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International Journal For Research in
Applied Science and Engineering Technology

INTERNATIONAL JOURNAL
FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Bioadsorption Behaviour and Thermodynamic Study Of Cadmium (II) on A.Barbadensis Miller Leaves Residue Powder

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Abstract: This present study aims to report batch adsorption of Cadmium Cd(II) on A.barbadensis Miller leaves residue powder (ABL). Adsorption behaviors were determined by varying operating parameters such as pH, initial concentration, doses, temperature and contact time. At 0.6 g bioadsorbent dose and initial concentration of Cd (II) ions 100 mg/l , Equilibrium time and Optimum pH value was found to be 120 min and pH 6 at 293 K. 82.1 to 59.2 % removal of Cd (II) were observed when temperature increases from 293 to 333 K . Thermodynamics parameters were obtainted to be better understanding mechanism of adsorption .The standard Gibbs free energy ΔG° value for the adsorption processes of Cd(II) was obtained negative value, ΔG° confirms the feasibility of the adsorption process and spontaneous nature of adsorption. The values of ΔH° and ΔS° for Cd(II) were obtained as -23.911,kJ/mol and -0.026,kJ/mol respectively. The negative value of ΔH° indicates exothermic nature of adsorption and negative value ΔS° value confirms the decrease randomness at the solid-liquid interface during adsorption on A.barbadensis Miller leaves residue .
Keywords : Bioadsorption, A.barbadensis Miller leaves powder , Cadmium , Gibbs free energy, Thermodynamics

I. INTRODUCTION

Heavy metals are source of generated by direct discharge of municipal and industrial wastewater. At elevated concentrations, soluble metal compounds can be deleterious to human health as well as to aquatic and marine environments. Cadmium (Cd) is one of the heavy metals considered to be toxic to humans and aquatic life[1].The major sources of water contamination by heavy metal Cd are a number of industries, such as welding and soldering, electroplating photography, production of iron, steel and cement, use of superphosphate fertilizers and pesticides, and production of nickel–cadmium batteries[2]. According to WHO's recommendation Cd(II) limit in drinking water is 0.005 mg/L.[3] Chronic exposure to Cd can affect the nervous system, liver, cardiovascular system and may lead to renal failure and death in mammals and humans.[4] Traditionally, the most widely applied methods for heavy metal removal from wastewaters are chemical and electrochemical precipitation , cationic and anionic ion-exchange resins, membrane filtration, and sorption [5]. Whereas, some methods such as ion-exchange and reverse osmosis are costly, others such as precipitation techniques have problems for disposal of metal-containing sludge.[6] Biosorption methods are considered flexible, easy to operate, with much less sludge disposal problems. Besides different types of commercial adsorbents such as granular activated carbon or powdered activated carbon, several low-cost adsorbents generated by forestry and agricultural activities able to sequester heavy metals from contaminated waters have been extensively studied.[7] *Aloe barbadensis* miller is a plant, which belongs to the family of Liliaceae, it is succulent with a whorl of elongated, pointed leaves. It is a perennial medicinal herb found almost everywhere in India. It is a xerophyte and can be grown even in dry lands under rain fed conditions. It is an erect plant with an ultimate height of 0.8m/2.6ft and spread of 0.8m/2.6ft with green, dagger-shaped leaves that are fleshy, tapering, spiny, marginated and filled with a clear viscous gel[8]. The objective of the present study is to investigate the feasibility of A.barbadensis Miller leaves (ABL) powder as an alternative adsorbent for the removal of Cd from wastewaters. ABL contains various organic compounds (lignin, cellulose, and hemicellulose) with polyphenolic groups that might be useful for binding heavy metal ions. Batch experiments were carried out for thermodynamic studies on the removal of Cd from aqueous solutions. The influence of various contributing parameters such as pH, adsorbent concentration, contact time, and initial Cd concentration were investigated.

II. MATERIALS AND METHOD

A. Adsorbate

The chemical used in the study were of guaranteed reagent grade . stock solution of Cd (II) were made by dissolving exact amount $Cd(NO_3)_2$. $4H_2O$ in Distilled water. Solution were prepared by diluting stock solution of Cd (II) with double- distilled water .The pH of solution was adjusted with 1 N HCl and NaOH solution.

B.   Preparation of Adsorbent

ABL waste obtained from the Aryuvedic Juice Industries in New Delhi , ABL waste were washed several times followed by distilled water to remove particulate material from their surface , After that , They were dried in an oven 85 ^{0} C for 24 h. The dried leaves were ground and sieved to a particles size 150 µ m. Dried powder was stored in a dry place air tied box and to used for batch experiments.

C.   Batch Experiments

Batch adsorption experiments were carried out at constant temperature (30±1 ∘C) by adding different amounts of ABL (0.2–2 g/L) to 100 mL conical flasks containing aqueous solutions with varying initial Cd concentrations (20–200 mg/L). pH values of ABL Cd aqueous solutions were adjusted to desired levels (pH 1–10) using 0.1 N HCl or 0.1N NaOH. The flasks were shaken on an BOD orbit shaker at 150 rpm for varying durations (15–200 min) to study the influence of contact time between adsorbent and Cd on adsorption efficiency. After specified contact times, aliquots of ABL Cd aqueous solutions were filtered through 125 mm filter papers (Whatman No.5), and the filtrates were analyzed for residual Cd using flame AAS Atomic Absorption Spectrophotometer ECIL, India, using air acetylene flame was used for the determination of Cd(II) ions in the samples,for adsorption efficiency assessment as shown in Fig1.

Adsorption efficiency was expressed as a percentage of adsorbed metal compared to initial metal concentration, whereas adsorption capacity was expressed as amount of Cd adsorbed per mass

unit of ABL using the following equations, respectively:

$$q_e = \frac{(C_0 - C_e)V}{M} \qquad (1)$$

$$\% \text{ of Removal (R)} = \frac{(Co - Ce)}{Co} \times 100 \qquad (2)$$

Where C_o initial concentrations of Cd (II) ion solution, (ppm), C_e concentrations of Cd (II) ion solution at equilibrium,(ppm), M amount of adsorbent (g), q_e amount of adsorbate Cd (II) ions adsorbed per unit weight of the sorbent at equilibrium,(mg /g), V volume of Cd (II) solution (ml). To determine the optimum parameter by effect of behaviour as shown in Fig 2 .
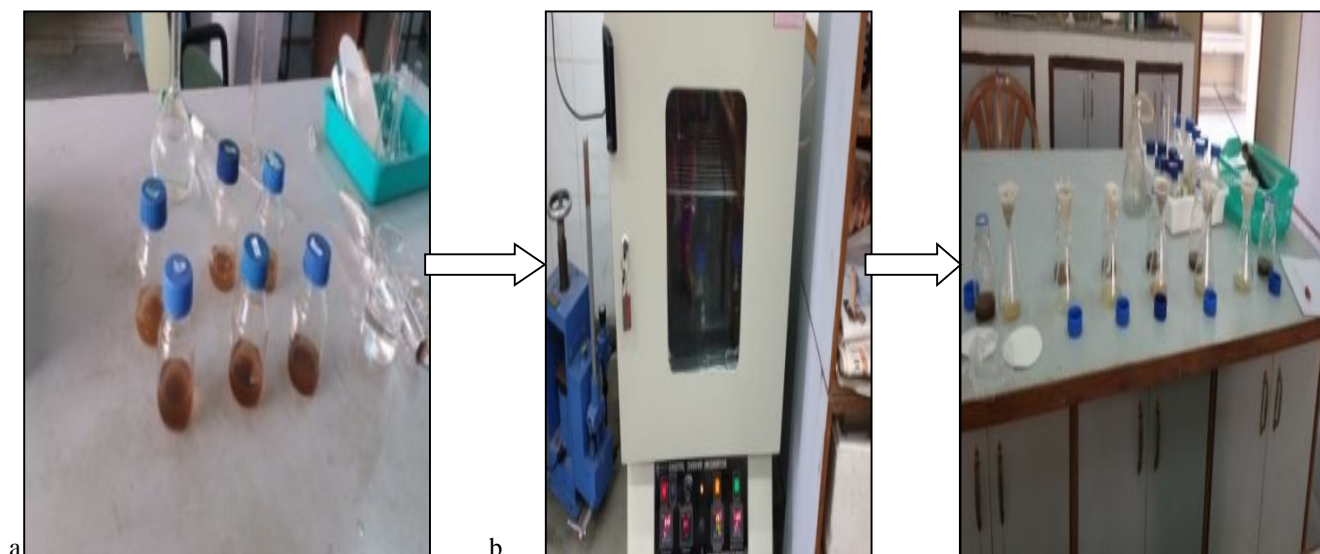

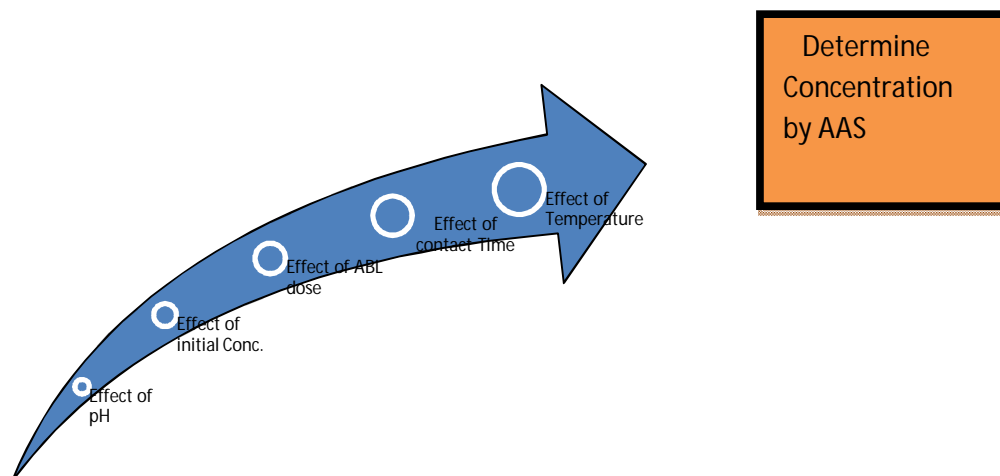Fig1:Bioadsorption process(a)adsorbate + adsorbent (b) Shaking for 120 min.(c) Filteration by Whatman paper .

Fig 2 : Bioadsorption Behaviour by removal of Cd (II)

III. RESULT AND DISCUSSION

A. *Effect of Initial pH of Suspension on Biosorption Efficiency*

pH parameters is an important influencing factor for heavy metal adsorption on ABL . In a certain pH range, most metal adsorption increases with increasing pH up to a certain pH value . In this study, the effect of pH on Cd adsorption by ABL is investigated by varying the pH of Cd solution (100 mg/L)–ABL (0.6g/L) and shaking the suspensions for contact times 120 min. Irrespective of allowed contact times, the percent adsorption of Cd was minimal (<49%) at pH 1–2, significantly increased to 78% in the pH range 2–5, and reached >95% at pH range 6–11 with a maximum of >99% at pH 9–10, . Decrease in adsorption at higher pH is due tothe formation of soluble hydroxyl complexes[9] Thus, the favorable pH for maximum Cd adsorption on the adsorbent under study was at 6, and this pH value was selected to further investigate the influence of other contributing parameters on the sorption process. The effect of pH on Cd removal efficiency at 120 min contact time is illustrated in Fig. 3.
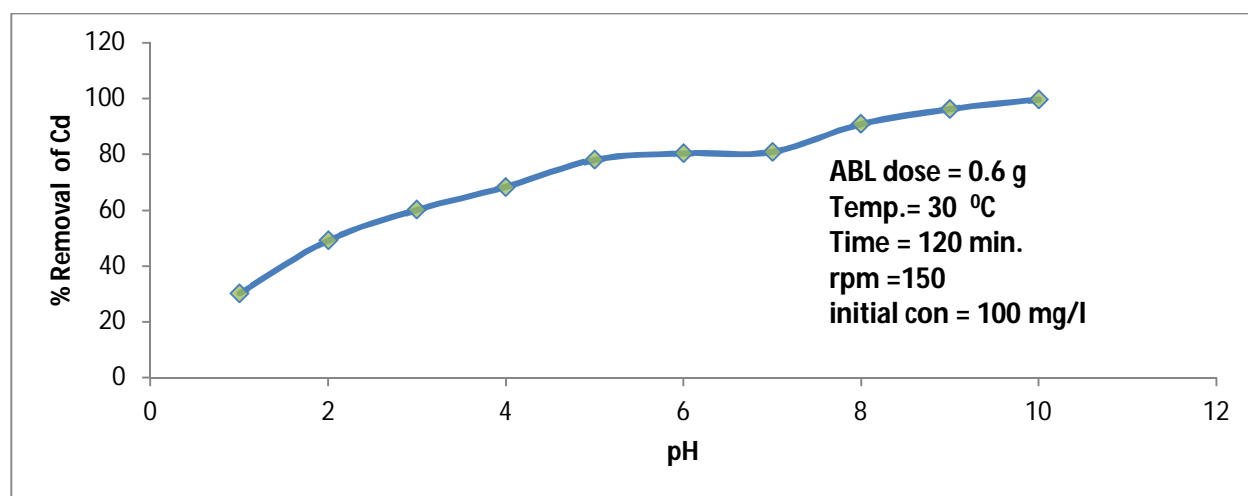

Fig 3 : Effect of pH variation on Cd removal through adsorption on ABL

B. *Effect of Contact Time on Sorption Efficiency*

The effect of contact time on efficiency of Cd (II) bio adsorption on ABL is investigated to study the rate of Cd removal. ABL of contact time at pH of 6 is illustrated in Fig. 4. From the plots, it is evident that for the investigated varying initial concentrations of Cd, maximum adsorption rates (78.2 %) are achieved almost in the first 120 min of contact for Cd concentrations of 100 mg / L . A

further increase in the contact time has a negligible effect on the rate of Cd adsorption. The rate of metal removal is higher in the beginning due to a larger surface area of the ABL being available for metal adsorption [10]. An equilibrium was established at 120 min as the adsorption did not change with further increase in contact time .
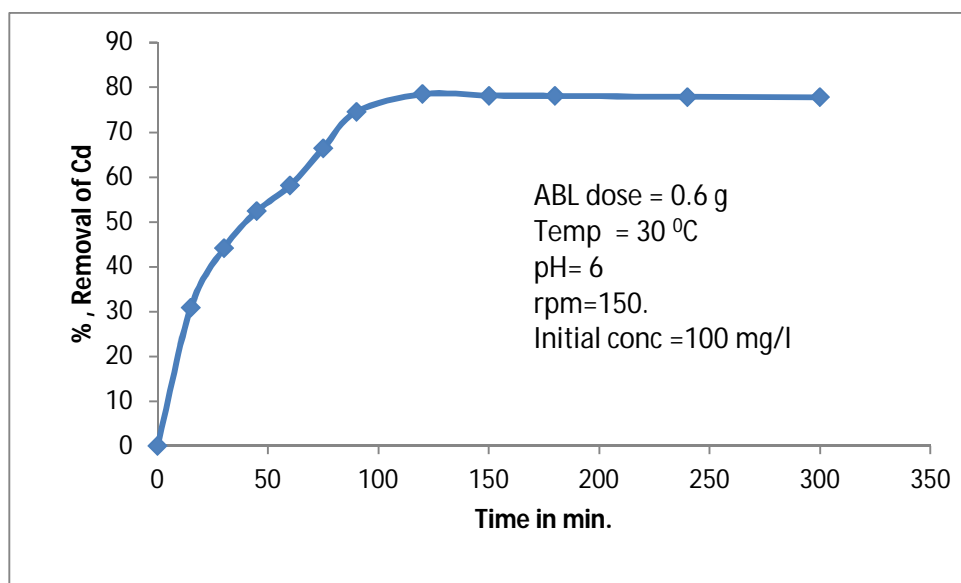

Fig 4: Effect of contact time on Cd removal using ABL

C.   Effect of Bioadsorbent

The effect of bioadsorbent dose onto Cd adsorption in Fig. 5. It is apparent that the percent removal of metal ions increases (60.3 to 88.3 %) from with increasing weight (0.2 g to2 g) of ABL due to the greater availability of surface area and thus exchangeable sites[11]. However, once almost all Cd is adsorbed, the contribution of additional adsorbent will be insignificant. On the other hand, the adsorption capacity, the amount adsorbed per unit mass of adsorbent, decreases mainly due to un-saturation of adsorption sites through the adsorption reaction. Another reason may be due to the particle interaction, such as aggregation, resulting from high sorbent concentration. Such aggregation would lead to decreases in total surface area of the sorbent and an increase in diffusion path length [12.] It can be noted from Fig. 5 that adsorption capacity, q, decreased from 30.5 to 4.44 mg/g as ABL concentration from 100 mg / L.
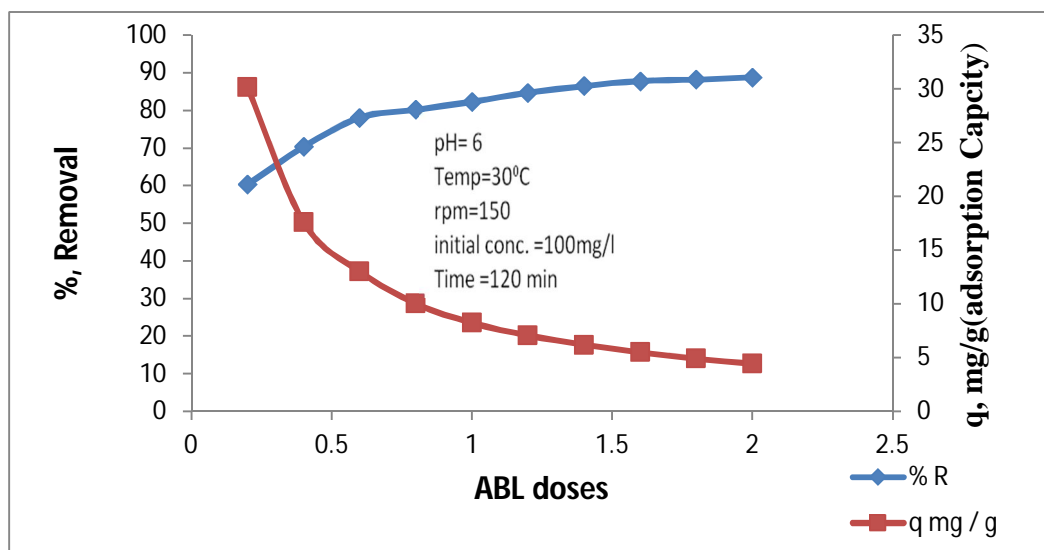

Fig.5. Effect of adsorbent dose on Cd removal using ABL at 120 min contact time.

International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor:6.887
Volume 5 Issue VIII, August 2017- Available at www.ijraset.com

D.   Effect of Initial Cadmium Concentration on Sorption Efficiency

The effect of initial Cd concentration (20–200 mg/L) was investigated at pH of 6.0 in the presence of 0.6 g ABL , and recorded outcomes are illustrated in Fig. 6. The plots reveal that for contact times, an increase in the Cd concentration from 20-200 mg/L results in a decrease in the percent metal removal from 80.1% to 60.2%, and an increase in adsorption capacity from 2.6to 20.6 mg/g. The decrease in the percentage removal of Cd can be attributed to saturation of available active sites on the adsorbent above a certain concentration of metal. The increase in adsorption capacity may be due to the higher adsorption rate and the utilization of all available active sites for adsorption at higher metal concentration[13.]
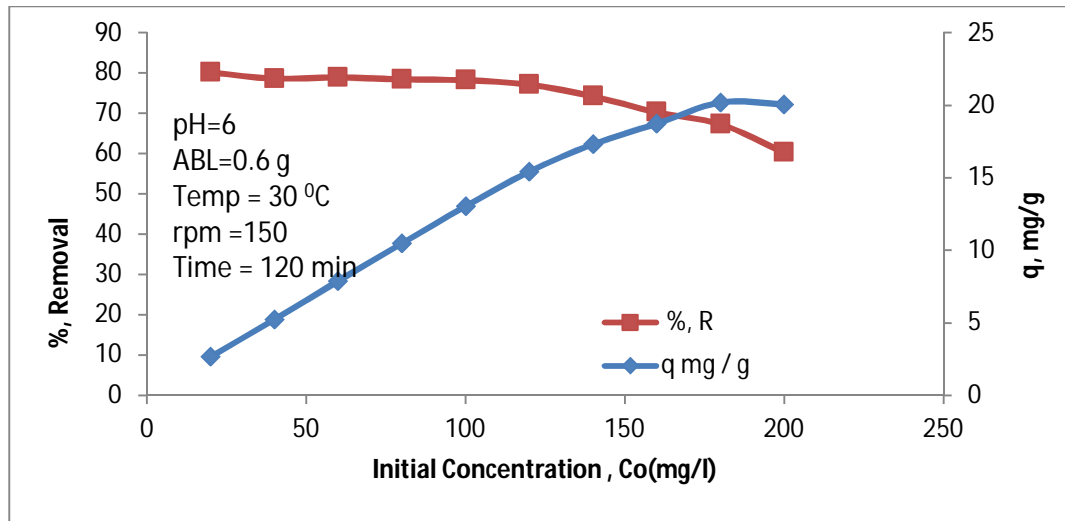

Fig. 6. Effect of initial Cd concentration on Cd removal using ABL .

E.   Effect of Temperature

The removal of Cd(II) by ABL were obtained at 293, 303 , 313.323,333 K (Fig. 7). At an equilibrium time of 120 min for initial Cd(II) concentration of 100 mg/l, the percentage removal decrease form 82.1 to 59.2 % with the increase in temperature from 293 to 333K .The sorption capacity decrease with increase in temperature indicating that the sorption process was exothermic . The decrease in adsorption capacity of ABL at high temperature may be attributed to enlargement of pore size or increase in the active surface for absorption at low temperature This could also be due to the enhanced mobility of the metal ions from the bulk solution Thermodynamics of the Adsorption of Cd(II) from Aqueous Solution on ABL towards the adsorbent surface and extent of penetration within ABL structure overcoming the rate of intraparticle diffusion [14] .
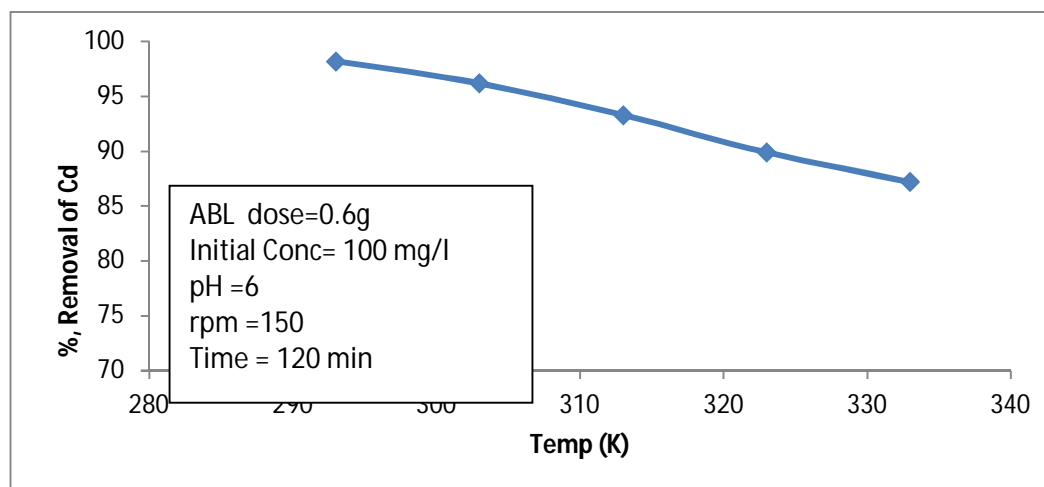

Fig. 7.Effect of temperature on Cd removal using ABL at contact times.

F.   *Thermodynamic Parameters of Adsorption*

The adsorption process of metal ions can be summarized by the following reversible process, which represents a heterogeneous equilibrium. Metal ions in solution ↔ Metal ions adsorbent The apparent equilibrium constant (*Kc*) of the adsorption is defined as by the following reversible process, which represents a heterogeneous equilibrium.

Metal ions in solution ↔ Metal ions adsorbent

$$K_c \;=\; \frac{q_e}{C_e} \tag{16}$$

$$\Delta G^0 \;=\; -RT \, \ln K_c \tag{17}$$

$$\ln K_c \;=\; \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{18}$$

where K_c equilibrium constant, ΔG^0 Gibb's free energy (kJ/mol), ΔS^0 entropy(kJ/mol), ΔH^0 enthalpy(kJ/mol) and R ideal gas constant . The values of ΔH^o and ΔS^o were calculated from the slope and intercept of the plot $\ln K_c$ vs 1/T of the Fig.10 and are listed in Table.1

T (K) the absolute temperature, *R* the gas constant (8.314 J/mol K), $\Delta S o$ the entropy change (J/mol) and $\Delta H o$ the enthalpy change (kJ/mol). $\Delta H o$ and $\Delta S o$ values were obtained from the slope and intercepts of van't Hoff plot, ln *Kc* versus *1/T* (Fig. 8).

Table I

Thermodynamic parameters for adsorption of Cd (II) on ABL

Temp (K)	ΔG KJ/MOL	Δ H , Kj / mol	ΔS , Kj / mol
293	-16.17294154	-23.911	-0.026
303	-16.10577033		
313	-15.78394153		
323	-15.42462864		
333	-15.19451962		

The Gibbs free energy indicates the degree of spontaneity of the adsorption process and the higher negative value reflects a more energetically favorable adsorption .[15]
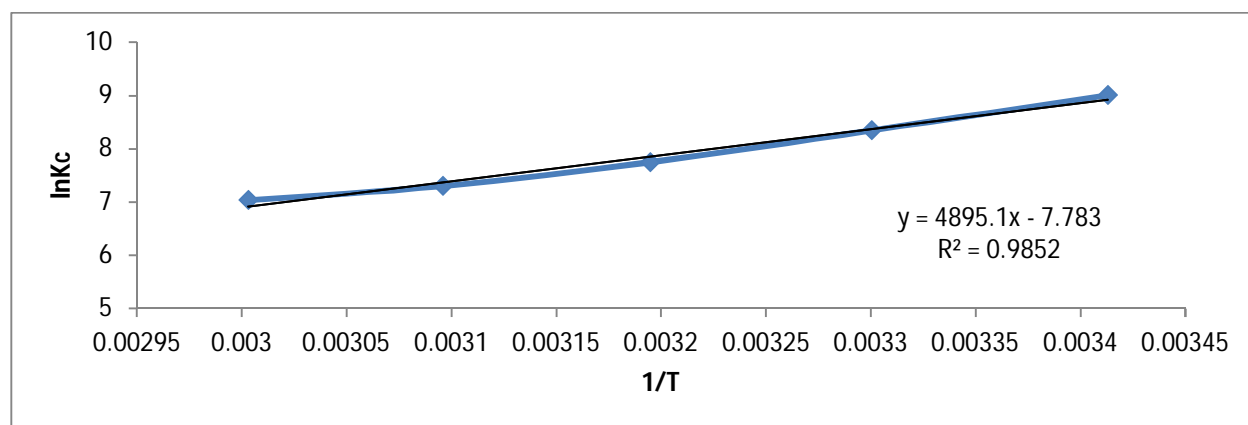

Fig 8 :   van't Hoff plots for Cd(II)

The values of ΔH^o and ΔS^o for Cd(II), was obtained as -23.911 kJ/mol and -0.026 KJ/mol respectively. The negative value of ΔH^o indicates exothermic nature of adsorption and negative value of $\Delta S o$ value confirms the decrease randomness at the solid liquid interface during adsorption [16].

IV. CONCLUSION

The present study revealed that the Cd (II) uptake onto ABL bioadsorbent provide good retention capacity at normal pH 6. According to the thermodynamic study the reaction was exothermic as low temperature favored the uptake of Cd (II) and negative ΔH^0 values , spontaneous and feasibile as shown by the negative values of the ΔG^0 of the adsorption Process . The method presented in this work might be of interest for industrial and for environmental applications for the removal of toxic metal ions from the environment. Using plant leaves for the removal of metal ions have the advantages of being available, cheap and efficient.

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