INTRODUCTION

Cadmium is one of the most priority heavy metals due to its high toxicity. Though it, is an essential heavy metal for living organisms, its increased levels have detrimental effects on living organisms (Purkayastha et al., 2014). Cadmium is found naturally by the process of rock and soil erosion. The cadmium concentration in the environment also gets elevated due to forest fires and volcanic eruptions (Rao et al., 2014). The various sources of cadmium are the electroplating industry, battery manufacturing units, textile operation, refineries, by-products from fertilizer industry and textile units (Patterson 1985, Poon, 1986). As per WHO (2011) guidelines for drinking water, the permissible limit of cadmium in drinking water is 0.03mg/L.

One of the important properties of cadmium is its solubility. Its compounds show variation in solubility ranging from high degree of solubility to insoluble (Zheng et al., 2014) According to EPA (Environment Protection Agency) it is regarded as a human carcinogen (Group B1) (Pandey et al., 2008). Cadmium toxicity includes bronchitis, pulmonary oedema, emphysema (Tchounwou et al., 2012). Cadmium also causes Itai-Itai disease. Cadmium poses serious health threats even at very low concentrations (Ajay Kumar et al., 2009). As studied by (Friberg et al., 1986) in natural unpolluted water the cadmium concentration is below 0.001mg/L. The toxic nature of cadmium makes it essential to remove from various industrial effluents before it is dumped into water bodies. Nowadays, various conventional water treatment methods are available to remove heavy metals from the industrial effluents. It includes reverse osmosis, ultrafiltration and electrodialysis; (Bazrafshan et al., 2015). These conventional methods possess both advantages and disadvantages.
The major drawbacks are its high operation charges, energy consumption, less effectiveness for low metal ion concentration, etc. To overcome the problem, the adsorption process has come up as an effective tool for heavy metal removal from various effluents. Adsorption has the significant advantage of being low-cost implementation, less energy usage, and effective at low metal concentrations. Available literature showed that there are a large number of naturally occurring adsorbents which are used for the removal of heavy metal cadmium from aqueous solution. Biomaterials like rice husk (Ajmal et al., 2003), sugarcane bagasse (Krishnan and Anirudhan, 2003), cashew nutshell (Tangjunk et al., 2009), waste tea (Ahlwalia and Goyal, 2005), agricultural wastes (Yingjie Dai et al., 2018) coffee ground (Azouau et al., 2010), areca catechu (Chakravarty et al., 2012), pine cone (Thakur et al., 2020), Peganum harmala seeds (Zamani et al., 2012), rice bran biochars (Amen et al., 2020), orange peel (Gupta and Nayak, 2012), algae (Sulaymon et al., 2013). The present work emphasizes removing cadmium from synthetic water using leaves of Averrhoa carambola as an adsorbent by the process of adsorption. The factors which affect the process of adsorption are pH, contact time, metal ion concentration and dose of adsorbent. Averrhoa carambola belongs to the Oxalidaceae family. A. carambola is commonly known as star fruit. It contains a several high oxalic acids. Previous studies on chemical constituents of carambola leaves show the presence of steroids, triterpenes (Moresco et al., 2012) cyanidin glycosides (Dan Yang et al., 2017), O-glycosyl flavonoids (Yang et al., 2015), and C-flavones (See Wan Yan et al., 2013). The presence of the above chemical constituents suggests that it may act as a good adsorbent in removing the cadmium from the synthetic water; hence it was taken as bio adsorbent in the present work.

MATERIALS AND METHODS

Preparation of stock solution
A stock solution of cadmium of 1000 mg/L was prepared by dissolving Cd (No3)2 salts in 1000 ml of distilled water. Using a stock solution of 1000 mg/L, lower concentrations of 5 mg/L, 10 mg/L, 15 mg/L, 20 mg/L, 25 mg/L and 30 mg/L were prepared by serial dilutions of stock solution. The pH of the solution was adjusted using 0.1 M NaOH and 0.1 M HCl.

Preparation of adsorbent
A. carambola waste leaves were collected from a village area in Sonapur, Kamrup rural, Assam. The collected leaves were washed with tap water to remove dirt and impurities. They were then washed with distilled water and kept for sun drying for three days followed by oven drying for a week. The oven dried sample were ground to powder using a mixer grinder. The powdered leaves were again washed with distilled water to remove colour of the leaves that may hamper AAS analysis. The washed powdered leaves were oven dried till the moisture was completely removed. The completely dried powdered leaves were sieved using 75 μm and kept in a plastic container and stored inside a desiccator for future use (Rao et al., 2010) The leaves powder of carambola is named waste A. carambola leaves powder (WACLP).

Experiment
Batch experiments were conducted under various experimental conditions like pH dose of adsorbent, initial metal ion concentration and contact time. In a 250ml conical flask, 100 ml cadmium nitrate stock solution was taken followed by WACLP powder. The mixture was set inside the shaker for 180 mins at 120 rpm. The pH varied from 2-6. Adjustment of pH was done using 0.1M NaOH and 1 M HCl. The experiment was carried out for the initial concentration ranging from 5-30 mg/L and a dose of 0.5 -0.4 gm. After reaching equilibrium time, the mixture was filtered using Whatman filter paper 41 and the filtrate was analyzed for cadmium concentration in AAS. The raw and metal adsorbed adsorbent (WACLP) was characterized by a carbon-hydrogen nitrogen analyzer (CHNS) and SEM-EDAX studies.

Analytical methods
The removal efficiency of the WACLP by adsorption process can be evaluated using Equations 1 and 2 (Gupta et al., 2022)

\[
\% (R) = \left(\frac{C_0 - C_e}{C_0}\right) \times 100
\]

where, \(C_0\) is the initial metal ion concentration (mg/L), \(C_e\) is concentration of metal ion at equilibrium(mg/L), and % R is the percentage removal

The amount of metal adsorbed on the surface of adsorbent is calculated as

\[
q_e = \left(\frac{C_0 - C_e}{M}\right) \times V
\]

Where, \(q_e\) is the amount of metal adsorbed by adsorbent, \(C_0\) is the initial metal concentration (mg/L), \(C_e\) is the metal concentration at equilibrium (mg/L), M is the mass of the adsorbent (g), V is the volume of solution (L).

RESULTS AND DISCUSSION

Elemental analysis
The elemental analysis of the adsorbent using carbon, hydrogen, nitrogen and sulphur analyzer (CHNS) showed that 40.45% of carbon content in the adsorbent imparted good adsorbent capacity. The other elements

included hydrogen (6.53%), Nitrogen (2%) and Sulphur (.05%) which were less in amount.

**Energy Dispersive Xray of raw and cadmium loaded sample**
The elemental analysis was determined by Energy Dispersive Xray (EDAX). The EDAX spectra image showed that the major elements present are chlorine, potassium, silicon, phosphorus, calcium, magnesium, sulphur, oxygen (Fig 2). It is clear from Figure 2 and Fig 3 that the elements like silicon, calcium, magnesium, oxygen, etc. were replaced by cadmium through an ion exchange mechanism and the peak intensity got reduced after the uptake of cadmium ions. The reduction in the intensity of the peak could be due to the binding of the cadmium ions onto the surface of adsorbent. Similar reports were marked by Zulfi et al., 2013 on Annona muricata L. seeds for Pb (II) and Cu (II) ions.

**Scanning Electron Microscopy**
The Scanning Electron Micrography (SEM) of cadmium loaded biosorbent taken at 20kv and 1000x magnification of Cd (II) before adsorption and showed uneven and porous structures. The irregular texture and cavity-like structures were modified into smooth texture after adsorption. The cavity-like structures acted as adsorption sites for the cadmium. SEM micrographs suggested a porous, heterogeneous rough surface which made it potential to adsorb cadmium ions. After cadmium treatment adsorbent appeared to be smooth and altered in the texture. Similar reports were observed in Lemna polyrrhiza L. for cadmium metal removal (Unadkat et al., 2018)

**Batch equilibrium studies**

**Effect of pH on cadmium adsorption by WACLP**
The process of adsorption is highly influenced by pH of the solution. The pH undertaken in the present study varied from (1-6). At low pH, Cd (II) ions compete with H^+ ions which are more in numbers for the adsorption sites on the surface of the adsorbent. This causes low adsorption in the lower pH range. As the pH increases, the concentration of H^+ ions decreases and the competition for the adsorption sites between H^+ and Cd (II) ions reduces. This results in the occupation of adsorption sites by Cd (II) ions. The availability of more negative charge on the surface of the adsorbent results in a strong bond of attraction between Cd (II) ions and the adsorption sites. Above pH 6 precipitation of metal hydroxide takes place. As studied by Pavasant et al., (2006) formation of metal hydroxide could occur above pH of 6.5. Hence, In the present work experiment was conducted at below pH 6. As studied by various researchers, pH value of 5 is considered good for equilibrium and Kinetics studies (Ajay Kumar et al., 2009). According to Salim et al. (2008) cadmium removal by combination of leaves was maximum at pH 5. Panda et al. (2006) studied the husk of Lathyrus sativus and

![Image of Wastes Averrhoa Carambola leaves powder (WACLP) powder](image1)

**Fig. 1. Wastes Averrhoa Carambola leaves powder (WACLP) powder**

![Image of Energy dispersive X ray (EDAX) of raw wastes leaves of Averrhoa carambola (WACLP)](image2)

**Fig. 2. Energy dispersive X ray (EDAX) of raw wastes leaves of Averrhoa carambola (WACLP)**

![Image of Energy Dispersive X ray (EDAX) of cadmium loaded spectra](image3)

**Fig. 3. Energy Dispersive X ray (EDAX) of cadmium loaded spectra**
showed maximum adsorption at pH value of 5. Bilal et al. (2021) showed optimum pH of 6 for the removal of cadmium by Capparis decidua and Ziziphus mauritiana. Ali et al. (2022) also reported the adsorption of cadmium onto guava leaves at pH value of 5.6.

Effect of initial metal on adsorption by WACLP
The effect of initial metal ion concentration on adsorption was studied in the range of 5 to 30 mg/L. Experimental values showed that the removal percentage increases as the initial metal concentration increases from 5 mg/L to 10 mg/L. Further increase in metal ion concentration does not increase the metal removal percentage. This can be because the binding sites get saturated on the adsorbent surface. From Fig. 6, it was evaluated that the removal efficiency decreased from 92.6% to 91% as the initial metal ion concentration increased from 5 to 30 mg/L. The maximum removal was at 15 mg/L and hence 15 mg/L was considered as optimum metal ion concentration for equilibrium and kinetic studies. The reason for the decrease in removal percentage as metal ion concentration increases is the accumulation of adsorbent particles at higher metal ion concentration (Ajay Kumar et al., 2009). The binding sites get occupied at lower metal ion concentrations.

Effect of adsorbent dose on cadmium adsorption by WACLP
The effect of adsorbent dosages on the concentration of Cd (II) ions is presented in Fig. 8. The dose of the adsorbent varied from 0.5 to 4 g/L. Fig. 7 indicated that as the dose of the adsorbent increased from 0.5 to 2 gm there is increase in the percentage removal of cadmium. Further, when the dose was increased, the removal percentage was reduced due to the loading of the adsorbent particles and due to the intercellular dissociation binding capacity of the metal ion affected (Zhao et al., 2017). The maximum removal percentage was at 2 gm dose of adsorbent. The significant increase in Cd (II) adsorption took place when the dose increased from 0.5 to 2g/L. Similar reports have been observed for cadmium ion adsorption onto mushrooms (Vimala and Das., 2009) and mango peel waste (Iqbal et al., 2009).

Effect of contact time on cadmium adsorption by WACLP
The effect of contact time on the removal of cadmium was studied at contact times ranging from 30-180 mins. Fig. 8 showed the removal percentage by WACLP increased as the time increases from 30 mins to 90 mins. During the initial period the increase in removal of cadmium was due to the availability of active binding sites on the adsorbent surface. Gradually, the sites get occupied by metal ions and hence further increase in time does not increase the cadmium adsorption. The equilibrium time for maximum cadmium removal was 90 mins. This suggests that no adsorption occurred after 90 mins as most of the vacant sites were filled up at 90 mins (Al-Homaidan et al., 2015).

Adsorption isotherm
Langmuir, Freundlich and Temkin Isothermal models were studied to fit the experimental data. The Langmuir isotherm assumes monolayer adsorption without interaction between adsorbed ions (Langmuir, 1918). The equation is expressed as:

$$\frac{Ce}{q_e} = \frac{1}{q_L K_L} + \frac{C_e}{q_L}$$

Where, $C_e$ represents the equilibrium concentration of the metal ions (mg/L), $q_e$ represents the amount of metal ions adsorbed by a unit mass adsorbent (mg/g), $q_L$ denotes the maximum amount of the metal ions adsorbed by the unit mass adsorbent (WACLP) in (mg/g), and $K_L$ represents the Langmuir constant (L/mg). Langmuir constant is related to affinity of the binding sites and sorption energy.

A plot between $1/q_e$ and $1/C_e$ gives the value of slope and intercept. One of the important parameters of Langmuir is the separation factor $R_L$. It is expressed by the equation (4) given below

$$R_L = \frac{1}{1+bC_i}$$

Where, $C_i$ is the initial concentration (mg/L). Values of separation factor provides an idea about the type of adsorption. The value of $R_L$ ranges from (0-1). If the value is 0, adsorption is irreversible, favourable adsorption when $0<R_L<1$, linear when $R_L$ is 1 and unfavourable when $R_L$ is above 1.

The Freundlich isotherm depends on the interaction between adsorbed ions. It is expressed as by equation (5).

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

Where, $K_f$ and $n$ are Freundlich constants. $K_f$ is adsorption capacity and $n$ being dimensionless constant relating to adsorption intensity. A plot between $\log q_e$ and $\log C_e$ gives the value of slope and intercept (Freundlich, 1906).
Temkin isotherm
It assumes that heat of adsorption of all the molecules on the adsorbent surface decreases linearly. The linear form is expressed by Equation 6

\[ q_e = \left(\frac{RT}{b}\right) \times \ln A + \left(\frac{RT}{b}\right) \times \ln C_e \]  (6)

Where \((RT/b) = B\), \(R\) is universal gas constant, \(T\) is the absolute temperature and \(b\) is Temkin constant. \(B\) (j/mol) is constantly related to the heat of adsorption. \(A\) (L/mg) is equilibrium binding constant.

Table 2 inferred that the maximum adsorption capacity \((q_{max})\) on the surface of \(A.\ carambola\) was estimated to be 10 mg/g. Lower 
\((q_{max})\) ion adsorption capacity have been reported for other adsorbent such as, Wheat bran (0.7 mg/g) (Singh et al., 2006), Rice polish (0.972 mg/g) (Singh et al., 2005). Based on regression coefficient \((R^2)\) values, the adsorption isotherm was best fitted to the Langmuir isotherm model with an \(R^2\) value of 0.976. Previous studies on the removal of Cd (II) by the modified algae and ash as adsorbent indicated the Langmuir model as the Best fitted model for adsorption for removal of Cd (II) ions (Maria Harja et al., 2015).

<table>
<thead>
<tr>
<th>Langmuir isotherm</th>
<th>(q_{max}) (mg/g)</th>
<th>(K_L) (L/mg)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WACLP</td>
<td>10.35</td>
<td>0.976</td>
<td>0.193</td>
</tr>
<tr>
<td>Freundlich isotherm</td>
<td></td>
<td>(K_f)</td>
<td>(R^2)</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>0.966</td>
<td>1</td>
</tr>
<tr>
<td>Temkin isotherm</td>
<td></td>
<td>(B_T) (J/mol)</td>
<td>(K_T) (L/mg)</td>
</tr>
<tr>
<td></td>
<td>1.458</td>
<td>1.58</td>
<td>0.974</td>
</tr>
</tbody>
</table>

Table 3. Pseudo first order kinetic parameters for biosorption of Cd (II) by WACLP

<table>
<thead>
<tr>
<th>(C_d) (mg/L)</th>
<th>(q_{(exp)}) (mg/g)</th>
<th>(q_{(cal)}) (mg/g)</th>
<th>(K_f)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.2274</td>
<td>0.021126</td>
<td>0.0065</td>
<td>0.97154</td>
</tr>
<tr>
<td>10</td>
<td>2.18</td>
<td>0.066848</td>
<td>1.16</td>
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<tr>
<td>15</td>
<td>0.695</td>
<td>0.308822</td>
<td>1.28</td>
<td>0.96544</td>
</tr>
<tr>
<td>20</td>
<td>0.92</td>
<td>0.37723</td>
<td>1.38</td>
<td>0.78706</td>
</tr>
<tr>
<td>25</td>
<td>1.14</td>
<td>0.563099</td>
<td>0.0000085</td>
<td>0.86263</td>
</tr>
<tr>
<td>30</td>
<td>1.37</td>
<td>0.578625</td>
<td>1.3</td>
<td>0.912045</td>
</tr>
</tbody>
</table>
Table 4. Pseudo second order kinetic parameters for biosorption of Cd (II) by WACLP

<table>
<thead>
<tr>
<th>C1 (mg/L)</th>
<th>qe(exp)(mg/g)</th>
<th>qe(cal)(mg/g)</th>
<th>k1</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.22745</td>
<td>0.248843</td>
<td>0.004798</td>
<td>0.99971</td>
</tr>
<tr>
<td>10</td>
<td>0.462</td>
<td>0.451875</td>
<td>0.00575</td>
<td>0.99997</td>
</tr>
<tr>
<td>15</td>
<td>0.695</td>
<td>0.620544</td>
<td>0.00675</td>
<td>0.99976</td>
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<tr>
<td>20</td>
<td>0.92</td>
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<td>0.991</td>
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<td>25</td>
<td>1.14</td>
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<td>0.00834</td>
<td>0.99999</td>
</tr>
<tr>
<td>30</td>
<td>1.37</td>
<td>2</td>
<td>0.00865</td>
<td>0.99986</td>
</tr>
</tbody>
</table>

Adsorption kinetics

Two important kinetic models were studied to evaluate the adsorption process. The Kinetic experiment was investigated for the concentration range 5-30 mg/L and operating optimum conditions of pH 5, a dose of 2 gm and an equilibrium time of 90 mins at 120 rpm. The equation for Pseudo first order is expressed by equation

$$\log(qe - qt) = \log(qe) - \frac{K_1}{2.303t}$$  \hspace{1cm} (7)

where, qe (mg/g) and qt (mg/g) are adsorption capacity of Cd (II) ions at equilibrium and time t. K1 is rate constant. A plot between ln(qe-qt) versus time gives slope and intercept, k1, qe.

The Pseudo second order kinetics is expressed by equation

$$\frac{t}{qt} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (8)

where, k2 is second order rate constant. A plot between t/qt and t gives slope and intercept and k2 value from slope and intercept. The slope was obtained as 1/qe and 1/k2 qe² as the intercept

Table 3 and Table 4 present the summary of kinetic parameters. The plots are shown in Fig 10. The pseudo-second order regression coefficients were higher than the first-order. Moreover, the calculated values of adsorption capacities qe at equilibrium of pseudo-second order were close to the experimental qe values. Hence, the adsorption of Cd (II) on WACLP followed pseudo-second order kinetics and was based on chemisorption and there was ion exchange between adsorbent surface and metal solution (Abbas et al., 2019).

A similar study on cadmium adsorption by Erythrina variegata orientalis leaf powder (Kumar et al., 2009); Psidium guajava L leaf powder (Rao et al., 2010) and bamboo stem biomass (Akinyeye et al., 2019) showed pseudo-second order reactions. Removal of cadmium and copper by biosorption on Typha angustifolia leaves also showed pseudo-second order kinetics (Guechi et al., 2020).

Conclusion

The present study concluded that adsorption by leaves powder of carambola named waste A. carambola leaves powder (WACLP) depended on various parameters like pH, initial metal ion concentration, contact time and dose of the adsorbent. The removal percentage was maximum at 15 mg/L concentration and an in-
crease in further initial concentration did not increase removal capacities. Results showed best fits to Langmuir isotherm suggesting monolayer adsorption. Further, the adsorption by WACLPL also best fitted to Pseudo second order kinetics. Henceforth, WACLPL bore good potential in the removal of Cd (II) from synthetic water.

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Conflict of interest

The authors declare that they have no conflict of interest.

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