Removal of Heavy Metal Ions from Leachate using Natural Adsorbent Delonix Regia

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Abstract

In the present work, the adsorption of nickel ions from leachate sample by activated carbon prepared from seeds of Delonix Regia was studied. The activated carbon prepared by pretreatment with KOH was subjected to SEM, XRD and FTIR analysis. The influences of different experimental parameters on nickel uptake were investigated such as sorption time, final solution pH, adsorbent dosage and temperature. The experimental data were correlated to different kinetic and adsorption models and the corresponding kinetic parameters were determined. The % removal was found to be 75.03% and follows pseudo-first order kinetic model for Ni. These parameters are considered fundamental for further studies involving the scale-up of the process for continuous studies.

Keywords: Delonix Regia seeds Activated Carbon (DRAC), Leachate, Ni adsorption

I. INTRODUCTION

Landfill leachate is considered as a potential pollutant when it percolates through a waste disposal site depending on composition and extent of decomposition of refuse and hydrological factors. There is growing concern for surface and ground water pollution for which better understanding and prediction regarding its treatment is of prior importance. As water percolates through a waste deposit it leaches various components present in it thus exhibiting high concentration of dissolved organics, toxics, metals, color, odor, turbidity, pH, etc.[1][2]

The different methods for removal of heavy metals from wastewater include precipitation, coagulation, reduction membrane process, ion exchange and adsorption. Adsorption as compared to other methods has advantages due to its simple design and operation, sludge free and cost effectiveness [3]

Leachate can be defined as a potential hazardous waste from landfill sites. If not dealt properly they can cause pollution to groundwater, health problems and effect the environment. It is important that leachates are treated and contained to prevent these occurrences. Leachate pollution is the result of biological, chemical and physical processes that take place in landfills combined with waste composition and landfill water regime. [4]

A wide range of new tertiary treatment processes has been developed on the enhanced coagulation–flocculation, clarification and biological processes (aerated lagoons, activated sludge, anaerobic filters, stabilization ponds, up flow anaerobic sludge blanket, sequence biological reactor, rotating biological contactors, and nitrification or denitrification processes) as possible circumstance for leachate treatment, mainly hinges of its reliability, simplicity, high cost-effectiveness, reduction of stabilization time and acceleration of biogas production[5][6]

Several studies have demonstrated use of natural adsorbent for removal of heavy metals in leachate.[7-18]. Mohan et al[19] studied removal of heavy metal ions from municipal solid waste leachate using coal fly ash as an adsorbent. Foo et al [20] carried out the study of leachate treatment using activated carbon. Nitrogen removal and heavy metals in leachate treatment using SBR technology was done by Morling and group [21]. Nagwan et al [22] tried to remove some heavy metals from leachate. Daga and group [23] reviewed low cost adsorbent for heavy metal removal from waste water.

Most of the world production of Nickel is used for producing alloys in coins, jewellery and stainless steel, in electropolating as protection against corrosion, production of Raney Nickel catalyst, etc. The most commonly reported health effect with Ni exposure is contact dermatitis, respiratory problems like chronic bronchitis, pulmonary fibrosis and impaired lung functions which has been observed in Ni welders. The carcinogenicity of Ni has been well documented in occupationally exposed individuals.

The purpose of this study is therefore to investigate the removal of nickel from hazardous landfill leachate using activated carbon prepared from seeds of Delonix Regia(Binomial name), Gulmohar (Royal Poinciana) (family Fabaceae), which is a tropical or subtropical flowering plant as a natural adsorbent.
II. MATERIALS AND METHOD

A. Characterization of Leachate

The leachate samples were collected from Urali-Devachi, solid waste disposal site for Pune municipal area. The characteristics study of Urali-Devachi sample is shown in Table 1. The analysis of the heavy metals in the leachate sample was done by AAS, Chemito AA 201.

<table>
<thead>
<tr>
<th>Life span/ Parameter</th>
<th>Recent</th>
<th>Intermediate</th>
<th>Old</th>
</tr>
</thead>
<tbody>
<tr>
<td>Age (Years)</td>
<td>&lt;5</td>
<td>5-10</td>
<td>&gt;10</td>
</tr>
<tr>
<td>pH</td>
<td>6.5</td>
<td>6.5-7.5</td>
<td>&gt;7.5</td>
</tr>
<tr>
<td>COD (mg L⁻¹)</td>
<td>&gt;10,000</td>
<td>4,000-10,000</td>
<td>&lt;4,000</td>
</tr>
<tr>
<td>BOD₅/COD</td>
<td>&gt;0.3</td>
<td>0.1-0.3</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Organic Compounds</td>
<td>80% volatile fatty acids</td>
<td>5-30% VFA+ Humic and Fulvic acids</td>
<td>Humic and Fulvic acids</td>
</tr>
<tr>
<td>Ammonia Nitrogen (mg/l)</td>
<td>&lt;400</td>
<td>N.A.</td>
<td>&gt;400</td>
</tr>
<tr>
<td>TOC/COD</td>
<td>&lt;0.3</td>
<td>0.3-0.5</td>
<td>&gt;0.5</td>
</tr>
<tr>
<td>Kjeldahl Nitrogen (g/l)</td>
<td>0.1-0.2</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>Heavy metals</td>
<td>Low</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>Biodegradability</td>
<td>Important</td>
<td>Medium</td>
<td>Low</td>
</tr>
</tbody>
</table>

B. Characterization of DRAC

Various researchers have worked for characterization of natural adsorbents. Ahmedna and group worked for production of granular activated carbon from agricultural by products. [24-38]

SEM micrographs have a large depth of field yielding a characteristic three dimensional appearance useful for understanding the surface structure of a sample. SEM and EDAX were carried out on JULJSM – 6360A (Japan) and the results are shown in Figure 1(A) and Figure 2(A) with Table 3 for Activated carbon and in Figure 1(B) and Figure 2(B) with Table 4 for Activated carbon.

XRD for activated carbon and DRAC were carried out on Bruker AXS D8 Advanced, made in Germany and recorded from20 valves. [0° and 80° with intensity range 0° to 200°] and graphs were plotted as shown in Figure 3. FTIR was carried out on Perkin Eimer, FT-IR system, Spectrum BX; Made in UK and following plot was obtained as shown in Figure 4 (A) and (B). N₂-BET was carried out on Micromeritics ChemiSorb 2720 instrument for powdered activated carbon and 16 mesh DRAC.

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Fig. 1 (A): SEM image of Activated Carbon [JULJSM – 6360A]  
Fig. 2 (A): EDA of Activated Carbon [JULJSM – 6360A]
Table – 4
Elemental Analysis of Activated Carbon by EDAX

<table>
<thead>
<tr>
<th>Element</th>
<th>Kev</th>
<th>Mass%</th>
<th>Element</th>
<th>Kev</th>
<th>Mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>0.277</td>
<td>62.26</td>
<td>Cl K</td>
<td>2.621</td>
<td>0.60</td>
</tr>
<tr>
<td>O K</td>
<td>0.525</td>
<td>12.77</td>
<td>Ca K</td>
<td>3.690</td>
<td>3.84</td>
</tr>
<tr>
<td>Mg K</td>
<td>1.253</td>
<td>0.63</td>
<td>Fe K</td>
<td>6.398</td>
<td>8.17</td>
</tr>
<tr>
<td>Al K</td>
<td>1.486</td>
<td>2.42</td>
<td>Cu K</td>
<td>8.040</td>
<td>1.24</td>
</tr>
<tr>
<td>Si K</td>
<td>1.739</td>
<td>2.85</td>
<td>Zr L</td>
<td>2.042</td>
<td>4.28</td>
</tr>
<tr>
<td>S K</td>
<td>2.307</td>
<td>0.94</td>
<td></td>
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</tr>
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</table>

Fig. 1: (B): SEM image of DRAC

Fig. 2: (B): EDAX of Gulmohar Seed Activated Carbon

Table – 5
Elemental Analysis of GSAC by EDAX

<table>
<thead>
<tr>
<th>Elements</th>
<th>Kev</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>0.277</td>
<td>60.76</td>
</tr>
<tr>
<td>O K</td>
<td>0.525</td>
<td>5.39</td>
</tr>
<tr>
<td>Cl K</td>
<td>2.621</td>
<td>11.51</td>
</tr>
<tr>
<td>K K</td>
<td>3.312</td>
<td>16.5</td>
</tr>
<tr>
<td>Cu K</td>
<td>8.040</td>
<td>2.64</td>
</tr>
<tr>
<td>Rh L</td>
<td>2.696</td>
<td>3.2</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100.00</td>
</tr>
</tbody>
</table>

Fig. 3: XRD of Activated Carbon [Insight] and DRAC
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III. EXPERIMENTAL STUDIES

A. Pretreatment of leachate

Pretreatment was done by heating. 250 ml of filtered sample to boiling and was then allowed to stand for 48 hrs. followed by oxidation with 20 ml of 0.1N KMnO₄. Activated Carbon from Delonix Regia Seed was prepared by treating it with potassium hydroxide. Initially the materials were washed thoroughly with water to remove the earthy matter and dried at 110°C. The dried material was then subjected to 1N KOH for 10 min. This material was then washed with dilute HCl to make the sample neutral. It was then carbonized at 500°C for 25 min in a muffle furnace. Finally the materials were ground in an agate mortar and particles sieved to 16 mesh size. This ground material was then impregnated with 0.1N KMnO₄.

B. Estimation of Nickel

Nickel estimation was carried out by DMG method using Atomic Absorption Spectrophotometer, Chemito AA 201. The Beer’s law calibration plot shows a regression of $R^2 = 0.992$ as shown in Figure 5. The concentration of Nickel in the Leachate sample was found to be 0.791667 ppm.

C. Study of Adsorption Isotherm:

The adsorption isotherm data are important to study the adsorption capacity and equilibrium coefficient for adsorption process. In the present work, three adsorption isotherms were utilized viz. Freundlich, Langmuir and D-R isotherm. In this study, adsorption isotherm models were evaluated using three parameters such as temperature variation, contact time variation and also using adsorbate concentration variation. (Kinhikar, 2012), (Kodolikar and Doss, 2019)

For the isotherm studies, varying amounts of DRAC in the range 1g to 6 g were taken in the conical flasks and added with 200 ml Leachate sample solution. The flasks were then subjected to agitation for a period of 6 hours to reach equilibrium. The equilibrium concentration was determined by analyzing Ni²⁺ ions in leachate sample by UV Visible Spectrophotometer. The Langmuir, Freundlich and D-R models were applied for adsorption equilibrium of DRAC. The results were obtained using the equation

$$q_e = \frac{(C_0 - C_e)V}{d}$$

Where $q_e$= concentration of Ni ion on DRAC in mg/l, $C_0$, $C_e$= initial and equilibrium concentrations of Ni ion in solution in mg/l, $V$= volume of solution in liters, $d$= amount of DRAC[g]. A plot of $q_e$ against $C_e$ is shown in Figure 6.

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**Fig. 4 (A):** FTIR image of Activated Carbon [Perkin Elmer, Spectrum BX]

**Fig. 4 (B):** FTIR image of Delonix Regia Seed Activated Carbon

**Fig. 5:** Adsorption isotherm of Ni on DRAC
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Langmuir Isotherm:
The Langmuir isotherm is applied to homogeneous sorption. It is the simplest theoretical model for monolayer adsorption which was developed from kinetic or thermodynamic derivation. The equation for Langmuir isotherm is given below,

\[
\frac{C_e}{q_e} = \left( \frac{C_e}{Q} \right) + \left( \frac{1}{bQ} \right)
\]

(2)

“Q” and “b” in this case can be determined from the plot of \( C_e/q_e \) versus \( C_e \) (Figure 7). “Q” indicates the maximum sorption upon complete monolayer saturation. Higher value of “b” indicates the adsorbent has high affinity for the adsorbate and vice versa.

Freundlich Isotherm:
It is an empirical isotherm model that considers heterogeneous adsorption and can be used for non-ideal adsorption. The equation for Freundlich isotherm is given below,

\[
q_e = K_f \cdot C_e^{1/n}
\]

(3)

The results revealed that the adsorption of nickel under optimum condition at 25°C obeyed Freundlich isotherm (Figure 8). This model represents the relationship between the amount of Nickel adsorbed per unit mass of the adsorbent \( (q_e) \) and concentration of Nickel \( (C_e) \). \( K_f \) and \( n \) are constant representing the adsorption capacity and intensity of adsorption. Higher value of \( n \) indicates greater degree of heterogeneity. For \( 1/n \) less than unity, adsorption is the predominant process that takes place otherwise desorption becomes predominant.

Dubini-Radushkevich Isotherm:
The D-R isotherm which assumes a heterogeneous surface is expressed as follows

\[
\ln q_e = \ln q_m - K \cdot e^2
\]

(5)

The parameter \( e \) can be found from equation,

\[
e = RT \ln \left( 1 + \frac{1}{C_e} \right)
\]

(6)

Where \( K \) Constant related to adsorption energy, \( q_e \) is amount of Ni ions adsorbed per unit mass of adsorbent (mg/g), \( q_m \) is the maximum adsorption capacity (mg/g), \( R \) is gas constant and \( T \) is absolute temperature.

Therefore D-R isotherm (Figure 9) can be used to predict equilibrium adsorption data at different temperatures. The model describes the adsorption of subcritical vapors onto micro pore solids following a pore filling mechanism. The plot of \( \ln q_e \) vs \( e^2 \) gives slope \( K \) (mol²/J²) and intercept \( q_m \).
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Fig. 8: Dubini - Radushkevich isotherm

With the plot the slope -K= -2E⁻⁹ which gives the value of K=2E⁻⁹ and intercept for lnqₘ = 1.9584 giving value of constant qₘ = 7.088; hence the equation for Dubini - Radushkevich Adsorption Isotherm can be given for this adsorption study with DRAC as follows:

\[
\ln q_e = 1.9584 - 2 \times 10^{-9} \times e^2 \quad [7]
\]

The results of all the three isotherm studies are tabulated in Table 3.

Table – 6

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>R²</td>
<td>0.7377</td>
</tr>
<tr>
<td>Freundlich</td>
<td>Kf (mg/g)(L/mg)⁰⁻¹</td>
<td>1.3174</td>
</tr>
<tr>
<td></td>
<td>1/n</td>
<td>1.077</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.988</td>
</tr>
<tr>
<td>Dubini - Radushkevich</td>
<td>E (KJ/mol)</td>
<td>0.9355</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7807</td>
</tr>
</tbody>
</table>

**D. Adsorption Parameter Studies:**

1) **Effect of pH**

To study the effect of pH on adsorption of DRAC in leachate, the experiments were conducted with varying pH. The results are depicted in Figure 10.

![pH Vs %removal](image)

**Fig. 9: Effect of pH**

2) **Effect of Speed of Agitation**

To investigate the effect of speed of agitation on adsorption of DRAC in leachate, the experiments were conducted with varying speed of agitation i.e. 500 rpm, 800 rpm and 1000 rpm with 6g of DRAC and 100ml of leachate sample as shown in Figure 11.
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Effect of Leachate Volume
To investigate the effect of leachate volume on adsorption of Ni by DRAC in leachate, the experiments were conducted with varying leachate volume from 50 ml to 200 ml with 6g of DRAC and 800rpm. The results are as shown in Figure 12.

Effect of Adsorbent Dosage
To investigate the effect of adsorbent dose on adsorption of DRAC in leachate, the experiments were conducted with varying adsorbent dosage from 0.5g to 6g. The results obtained are shown in Figure 13.

Effect of Temperature
To investigate the effect of temperature on adsorption of DRAC in leachate, the experiments were conducted with adsorbent dosage of 6g with varying temperature at 25°C, 35°C and 50°C. The result is shown in Figure 14.
E. Kinetic Studies:

The adsorption kinetic studies describe the solute uptake rate which in turn controls the residence time of adsorbate uptake at the solid-liquid interface. Adsorption kinetics is one of the important characteristics in defining efficiency of adsorption process and to understand the behavior of adsorbent.

For studying the rate of diffusion experiments were conducted with adsorbent dosage of 6g in 100 ml of leachate sample at a temperature of 25⁰C and speed of agitation at 800 rpm for a time period of four hours. This was studied to investigate the concentration of Ni remaining in solution vs. time on adsorption of DRAC in leachate as shown in figure 15. (Kodolikar and Doss, 2019), (Dwairiand et al, 2014), (Doss and Kodolikar, 2012), (Idrisand et al, 2012), (Sulaymon et al 2012), (Suyambu and Perumal, 2012).

1) Pseudo-First-Order Model:
The first kinetic model considered for this study is Pseudo first order model which is expressed as:

\[ \log(q_e - q) = \log q_e - K_f t \frac{2.303}{2.303} \]  
\[ q = (C_0 - C_e) \times \frac{V}{M} \]

Where \( C_0 \) and \( C_e \) are initial and equilibrium adsorbate concentration in solution, \( V \) is volume of solution, \( M \) is mass of adsorbent and \( K_f \) is a rate constant for pseudo-first-order model (1/min).

Fig. 14: Effect of Temperature

Fig. 15: Kinetic studies

Fig. 16: Pseudo-first order model
The figure 16 shows the result of pseudo-first order model when applied to the experimental data of adsorption.

2) Pseudo-Second-Order Model:

Pseudo-second order equation is based on the assumption that rate limiting step may be chemical adsorption. It is assumed that adsorption capacity is proportional to the number of active sites occupied on the adsorbent. The equation of pseudo-second order is given below.

\[
\frac{t}{q} = \frac{1}{K_s q_e^2} + \left(\frac{1}{q_e}\right) t
\]

(10)

Where, \(K_s\) is a rate constant for pseudo second order model (g/mg.min).

The initial sorption rate, the equilibrium sorption capacity and pseudo-second order rate constant can be determined from plot \(t/q\) vs. \(t\) [Figure 17]. As a result, the sorption system appears to follow pseudo-second order kinetics.

![Pseudo-second order model](image)

Fig. 17. Pseudo-second order model

The pseudo-second order model for adsorption of metal ions onto DRAC agrees well with experimental data due to greater value of \(R^2\) i.e., 0.997. These suggest that adsorption data is well represented by pseudo-second order kinetics and supports assumption that rate limiting step of metal adsorption may be chemical adsorption.

F. Continuous Adsorption Column Studies:

With the batch adsorption studies data, a continuous adsorption column was designed with varying parameters and the adsorption of Ni was studied in continuous mode at laboratory level.

(Dwairiand et al, 2014)

1) Preparation of Column for Adsorption Studies

An adsorption column of internal diameter of 22mm was taken and washed thoroughly with distilled water. The neck of the column is plugged with cotton wool. DRAC of 16mesh was filled into the column up to a height of 5cm. Then, 0.1N KMnO4 was allowed to flow through the column. After all the KMnO4 had drained the column was ready for use.

Leachate sample of known quantity is passed through the column. The outlet flow rate of column is set to 2.5ml/min. Sample were collected from the column initially at 2min till 1hr, then at 3min for 30min, then at 4min for 40min, then at 5min for 10min, then at 10min for 20min and lastly at 30min till the equilibrium is obtained. These samples are then analyzed using AAS. Similarly, process was repeated for column having internal diameter of 18mm and 30mm and a bed height of 5 cm, 10 cm and 20 cm for each.

2) Parameters Studied in Continuous Adsorption of Ni using DRAC

a) Break through Curve

An adsorption column of internal diameter 22mm was taken and 16mesh sieved DRAC was filled in the column up to a bed height of 20cm. A known quantity of leachate sample was passed through the column until the equilibrium was obtained. Outlet flow rate of column was set at 2.5ml/min. Samples were collected from the column initially at 2min till 1hr, then at 3min for 30min, then at 4min for 40min, then at 5min for 10min, then at 10min for 20min and lastly at 30min till the equilibrium are obtained. These samples were then analyzed in AAS.

A graph of concentration vs. time representing % removal of Ni through fixed bed column (20 cm height) of DRAC (pH-8.03, temperature:25°C, initial leachate concentration of 0.791667ppm) was obtained [known as Break Through Curve]. (Figure 18)
b) Effect of Column Diameter
This study was carried out to study the adsorption of Ni ion on DRAC when the column diameter was varied as 18mm, 22mm and 30mm. This parameter gives the optimum feasible column diameter for further studies. Results of one such variation in column diameter for constant bed height of 50mm is given in figure 19.

![Fig. 19: Effect of Column Diameter with bed height 50mm](image)

A matrix study was carried out by varying column diameter and bed height and the final optimized results were obtained as tabulated in Table 7.

c) Effect of Bed Height
This study was carried out to study the adsorption of Ni ion on DRAC when the adsorbent bed height was varied as 50mm, 100mm and 200mm. This parameter gives maximum the feasible bed diameter for further studies. One of the studies result with variation in bed height for constant column diameter of 30mm is given in figure 20.

![Fig. 20: Effect of Bed Height for Column diameter 30mm](image)
Table 7

<table>
<thead>
<tr>
<th>Column Diameter/Bed Height</th>
<th>50mm</th>
<th>100mm</th>
<th>200mm</th>
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<tbody>
<tr>
<td>18mm</td>
<td>55.5789</td>
<td>53.94739</td>
<td>60.45114</td>
</tr>
<tr>
<td>22mm</td>
<td>54.57066</td>
<td>73.50273</td>
<td></td>
</tr>
<tr>
<td>30mm</td>
<td>55.34807</td>
<td>55.52633</td>
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</table>

The maximum removal was obtained at bed height 200mm and bed diameter of 22mm. Here the removal of Ni ions was about 73.5%. Thus for continuous process an optimum column diameter 22mm and height 200mm was obtained.

d) Effect of Flow Rate

This study was carried out to study the adsorption of Ni ion on DRAC when the flow rate was varied as 2.5ml/min, 5.5ml/min and 8.5ml/min. This parameter gives maximum the feasible flow rate for further studies. The bed height and diameter of the column was fixed as 22mm internal diameter and a bed height of 200mm. The flow rate was varied from 2.5ml/min to 5.5ml/min and 8.5ml/min and %removal were calculated.

![% Removal vs Flow rate](image)

Fig. 21: Effect of Flow Rate

IV. RESULTS AND DISCUSSION

A. Characterization of DRAC

Figure 3 depicts the x-ray diffraction of the activated carbon obtained by calcinations of Delonix Regia at a temperature of 500°C for a time period of 10 minutes in a muffle furnace. Inset of the same figure represents x-ray diffraction pattern of authentic activated carbon commercially available. On comparing both the x-ray patterns, it is observed that the 2θ values of the peaks at ~ 12.2° and ~ 28.3° are in well agreement with the standard A.S.T.M data for authentic carbon. Thus, preliminary it has been confirmed that the calcined Delonix Regia contains activated carbon which is of the grade and quality comparable to authentic activated carbon commercially available. However, in calcined Delonix Regia pattern an additional peak at 2θ value of ~ 40.3° is observed which can be attributed to the transformation occurring due to line broadening. This line broadening or transformation is because of the formation of graphene i.e. as observed in the structure of graphite. The tetrahedral structure of carbon is getting distorted due to calcinations as one of the valencies of carbon is remaining unsatisfied. Moreover, this broadening is also correlated with microcrystalline nature of calcined DR. due to this line broadening physical form of the activated carbon is also changing from powder form to granular one. This granular form is amorphous in nature.

The FTIR showed characteristic peaks at around 1650 cm⁻¹ due to C=O stretch of carboxyl group and 2900 cm⁻¹ due to CH stretch and OH stretch of hydroxyl group which confirmed presence of surface functional groups like carboxyl and hydroxyl groups comparable to activated charcoal. BET was carried out on Micromeritics ChemiSorb 2720 instrument for powdered activated carbon and 16 mesh DRAC and the surface area were found to be 207.839 m²/gm and 6.8865 m²/gm respectively.

B. Adsorption Studies

The adsorption data was validated to Freundlich and Langmuir isotherms. The R² value of 0.998 for Freundlich shows to be a better fit than Langmuir and Dubini - Radushkevich. The adsorption equilibrium data of GSAC for removal of Ni ion were conveniently represented by Freundlich isotherm model as with regression of R² = 0.988.

\[
q_e = 1.3174C_e^{0.9285} \quad [11]
\]
C. Effect of parameters

1) Effect of pH
To investigate the effect of pH on adsorption of DRAC in leachate, the experiments were conducted with varying pH i.e. 3.8pH, 8.03pH and 9.54pH and it was found that the pH of leachate affects its uptake of activated carbon and in general the uptake decreases at lower as well as higher pH values. At lower pH, the uptake of Ni is less due to presence of H\(^+\) ions suppressing the ionization of Ni so that its uptake on polar adsorbent is reduced. At higher pH range, Ni forms salt. Thus, at pH 8.03 maximum percent removal was found. The results are depicted in Figure.

2) Effect of Speed of Agitation
To investigate the effect of speed of agitation on adsorption of DRAC in leachate, the experiments were conducted with varying speed of agitation from 500rpm, 800rpm and 1000rpm with 6gm of DRAC and 100ml of leachate sample. It was found that with an increase in the speed of agitation, the adsorption increases. A significant increase is observed at an agitation speed of 800rpm. Any further increase in speed of agitation did not cause a significant change in adsorption as at lower speed of agitation the availability of the adsorption sites is comparatively less as adsorbent is coarse while with high speed of agitation significantly high adsorption sites are available as increase in speed causes the crushing of the adsorbent. Further, it was observed that the rate of adsorption was not found proportional to increase adsorbent surface area as per the experimental results. In view it was justified that with increase in adsorption sites, the increase in adsorption is not proportionally high. The maximum % removal was found to be 78.94% at 800rpm.

3) Effect of loading
It was found that with an increase in the dose, the adsorption increases. A significant increase is observed at adsorbent dosage of 6gm. Any further addition of adsorbent did not cause a significant change in adsorption as at lower adsorbent dosage the concentration of Ni in leachate sample is high as compared to availability of the adsorption sites. Further, the rate of adsorption was not found proportional to increase in adsorbent dosage as per the experimental results. In view it was justified that with increase in adsorbent dosage the increase in adsorption is not proportionally high. The maximum removal was found to be at 6g of DRAC.

4) Effect of Temperature
To investigate the effect of temperature on adsorption of DRAC in leachate, the experiments were conducted with adsorbent dosage of 6g with varying temperature at 25\(^{\circ}\)C, 35\(^{\circ}\)C and 50\(^{\circ}\)C. It was observed that at 25\(^{\circ}\)C maximum adsorption occurred while adsorption decreased at higher temperatures.

D. Kinetics Studies
The kinetics were studied to investigate the concentration of Ni remaining in solution vs. time on adsorption of DRAC in leachate. The experiments were conducted with adsorbent dosage of 6gm, 100ml of leachate, temperature 25\(^{\circ}\)C, pH 8.03 and speed of agitation800rpm and it was found that with an increase in time, the concentration decreases. A significant decrease in concentration is observed initially and as the time increases after the equilibrium state is reached there is no significant change in the concentration. The maximum % removal was found to be 76.47 at 6hours.

E. Adsorption Column Studies
From the studies made with adsorption column it can predicted that for an adsorbent capacity considered in studies % removal was decreasing with increasing bed height at constant column diameter. But for constant bed height of the adsorbent in column as the column diameter was increasing % removal of Ni ions was increasing. The effect of flow rate variations suggest that % removal decreases with increase in flow rate as the load of adsorption increases on the same quantity of adsorbent in the column. The maximum % removal of Ni [73.50%] using DRAC as adsorbent was obtained at lowest flow rate of 2.2ml/min for Column diameter 22mm and Bed height 200mm.

V. CONCLUSIONS
The characterization by XRD shows that calcined DR is microcrystalline with graphene structure. This study shows that Ni ion can be removed from the leachate by adsorption on DRAC. The maximum removal of 73.50% was obtained at a temperature of 25\(^{\circ}\)C, pH of 8.03 using 6g of adsorbent for 100ml of leachate. The runs were carried out for 6hours for equilibrium studies. The adsorption equilibrium data of DRAC for removal of Ni ion adhere to Freundlich isotherm model. The adsorption system follows pseudo-second order kinetic model for Ni. The batch experiment showed that the adsorption of Ni ion over DRAC is influenced by various parameters like pH, amount of adsorbent, speed of agitation, contact time and temperature. For temperature of 25\(^{\circ}\)C maximum adsorption occurred while the adsorption decreased at higher temperatures. The adsorption of Ni on DRAC proceeds through film diffusion. The adsorption studies using column quantified that the bed height 200mm, column diameter 20mm and flow rate of 2.2ml/min give optimum % removal of Ni ions [73.50%] over DRAC in 6 hours. The DRAC can be used as a low cost adsorbent for removal of Ni ions from the leachate solution. These parameters can be extended for scale-up studies.
NOMENCLATURE

- **C₀, Cₑ**: initial and equilibrium concentrations of Ni ion in solution in [mg/l]
- **d**: amount of GSAC [g]
- **Kₐ**: Freundlich Adsorption constant [unit less]
- **n**: constant [unit less]
- **qₑ**: concentration of Ni ion on GSAC in [mg/l]
- **V**: volume of solution in [liters]

REFERENCES

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