.

$$C_e / q_e = 1 / bQ_m + (1 / Q_m) C_e \dots \dots \dots (1)$$

For the study of adsorption of  $Pb^{2+}$  &  $Cd^{2+}$  onto carbonized material of seeds of Casuarinas Equisetifolia graph was plotted  $C_e/q_e$  Vs  $C_e$ . The constants of Langmuir isotherm  $Q_0$ , and  $b$ , evaluated from graph.

	$Pb^{2+}$	$Cd^{2+}$
<b>M</b>	0.0874	0.0815
<b>C</b>	0.3788	0.589
<b>Q0</b>	11.4	11.25
<b>b</b>	0.2307	0.1383
<b>R<sup>2</sup></b>	0.9946	0.846

**Table: 1 Parameters in Langmuir isotherm of  $Pb^{2+}$  &  $Cd^{2+}$**

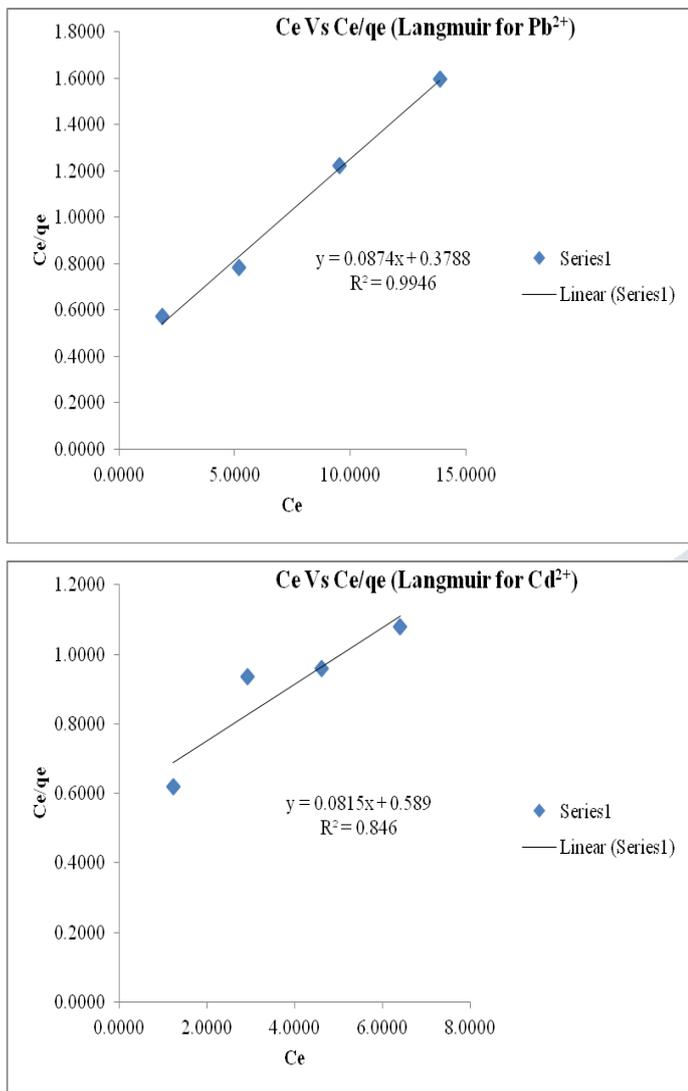


Figure 1. Ce Vs Ce/qe for Langmuir isotherm of Pb<sup>2+</sup> & Cd<sup>2+</sup> (Langmuir Isotherm)

RL (Halls Separation Factor) expressed in terms of dimensionless equilibrium parameter is Langmuir Isotherm

$$RL = 1/(1+bC_0)$$

$$RL = 0.0977$$

$$RL = 1/(1+bC_0)$$

$$RL = 0.1530$$

Value of RL for Pb<sup>2+</sup> & Cd<sup>2+</sup> is  $0 < RL < 1$

It means that Langmuir isotherm is favourable.

### 3.3 Freundlich Isotherm

A unique form of Langmuir adsorption isotherm is the Freundlich isotherm. This isotherm falls short at elevated stress & it obeys only at low pressure. It is used for multilayer adsorption. Dealings among adsorbed molecules the linear Freundlich isotherm is expressed as:

$$\log q_e = \log K_f + 1/n \log C_e \dots \dots \dots (2)$$

Where  $q_e = x / m$

The graph plotted  $\log q_e$  Vs  $\log C_e$  indicates that the adsorption of Pb<sup>2+</sup> & Cd<sup>2+</sup> on activated carbon of seeds of Casuarinas Equisetifolia also go after Freundlich adsorption isotherm model. The constants of Freundlich isotherm (K<sub>f</sub> and n) & Correlation coefficients are recorded.

	Pb <sup>2+</sup>	Cd <sup>2+</sup>
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<b>m</b>	0.6709	0.4909
<b>C</b>	0.2224	0.4096
<b>n</b>	1.4905	2.0371
<b>Kf</b>	1	1
<b>R<sup>2</sup></b>	0.98	0.9502

Table: 2 Parameters in Freundlich isotherm of Pb<sup>2+</sup> & Cd<sup>2+</sup>

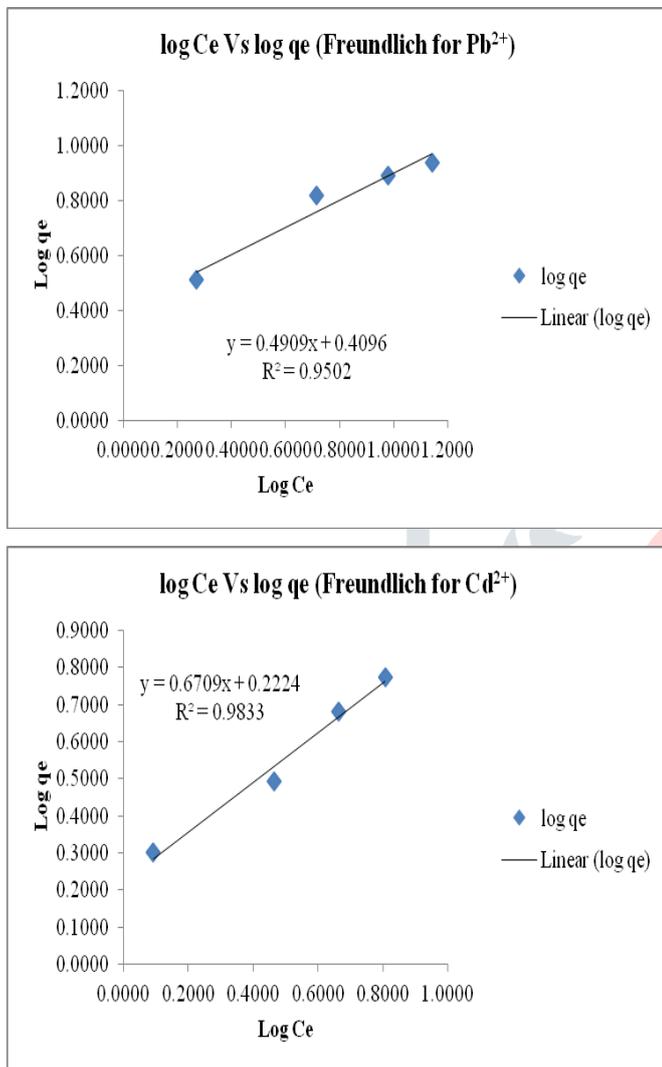


Figure 1. log Ce Vs log qe for Freundlich isotherm of Pb<sup>2+</sup> & Cd<sup>2+</sup> (Freundlich Isotherm)

Here, the value of  $1/n$  for Pb<sup>2+</sup> & Cd<sup>2+</sup>

$0 < 1/n < 1$  which is favorable.

Also, Value of  $R^2$  of Pb<sup>2+</sup> for Freundlich isotherm is less than Langmuir isotherm while for Cd<sup>2+</sup> it is greater than Langmuir isotherm.

### 3.4 Temkin Isotherm

It includes one aspect that believe interface take place among adsorbent & adsorbate. In this model heat of adsorption of molecules in the entire layer would shrink linearly in its place of logarithmic. Derivation of temkin isotherm is a uniform allotment of binding energy which was carried out by plotting the graph quantity adsorbed  $q_e$  Vs  $\ln C_e$ . Temkin isotherm model gives a linear form which is represented by the equation given below.

$$q_e = RT/b \ln KT + RT/B \ln C_e \dots \dots \dots (3)$$

Straight line graph, with slope indicating B & intercept is K. constants in Tempkin isotherm along with the relationship coefficients are as follows. The R<sup>2</sup> values 0.97 confirm that Tempkin isotherm provides a reasonable model for the adsorption of Pb<sup>2+</sup> & Cd<sup>2+</sup> on activated carbon prepared from seeds of Casuarinas Equisetifolia.

	Pb <sup>2+</sup>	Cd <sup>2+</sup>
<b>m</b>	2.7024	1.7069
<b>c</b>	3.0801	1.2216
<b>b</b>	0.917	1.452
<b>B</b>	2.7024	1.7069
<b>kT</b>	3.1260	2.0456
<b>R<sup>2</sup></b>	0.9724	0.9903

Table: 3 Parameters in Temkin isotherm Pb<sup>2+</sup> & Cd<sup>2+</sup>

Temp	30°	40°	50°	Temp	25°	30°	35°
<b>m</b>	2.154	2.5997	2.7024	<b>m</b>	1.9541	1.7069	1.5512
<b>C</b>	3.521	2.6448	3.0801	<b>C</b>	0.4454	1.222	1.434
<b>b</b>	1.134	0.953	0.917	<b>b</b>	1.268	1.452	1.597
<b>B</b>	2.184	2.5997	2.7024	<b>B</b>	1.9541	1.7069	1.5512
<b>kT</b>	5.0137	2.7659	3.1260	<b>kT</b>	1.2560	2.0456	2.5198
<b>R<sup>2</sup></b>	0.8713	0.9164	0.9724	<b>R<sup>2</sup></b>	0.9885	0.9903	0.9133

Table: 4 Comparison of Tempkin isotherm at different temperature of Pb<sup>2+</sup> & Cd<sup>2+</sup>

#### IV. Conclusions

Various Isotherm forms for the adsorption of Pb<sup>2+</sup> & Cd<sup>2+</sup> by using activated carbon set up from seeds of Casuarinas Equisetifolia from aqua solution were studied. Freundlich & Temkin isotherm model are best fitted with statistics obtained from experimentation.

1. The most select Pb<sup>2+</sup> & Cd<sup>2+</sup> ion concentration was found to be 100 ppm & 50 ppm.
2. Adsorbent quantity increases percent elimination of Pb<sup>2+</sup> & Cd<sup>2+</sup> increases, since it endow with more positions for adsorption. Utmost adsorption was observed at adsorbent dosage of 700 mg & 600 mg.
3. 120 min & 90 min is the equilibrium time necessitated for the adsorption of Pb<sup>2+</sup> & Cd<sup>2+</sup>.
4. The adsorption of Pb<sup>2+</sup> & Cd<sup>2+</sup> onto activated carbon get ready from Casuarinas Equisetifolia followed Freundlich and Temkin Adsorption Isotherm model.

The attained outcomes indicate that the activated carbon prepared from seeds of Casuarinas Equisetifolia is capable for the removal of Pb<sup>2+</sup> & Cd<sup>2+</sup> with high affinity and capacity indicating its potential use as a economically cheaper adsorbent in near future.

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