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Equilibrium and Thermodynamic Study of Cadmium Adsorption on *Dalbergia Sissoo* Sawdust

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ABSTRACT

In the present paper, the equilibrium and thermodynamic parameters of cadmium adsorption from aqueous solution on sodium hydroxide modified Dalbergia sissoo sawdust were evaluated on the basis of Langmuir, Temkin and Dubinin-Radushkevich isotherms. The adsorption of cadmium on sawdust was monolayer type, renewable and occurred by complexation mechanism. The analysis of thermodynamic data indicated that adsorption of cadmium on Dalbergia sissoo sawdust is spontaneous, exothermic and entropy driven. The linear form of Dubinin-Radushkevich isotherm was established which can be used for evaluation of saturated equilibrium concentration of adsorbate where all adsorption sites become fully occupied. The correlation between Langmuir and Temkin adsorption parameters was also explored which indicated that the magnitude of enthalpy of adsorption is equal to the heat of adsorption at half coverage. The results and interpretations based on present study may be used as a source for understanding the nature of adsorption phenomena.

1. Introduction

The discharge of toxic metal ions from industry and other institutions can affect the quality of water supply [1, 2]. Cadmium is one of the toxic metal ions that is released from different processing industries and ultimately enters into the human body through the food chain. Cadmium deteriorates normal function of our vital organs [3, 4]. A variety of physical and chemical methods are used for the treatment of industrial effluents, including chemical precipitation, adsorption, ion-exchange, membrane separation etc [5, 6]. Adsorption is considered one of the simple, efficient and cost effective techniques for the removal of pollutants from gaseous or liquid phase by solid substrate [7, 8]. It can be characterized on the basis of different models which utilize different approaches for physical interpretation of adsorption parameters [9-13].

The adsorption of heavy metal ions on natural materials is extensively being studied in search for low cost and potential adsorbents [14-16]. A low cost adsorbent is one which is abundant in nature, waste material or a byproduct of an industry and requires little processing. Sawdust is one of the low cost adsorbent which is abundantly available as a byproduct of wood mills [17-20]. *Dalbergia sissoo* sawdust has been studied as a potential adsorbent for the removal of nickel and copper from aqueous systems [21, 22]. Other agricultural and plant based materials like rice husk, sugarcane bagasse, pine bark etc. have also been recognized as potential adsorbents for the removal of heavy metal ions from aqueous systems [14-16].

The major constituents of agricultural and plant based adsorbents are lignin, cellulose and hemicellulose. Singh *et al*. (2014) reported that *Dalbergia sissoo* sawdust consists of cellulose (34.4%), hemicellulose (28 %), lignin (23.3 %) and ash (2 %) [23]. The methyl esters groups contained in lignin, cellulose and hemicellulose are converted to carboxyl functional groups on pretreatment with strong base [21]. These carboxyl functional groups play major role in the binding of metal ions to agricultural and plant based adsorbent via complexation and ion-exchange mechanism [16, 24, 25].

The aim of the present work was to investigate the equilibrium and thermodynamic characteristics of cadmium adsorption on *Dalbergia sissoo* sawdust modified with NaOH. The most common name of *Dalbergia sissoo* is Shisham. The pH, amount of adsorbent and concentration of NaOH required for the pretreatment of sawdust were optimized. The Langmuir, Temkin and Dubinin-Radushkevich isotherms were applied for the evaluation of various adsorption parameters. The correlation between Langmuir and Temkin isotherm parameters was also explored for interpretation of adsorption parameters.

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2. Material and Method

2.1 Equipments

The EG&G Princeton Applied Research model 174A Potentiostat/ Galvanostat and model RE 0089 x-y recorder were used for differential pulse voltammetric analysis of cadmium ion at hanging mercury drop electrode. Differential pulse voltammetry was used to measure the equilibrium concentration of cadmium using hanging mercury drop as a working electrode, Ag/AgCl(sat. KCl) as a reference electrode and platinum wire as counter electrode. The flask shaker Model SF1, Stuart Scientific, UK was used for sample shaking. Temperature was maintained using Thermostirrer Model BKL-235. The pH was measured with Metrohm model 781 pH/ion meter equipped with combination glass electrode and Pt1000 temperature sensor. The Sartorius Model CP224S balance was used for weighing. The samples were prepared in glass culture tubes with polyethylene caps.

2.2 Chemicals

All chemicals were of analytical grade purity obtained from Merck. The stock solution of 0.01 mol L^{-1} cadmium was prepared using $Cd(NO_3)_2.4H_2O$. The cadmium was used as adsorbate in the present study. All solutions were prepared in deionized water. NaOH and $HClO_4$ were used for adjustment of pH.

2.3 Adsorbent

The *Dalbergia sissoo* sawdust was used as adsorbent for the removal of cadmium from aqueous solution. The sawdust was in form of thin flakes with bulk density of 0.22 g cm^{-3} obtained from local wood mill.

2.4 Methodology of Adsorption Analysis

Samples with different initial concentrations of cadmium were prepared in glass culture tubes by dilution of different volumes of 0.01 mol L^{-1} stock solution of cadmium. The total volume of each sample was made up to 10 ml by addition of deionized water. Since there was very slight effect of shaking time on the adsorption of cadmium; therefore, all samples were shaken for one hour for establishment of equilibrium condition. Centrifugation was not required in the present study because clear solution of each sample can easily be pipette out for voltammetric analysis of equilibrium concentration of cadmium. The number of moles of cadmium adsorbed per gram of sawdust was calculated by using the following equation:

$$n = \frac{([A]_0 - [A]_e)V}{1000\,m} \quad (1)$$

where n (mol g^{-1}) is the number of moles of cadmium adsorbed per gram of adsorbent, m (g) is the weight of sawdust, $[A]_0$ and $[A]_e$ (mol L^{-1}) are the initial and equilibrium concentration of adsorbate respectively and V (ml) is the volume of sample solution.

2.5. Optimization of Sawdust Weight

The optimum weight of sawdust is the minimum quantity of sawdust used for adsorption study beyond which the magnitude of n is not affected significantly with increasing weight of adsorbent. In order to find the optimum weight of sawdust, the adsorption of cadmium was studied on different weights of sawdust at pH 5 from 10 ml sample containing 0.005 mol L^{-1} initial concentration of cadmium and the magnitude of n was evaluated as function of weight of sawdust. The data in Fig. 1 indicates that the effect of change in weight of sawdust on n is negligible at ≥ 0.25 g. Thus 0.25 g was considered as optimum amount of sawdust required for further adsorption study.

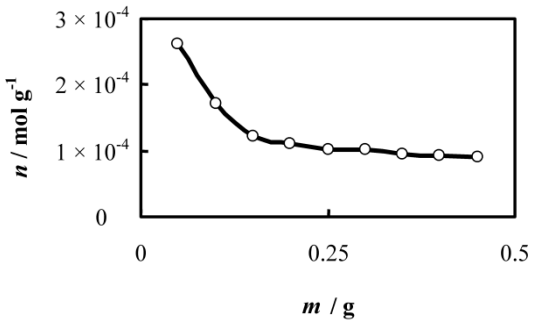

Fig. 1: Effect of weight of sawdust on the adsorption of cadmium (pH = 5, T = 298 K, V = 10 ml and $[A]_0$ = 0.005 mol L^{-1}

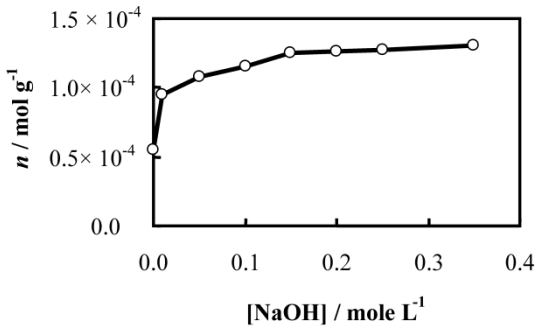

Fig. 2: Effect of concentration of NaOH used in the treatment of sawdust on the adsorption of cadmium (m= 0.25 g, pH = 5, T = 298 K, V = 10 ml and $[A]_0$ = 0.005 mol L^{-1}

2.6 Optimization of Concentration of NaOH Required for Modification of Sawdust

NaOH treatment was carried out for the removal of color base soluble materials and creation of more adsorption sites [18]. In order to optimize the concentration of NaOH solution required for pretreatment, one gram of sawdust was taken in 100 ml beakers containing 25 ml solution of different NaOH concentrations. The samples were heated on hot plate for one hour, filtered to remove color base soluble materials,

washed repeatedly with deionized water for neutralization and finally dried in oven. Then 0.25 g of each treated sawdust was shaken with 10 ml of 0.005 mol L^{-1} cadmium and the magnitude of *n* was measured as a function of concentration of NaOH used in the treatment of sawdust. The plot of *n* Vs. [NaOH] (Fig. 2) indicates that adsorption of cadmium on sawdust increases on treatment with NaOH. The effect of concentration of NaOH on magnitudeof *n* was insignificant beyond 0.2 mol L^{-1} NaOH. Thus 0.2 mol L^{-1} was considered as the optimum concentration of NaOH required for the modification of sawdust. The data in Fig. 2 indicates that adsorption of cadmium also occurs on untreated sawdust. However, adsorption of cadmium is improved significantly on treatment of sawdust with 0.2 mol L^{-1} NaOH.

3. Results and Discussion

3.1 Influence of pH on Adsorption of Cadmium on Sawdust

The influence of pH on adsorption of cadmium on sawdust modified with NaOH was studied using 0.25 g sawdust per 10 ml solution containing 0.005 mol L^{-1} initial concentration of cadmium. The data in Fig. 3 indicates that adsorption of cadmium increases with increasing pH and become constant in the pH range 4 to 6. Fig. 3 also indicates that extent of adsorption of cadmium is significantly low below pH 3.5. These effects of pH on adsorption of cadmium can be interpreted on the basis of complexation mechanism involving binding of cadmium ions with two adjacent carboxylic groups available on NaOH modified sawdust. The existence of ligands containing carboxylic functional groups in NaOH modified sawdust has been indicated by many authors [19, 24, 25]. At pH< 4, the carboxyl functional groups are protonated and not freely available for participation in the adsorption process [24, 25]. Due to this reason, the adsorption of cadmium is significantly low below pH 3.5.

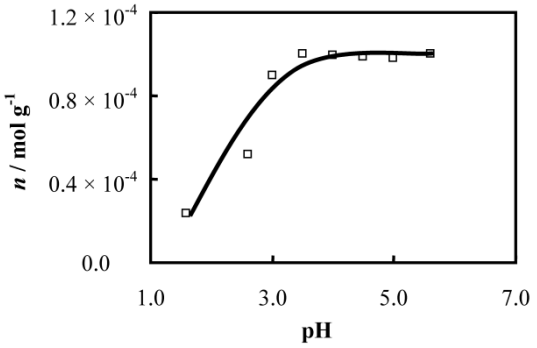

Fig. 3: Effect of pH on the adsorption of cadmium on sawdust modified with 0.2 mol L^{-1} NaOH (*m* = 0.25 g, *T* = 298 K, *V* = 10 ml and $[A]_0$ = 0.005 mol L^{-1})

3.2 Regeneration of Adsorption Sites on used Sawdust

The pH data given in Fig. 3 indicates that adsorption of cadmium is negligible at pH 1 maintained by using 0.1 mol L^{-1} strong acid ($HClO_4$). It means that one can remove the adsorbed cadmium by treatment of used adsorbent with 0.1 mol L^{-1} $HClO_4$. In the present work, the regeneration of sawdust was done by washing the used sawdust with deionized water followed by treatment with 0.1 mol L^{-1} $HClO_4$ and washing again with deionized water. Finally, the sawdust was treated with 0.2 mol L^{-1} NaOH at room temperature without boiling for creation of adsorption sites. The extent of adsorption of cadmium on regenerated sawdust was checked by shaking 0.25 g of regenerated sawdust with 10 ml of 0.005 mol L^{-1} cadmium solution. It was found that the amount of cadmium adsorbed on regenerated sawdust was equivalent to that on fresh NaOH modified sawdust. It means that regeneration process can be effectively utilized for recycling of used sawdust. It is difficult to find the number of cycles after which the sawdust completely loses its adsorption capacity. However, since adsorption occurs through carboxylic functional groups that are integral parts of structural constituents of sawdust, therefore, sawdust can be regenerated (or recycled) several times as long as the structural constituents containing carboxylic functional groups remain part of the sawdust.

3.3 Equilibrium Studies for the Identification of Adsorption Type

The adsorption process may be of single layer or multilayer. The fraction of adsorption layer formed at a given equilibrium concentration of adsorbate can be calculated on the basis of the following relation [12]:

$$\bar{n} = \frac{n}{n_m} \tag{2}$$

where $\bar{n}$ gives the fraction of adsorption layer formed at a given equilibrium concentration of adsorbate and n_m (mol g^{-1}) is the monolayer adsorption capacity. It has been shown that at any given equilibrium concentration of adsorbate, the magnitude of $\bar{n}$ can be represented by the following expression [12]:

$$\bar{n} = \frac{\beta_1[A]_e + 2\,\beta_2[A]_e^2 \cdots + N\beta_N[A]_e^N}{1 + \beta_1[A]_e + \beta_2[A]_e^2 \cdots + \beta_N[A]_e^N} \tag{3}$$

where β_1, β_2, …β_N are the overall equilibrium constants of the equilibrium expressions for the formation of given adsorption layer. The expression equivalent to Eq. (3) can also be used for analysis of titration curve of polyprotic acid [26]. On the basis of Eq. (3), the nature of adsorption can be identified by analyzing $\bar{n}$ as a function of equilibrium concentration of adsorbate. However, for

finding $\bar{n}$ one must know the magnitude of monolayer adsorption capacity of a given adsorbent. In order to solve this difficulty, it can be shown that in the region of low equilibrium concentration of adsorbate, the Eq.(3) reduces to following form of the Langmuir isotherm:

$$\bar{n} = \frac{K[\mathrm{A}]_e}{1 + K[\mathrm{A}]_e} \quad (4)$$

where K is the equilibrium constant maintained between adsorbate and adsorbent in the first layer. It is numerically equal to β_1. On equating Eq. (2) & (4) and making rearrangement, one can get following linear form of Langmuir isotherm [12,13]:

$$\frac{1}{n} = \frac{1}{n_m} + \frac{1}{n_m K[\mathrm{A}]_e} \quad (5)$$

The Langmuir isotherm can be used for finding magnitude of K and n_m by analyzing slope and intercept of the plot of n^{-1} Vs. $[\mathrm{A}]_e^{-1}$ (Fig. 4). In case of monolayer adsorption, the Eq. (5) is valid over the whole range of equilibrium concentration of adsorbate while in multilayer adsorption process; it is valid only at low equilibrium concentration of adsorbate [12]. It is, therefore, concluded that the correct value of n_m can be evaluated only by analyzing the Langmuir isotherm at low equilibrium concentration range for further adsorption layer analysis.

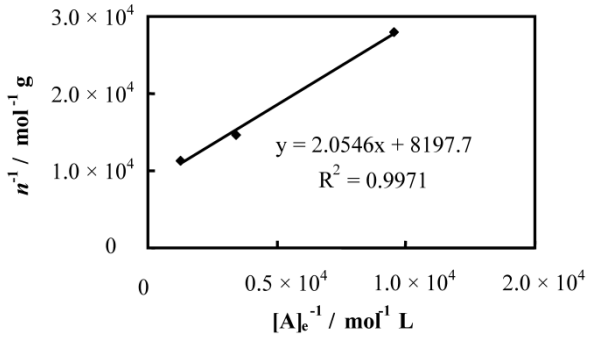

Fig. 4: Plot of n^{-1} Vs. $[\mathrm{A}]_e^{-1}$ for evaluation of monolayer capacity of *Dalbergia sissoo* sawdust modified with 0.2 mol L^{-1} NaOH (m = 0.25 g, pH = 5 and T = 298 K

In view of the above, the nature of adsorption in the present study was investigated by studying the adsorption of cadmium on 0.25 g sawdust at pH 5 from 10 ml solution containing different initial concentrations of cadmium. The samples were prepared by dilution of 1, 2, 3… up to 9 ml of 0.01 mol L^{-1} stock solution. Only the first three points were analyzed on the basis of Eq. (5) so that multilayer formation at higher equilibrium concentrations of cadmium could be identified by subsequent analysis of Eq. (2). The magnitude of K and n_m were calculated by analyzing slope and intercept of plot n^{-1} Vs. $[\mathrm{A}]_e^{-1}$ (Fig. 4) and found to be 4.0×10^3 mol $^{-1}$ L and 1.22×10^{-4} mol g $^{-1}$ respectively.

Once knowing the magnitude of monolayer capacity, one can calculate $\bar{n}$ on the basis of Eq. (2) at different equilibrium concentrations of cadmium. Since the magnitude of $\bar{n}$ indicates the fraction of adsorption layer formed at a given equilibrium concentration of adsorbate, therefore, one can predict the number of adsorption layers from the plot of $\bar{n}$ Vs. $[\mathrm{A}]_e$.

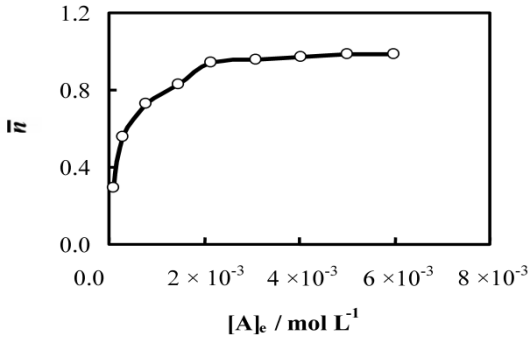

Fig. 5: Plot of $\bar{n}$ Vs. $[\mathrm{A}]_e$ indicating the formation of only single layer of cadmium adsorbed on *Dalbergia sissoo* sawdust modified with 0.2 mol L^{-1} NaOH (m = 0.25 g, pH = 5, T = 298 K)

It is clear from data in Fig. 5 that the magnitude of $\bar{n}$ approaches to unity at higher equilibrium concentration of cadmium. It is, therefore, concluded that adsorption of cadmium on sawdust leads to the formation of only single adsorption layer and there is no sign of multilayer formation.

Table 1: Comparison of adsorption capacity of NaOH modified *Dalbergia sissoo* sawdust with other reported costly adsorbent for removal of cadmium from aqueous system

Type of adsorbent	n_m / mol g^{-1}	References
Natural Zeolite	4.6×10^{-5}	Minceva et al. [27]
Granulated Activated Carbon	1.5×10^{-4}	Minceva et al. [27]
Carbon Nanotube	9.8×10^{-5}	Li et al. [28]
Dalbergia sissoo Sawdust	1.22×10^{-4}	Present study

3.4 Comparison of Adsorption Capacity of Sawdust with Other Costly Adsorbents

The monolayer adsorption capacity of *Dalbergia sissoo* sawdust is compared with other costly adsorbents in Table 1. The data contained in Table 1 indicates that the adsorption capacity of NaOH modified *Dalbergia sissoo* sawdust is comparable to granulated activated carbon and carbon nanotube which are costly adsorbents [27, 28]. Thus *Dalbergia sissoo* sawdust can be used as a potential adsorbent for the removal of cadmium from aqueous system.

3.5. Dubinin-Radushkevich Isotherm Treatment

Dubinin and Radushkevich put forward an empirical equation in 1947 which is commonly known as the DR

equation [29, 30]. For monolayer adsorption, the Gaussian form of DR equation can be expressed as:

$$\bar{n} = \exp\left[-\left(\frac{\varepsilon}{E}\right)^2\right] \quad (6)$$

where E is the energy of adsorption and ε is the differential molar work of adsorption, also known as Polanyi adsorption potential. In case of adsorption from solution, the magnitude of ε at a given equilibrium concentration of adsorbate can be evaluated on the basis of the following relation [29, 31-33]:

$$\varepsilon = -\Delta G^\circ = R\,T \ln\left(\frac{[A]_s}{[A]_e}\right) \quad (7)$$

where $[A]_s$ (mol L^{-1}) is the saturated equilibrium concentration of adsorbate at which adsorption approaches to its maximum limit. On substitution of ε from Eq. (7) into Eq. (6) and rearranging, one can get:

$$\left[-\ln\left(\bar{n}\right)\right]^{1/2} = \frac{R\,T}{E}\ln\,[A]_s - \frac{R\,T}{E}\ln\,[A]_e \quad (8)$$

Since magnitude of monolayer adsorption capacity is known from Langmuir adsorption isotherm, therefore, one can calculate the magnitude of $\bar{n}$ on the basis of Eq. (2) at different equilibrium concentrations of cadmium. The initial five points of the adsorption isotherm corresponding to the rising portion of Fig. 6 were used to analyze Eq. (8) for finding the magnitude of $[A]_s$ and E by analyzing slope and intercept of the plot shown in Fig. 6 using the following relations:

$$[A]_s = \exp\left(-\frac{\text{Intercept}}{\text{slope}}\right) \quad (9)$$

$$E = -\frac{R\,T}{\text{Slope}} \quad (10)$$

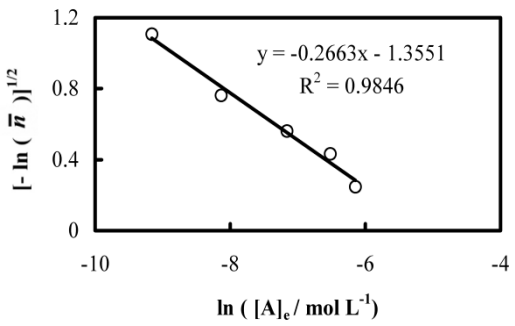

Fig. 6: Dubinin-Radushkevich adsorption isotherm for evaluation of energy of adsorption of cadmium on *Dalbergia sissoo* sawdust modified with 0.2 mol L^{-1} NaOH (m = 0.25 g, pH = 5,T = 298 K and n_m= 1.22 ×10^{-4} mol g^{-1})

The units of data along x and y axes must be taken into account while calculating the desired parameters from slope and intercept. The energy of adsorption obtained by analyzing Eq. (10) was found to be 9.3 kJ mol^{-1}. The magnitude of $[A]_s$ obtained by analyzing Eq.(9) was equal to 6.2 × 10^{-3} mol L^{-1}. It means that all adsorption sites available on sawdust become fully occupied on establishment of ≥ 6.2 × 10^{-3} mol L^{-1} equilibrium concentration of cadmium in the solution.

3.6 Temkin Isotherm Treatments for Evaluation of Thermodynamic Parameters

Since adsorption of cadmium on sawdust is monolayer type, therefore, one can utilize Temkin adsorption isotherm for the evaluation of ΔH^o and ΔS^o. The Temkin isotherm is given as [13]:

$$n = n_m\left(\frac{R\,T}{q_0}\ln\,(K^\circ)+1\right) + \frac{n_m\,R\,T}{q_0}\ln\,[A]_e \quad (11)$$

where q_0 (J mol^{-1}) is the positive quantity of heat evolved at zero coverage while K^o (L mol^{-1}) is the equilibrium constant when coverage (θ) approaches to unity as defined by the following expression [13]:

$$K_\theta = K^\circ \exp\left(\frac{q_0\,(1-\theta)}{R\,T}\right) \quad (12)$$

Since adsorption is monolayer type, therefore, θ can be calculated on the basis of the following relation:

$$\theta = \frac{n}{n_m} \quad (13)$$

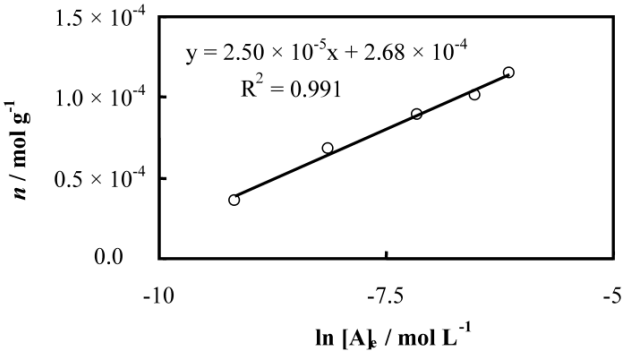

Fig. 7: Plot of n Vs. ln $[A]_e$ for evaluation of Temkin isotherm parameters of cadmium adsorption on *Dalbergia sissoo* sawdust modified with 0.2 mol L^{-1} NaOH (m = 0.25 g, pH = 5, T = 298 K and n_m= 1.22 ×10^{-4} mol g^{-1})

The parameters K^o and q_0 given in Eq. (12) are related to thermodynamic parameters according to following expressions:

$$K^\circ = \exp\left(\frac{\Delta S^\circ}{R}\right) \quad (14)$$

$$q_0 = -\Delta H^{o}_{(\theta=o)} \quad (15)$$

where $\Delta H^{o}_{\theta=0}$ (J mol^{-1}) is the enthalpy change at zero coverage and ΔS^{o} (J K^{-1})is the coverage independent entropy change . The magnitudes of q_0 and ΔS^{o} can be calculated by analyzing slope and intercept of the plot of n Vs. ln[A]$_e$ respectively as shown in Fig.7. The Temkin's isotherm is valid only in the intermediate range of coverage, therefore, only initial five points of the adsorption data shown in Fig. 5 were used to get plot of n Vs. ln[A]$_e$. The data presented in Table 2 indicates that ΔS^{o} is a positive quantity for the adsorption of cadmium on sawdust. Since ΔS^{o} is coverage independent, thus one can calculate coverage independent ΔH^{o} on the basis of following general thermodynamic relationship:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (16)$$

where ΔG^{o} is the Gibbs free energy change. The magnitude of coverage independent equilibrium constant (K) obtained from Langmuir isotherm at 298 K was used to calculate the magnitude of Gibbs free energy change at 298 K (ΔG^{o}_{298}) using the following general relation:

$$\Delta G^\circ = -RT\ln K \quad (17)$$

where R (8.3143 J mol^{-1} K^{-1}) is the universal gas constant and T (K) is the temperature. The magnitude of free energy change at 298 K (ΔG^{o}_{298}) was -20.5 kJ mol^{-1}. The data presented in Table 2 indicates that the magnitude of ΔH^{o} obtained by analyzing Eq. (16) is negative. It was, therefore, concluded that adsorption of cadmium on NaOH modified *Dalbergia sissoo* sawdust is spontaneous, exothermic, and entropy driven process.

Table 2. Equilibrium and thermodynamic parameters of cadmium adsorption at 25 ºC on *Dalbergia sissoo* sawdust modified with 0.2 mol L^{-1} NaOH

Parameters	Observed values
n_m / mol g^{-1}	1.22×10^{-4}
K / L mol^{-1} at 25 ºC	4.0×10^{3}
q_0 / kJ mol^{-1}	12.1
K^{o} / L mol^{-1}	335.5
ΔS^{o} / J mol^{-1} K^{-1}	48.4
ΔH^{o} / kJ mol^{-1}	-6.1
ΔG^{o}_{298} / kJ mol^{-1}	-20.5

3.7 Correlation between Langmuir and Temkin adsorption parameters

The Langmuir and Temkin adsorption parameters can be correlated on the basis of the following relation obtained by substitution of ΔG^{o} from Eq. (17) into Eq. (16) and rearranging:

$$K = K^\circ \exp\left(\frac{-\Delta H^\circ}{RT}\right) \quad (18)$$

where K_0 is related to the coverage independent entropy as defined in Eq. (15). It is clear from experimental data given in Table 2 that:

$$-\Delta H^\circ \cong \frac{q_0}{2} \quad (19)$$

Thus Eq. (18) can be rewritten as:

$$K = K^\circ \exp\left(\frac{q_0}{2RT}\right) \quad (20)$$

The magnitude of K calculated on the basis of Eq. (20) is found to be 3856 L mol^{-1} which is close to the experimental value of K given in Table 2. The right hand side of Eq. (20) can also be obtained by setting θ = 1/2 in Eq. (12). Thus one can say that K is the equilibrium constant at half coverage. On the basis of Langmuir equation, it can be shown that at half coverage, K is equal to the reciprocal of equilibrium concentration of adsorbate i.e.

$$K = \frac{1}{[A]_e} \ (\text{at } \theta = \frac{1}{2}) \quad (21)$$

The magnitude of [A]$_e$ at half coverage was calculated by taking reciprocal of K and found to be 2.5×10^{-4} mol L^{-1} for the adsorption of cadmium on sawdust. On substitution of K from Eq. (20) into Eq. (4), one can get the following relationship between the Langmuir and Temkin adsorption parameters:

$$\bar{n} = \frac{[A]_e \ K^\circ \exp\left(\frac{q_0}{2RT}\right)}{1 + [A]_e \ K^\circ \exp\left(\frac{q_0}{2RT}\right)} \quad (22)$$

On substituting $\bar{n}$ from Eq. (2) into Eq. (22) and making rearrangements, one can get following relation:

$$n = \frac{n_m \ [A]_e \ K^\circ \exp\left(\frac{q_0}{2RT}\right)}{1 + [A]_e \ K^\circ \exp\left(\frac{q_0}{2RT}\right)} \quad (23)$$

The Eq. (23) can be used for finding the number of moles of adsorbate adsorbed at a given temperature and equilibrium concentration of adsorbate. The magnitude of q_0 in unit of J mol^{-1} instead of kJ mol^{-1} should be used to analyze Eq. (23). A few points of cadmium adsorption on

modified sawdust at 55 ºC were calculated on the basis of Eq. (23) and are presented in Table 3 for comparison with experimental data. There was close agreement between calculated and experimental data which indicates the importance as well as validity of observed Langmuir and Temkin adsorption parameters.

Table 3. Comparison of experimental and few calculated data of cadmium adsorption at 55 ºC on *Dalbergia sissoo* sawdust modified with 0.2 mol L^{-1} NaOH (m= 0.25 g, pH = 5 and V = 10 ml. The calculated data was obtained on the basis of Eq. (23) using $n_m = 1.22 \times 10^{-4}$ mol g^{-1}, $K^o = 343.8$ L mol^{-1}, $q_0 = 12100$ J mol^{-1}, $R = 8.3143$ J mol^{-1} K^{-1} and $T = 328$ K).

Initial conc. $[A]_0$ / mol L^{-1}	Equil. conc. $[A]_e$ / mol L^{-1}	Amount of cadmium adsorbed n / mol g^{-1}	
		Experimental	Calculated
1.0×10^{-3}	1.83×10^{-4}	3.27×10^{-5}	4.33×10^{-5}
3.0×10^{-3}	6.80×10^{-4}	9.28×10^{-5}	8.26×10^{-5}
5.0×10^{-3}	2.20×10^{-3}	1.12×10^{-4}	1.06×10^{-4}
7.0×10^{-3}	4.10×10^{-3}	1.16×10^{-4}	1.13×10^{-4}
9.0×10^{-3}	6.04×10^{-3}	1.18×10^{-4}	1.16×10^{-4}

4. Conclusions

Adsorption of cadmium on NaOH modified *Dalbergia sissoo* sawdust was studied for evaluation of equilibrium and thermodynamic parameters. Adsorption of cadmium on sawdust was monolayer type, renewable and occurred by complexation mechanism. The monolayer capacity of sawdust was comparable to costly adsorbents. The Dubinin-Radushkevich isotherm treatment indicated that all adsorption sites available on sawdust become fully occupied on establishment of 6.2×10^{-3} mol L^{-1} equilibrium concentration of cadmium. The correlation between Langmuir and Temkin adsorption isotherms was also explored for analysis and interpretation of adsorption parameters The thermodynamic data indicated that adsorption of cadmium on modified *Dalbergia sissoo* sawdust is exothermic, spontaneous and entropy driven. It was concluded that NaOH modified *Dalbergia sissoo* sawdust can be used as a potential adsorbent for the removal of cadmium from aqueous system.

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