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Adsorption of 2-picoline from wastewater by agro coal ash: parametric, kinetic, equilibrium and thermodynamic features

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ABSTRACT

2-Picoline is a derivative of pyridine. Due to the hazardous nature, the removal of 2-picoline from wastewater is important. In the present study, the ability of agro coal ash as an adsorbent for the removal of 2-picoline from wastewater in a broad range of concentration (50–300 mg/L) was investigated. The influence of various experimental parameters like initial pH, adsorbent dose, contact time, initial concentration and temperature on the removal of 2-picoline on agro coal ash were studied. The optimum conditions for the maximum removal of 2-picoline were found to be: initial pH 6, contact time = 7 h and adsorbent dose = 2 g/L. Adsorption of 2-picoline followed pseudo-second-order rate kinetics. The Langmuir and Freundlich adsorption equilibrium isotherm models were analysed. The values of the change in Gibb's free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were calculated. Thermodynamic studies revealed that adsorption of 2-picoline on agro coal ash is an endothermic process.

Keywords: 2-Picoline; AGCA; Pyridine; Adsorption isotherms; Adsorption equilibrium

1. Introduction

Pyridine is a basic heterocyclic organic compound and it is structurally related to benzene with one C–H group replaced by nitrogen atom. It was discovered in 1849 by the Scottish chemist, Thomas Anderson, as one of the constituent of bone oil. 2-Picoline is a derivative of pyridine and a structural isomer. It is also known as α-picoline [1]. 2-Picoline has a ring-like structure and it is a colourless liquid with a strong unpleasant odour [2]. Its boiling point is 129.5˚C and the density is 0.946 at 20˚C [3]. It is freely soluble in water. 2-Picoline is used as a solvent and as a raw material for various chemicals used in industries like polymers, textiles, fuels, agro chemicals, pharmaceuticals and colorants [4]. Pyridine is a hazardous compound. Its derivatives have harmful effects on the liver, kidneys, immune system, eye (irritant), ingestion, inhalation and reproductive system [4–6]. Industrial wastewater containing 2-picoline shows toxicity to aquatic life and creates nuisance [7–9].

The pyridine concentration in the wastewaters emanating from industry is generally in the range of 20–200 mg/L [10]. During the emergency spill, the concentration increases to 1,000 mg/L. According to

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the Central Pollution Control Board norms, the concentrations of pyridine and its derivatives in wastewater should be less than 1 mg/L. Removal of 2-picoline from wastewater is therefore of great importance from the environmental point of view. Different treatment methods are available for the removal of pyridine derivatives from wastewater like adsorption [11,12], biodegradation [13], ion exchange [14], ozonation [15] and electrochemical oxidation [16]. Adsorption can be a preferred treatment technique, provided that the adsorption process is cost effective. Agro coal ash is easily available and it shows excellent adsorption characteristics. It was also used by several investigators as an adsorbent for the removal of dyes from wastewater.

Hence, agro coal ash is used as an adsorbent for the removal of 2-picoline from wastewater. The effects of various operating parameters on adsorption, such as pH, concentration, time and adsorbent dose were investigated in a batch process. Kinetics and equilibrium isotherm for adsorption were studied. The Langmuir and Freundlich isotherm models were tested for their applicability. Thermodynamic results show that AGCA is an effective adsorbent for the removal of 2-picoline from wastewater.

2. Materials and methods

2.1. Adsorbent

Agro coal ash is the mixture of wood ash and ground nut shell ash. It was collected from a local source at Nashik, Maharashtra, India. The agro coal ash was washed with hot-distilled water (75°C) and then dried in sunlight until all the moisture was evaporated. Then, these materials were grinded and sieved to the desired particle size.

Physico-chemical characteristics of AGCA were determined using standard procedures. Particle size analysis was carried out using standard sieves and the bulk density was determined by using a MAC bulk density meter. Proximate analysis was carried out using standard procedures [17]. The surface area of the particles was measured by the Brunauer–Emmett–Teller (BET) method using Micromeritics software.

2.2. Adsorbate

2-Picoline (chemical formula, C5H5N; molecular weight, 79.1) was supplied by Modern Science Laboratory, Nashik, India. Stock solutions (1,000 mg/L) of 2-picoline were prepared by dissolving an accurate weighed quantity in double-distilled water. Experimental solutions of the desired concentrations were prepared by the successive dilutions of stock solution with double-distilled water.

2.3. Analytical measurements

2-Picoline in the aqueous solution was analysed using a UV spectrophotometer. The wavelength corresponding to maximum absorbance for 2-picoline was found to be 262 nm. From the plot of absorbance and concentration of 2-picoline, the linear region of the curve determines the 2-picoline concentration in aqueous solution. Samples of higher concentration beyond the linear region of a calibration curve were diluted with distilled water for accurate determination of concentration from the linear portion of the calibration curve.

2.4. Batch adsorption study

All the adsorption experiments were carried out at 283, 293 and 303 K with different initial concentrations. The pH values were adjusted by using 0.1 N H_2S0_4 or 0.1 N NaOH solution. An equal amount (2 g) of AGCA was introduced into 100 mL bottles and 50 mL of 2-picoline solution of a desired concentration (50–300 mg/L) was added to each bottle and shaken for 7 h. Immediately after this, the sample was filtered and the clear solution (filtrate) was analysed using a spectrophotometer. Control samples with picoline solutions and without adsorbent were also included. No adsorption occurred on either glassware or filtration systems. The amount of the adsorbed picoline by AGCA at any time was calculated by using the following equation [2]:

$$q_e = \frac{(C_0 - C_e)v}{m} \tag{1}$$

where q_e is the amount of 2-picoline adsorbed (mg/g), C_0 is the initial concentration (mg/L), C_e is the equilibrium concentration (mg/L), v is the volume (L) and m is the mass of the adsorbent (g).

3. Results and discussion

3.1. Characterisation of adsorbents

The physico-chemical properties of AGCA such as the BET surface area, bulk density, moisture volatile matter, particle size, ash and fixed carbon content were determined and are shown in Table 1.

Table 1
Characterisations of AGCA adsorbent

Properties	AGCA
BET surface area (m^2/g)	58.2
Bulk density (kg/m^3)	157.2
Moisture volatile matter (%)	1.3
Ash content (%)	82.3
Fixed carbon content (%)	11.8
Average particle size (μm)	395.25

The fractional sieve analysis of the particles of AGCA was done and found as follows: −600 and +425 μm (36%) −425 and +180 μm (64%). Also, the chemical compositions of AGCA were done and found as follows: SiO_2 (42.12)%, MgO (8.50%), Al_2O_3 (12.15%), Fe_2O_3 (5.45%), CaO (10.75%), K_2O (9.2%), Na_2O (6.2%), TiO (2.5%) and Cl (3.13%).

3.2. Effect of initial pH

2-Picoline (α-picoline) behaves like a base and the transition of 2-picoline to $2PiH^+$ is pH dependent, with a maximum amount of $2PiH^+$ occurring in the pH range of 2–12 [18]. The pH of the solution affects the surface charge of the adsorbents and hence the adsorption proceeds through dissociation of functional groups, viz. surface oxygen complexes of acid character such as carboxyl and phenolic groups or basic character such as pyrones or chromes, on the active sites of the adsorbent. The pH value can affect the structural stability of 2-picoline and, therefore, its concentrations. Effects of the initial pH (pH_0), in the range of 2–11, on the removal of 2-picoline is shown in Fig. 1 at 303 K for $C_o = 100$ mg/L and $m = 2$ g/L. Equilibrium was attained at $t = 7$ h. A maximum 2-picoline adsorption of ~70% was found to occur at the natural pH_0 ($pH \approx 6$) of synthetic wastewater. The adsorption efficiency decreases drastically when pH_0 decreases ($pH_0 < 5$) with a minimum 2-picoline removal of 42% at pH_0 2. The maximum affinity to 2-picoline was found at $pH_0 \sim 6$. So, based on the experimental observations, further experiments were performed at $pH_0 \sim 6$.

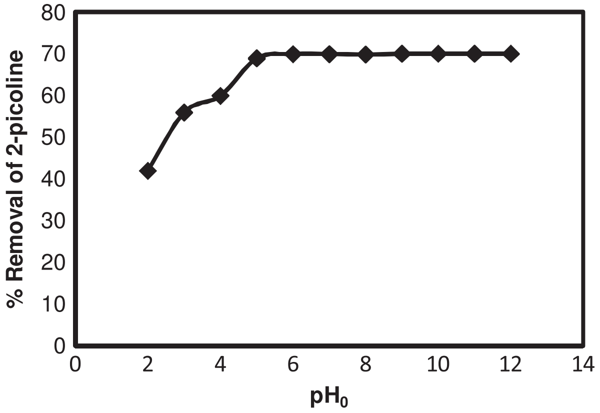

Fig. 1. Effect of initial pH of aqueous solution on the removal of 2-picoline by using AGCL ($C_0 = 100$ mg/L, $T = 303$ K, $m = 2$ g/L and $t = 7$ h).

3.3. Effect of adsorbent dose

Adsorbent dosage is an important parameter, because this factor determines the capacity of an adsorbent for a given initial concentration of the adsorbent. The effect of m on the uptake of 2-picoline by AGCA for $C_0 = 100$ mg/L is shown in Fig. 2. The 2-picoline removal is observed to increase rapidly with an increase in m up to about 2 g/L. An increase in the adsorption with the adsorbent dosage can be attributed to the availability of more adsorption sites and greater surface area for contact. At $m > 2$ g/L, the incremental 2-picoline uptake is very small, as the 2-picoline surface concentration and the 2-picoline bulk solution concentration come to equilibrium with each other. Thus, the optimum m for C_0 of 100 mg/L may be taken as 2 g/L.

3.4. Effect of initial concentration and temperature

The effect of C_0 ($50\,mg/L \leqslant C_0 \leqslant 300\,mg/L$) and temperature ($283\,K \leqslant T \leqslant 303\,K$) on the equilibrium uptake of 2-picoline by the AGCA at $m = 2$ g/L and $t = 7$ h was studied and a plot of the removal of 2-picoline and the sorptive uptake of 2-picoline by AGCA vs. C_0 with temperature as a parameter is shown in Figs. 3 and 4. It is evident that the sorption of 2-picoline and hence the 2-picoline removal from the solution increases with an increase in C_0 and temperature.

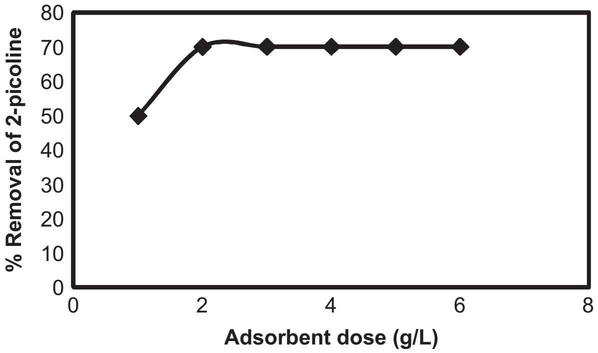

Fig. 2. Effect of adsorbent dose on the removal of 2-picoline by using AGCL ($C_0 = 100$ mg/L, $T = 303$ K and $t = 7$ h).

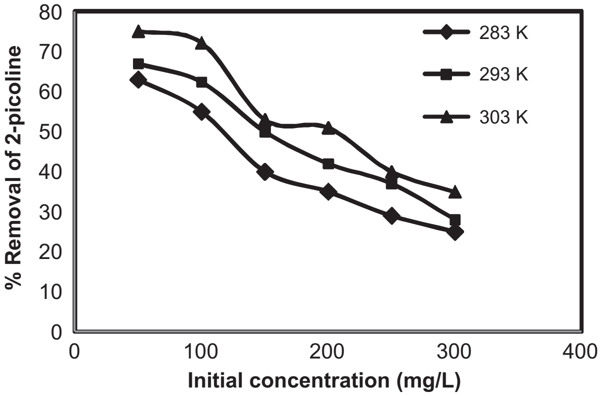

Fig. 3. Effect of initial concentration and temperature on the removal of 2-picoline by using AGCL ($m = 2\,\text{mg/L}$, $\text{pH}_0 = 6$ and $t = 7\,\text{h}$).

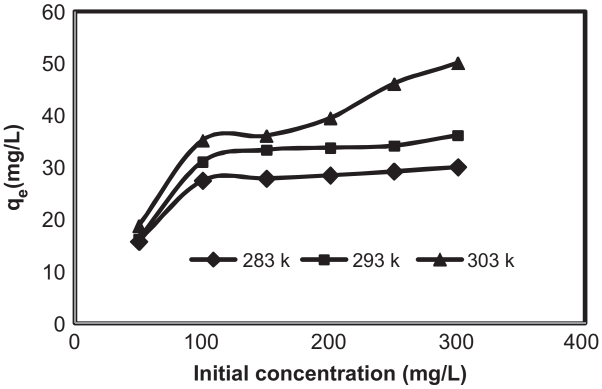

Fig. 4. Effect of initial concentration and temperature on the adsorption of 2-picoline on AGCL at equilibrium ($m = 2\,\text{mg/L}$, $\text{pH}_0 = 6$ and $t = 7\,\text{h}$).

It may be noted that as C_0 and/or temperature increases, the 2-picoline loading onto AGCA (i.e. q_e) increases. This means that the 2-picoline sorption capacity of the AGCA increases significantly with an increase in C_0, but only weakly with an increase in the temperature of the solution. This is because of the fact that a given mass of adsorbent adsorbs only a fixed amount of adsorbate. It is obvious that a higher percentage of 2-picoline was removed with a decrease in C_0. However, the amount of 2-picoline adsorbed per unit adsorbent mass increased with an increase in C_0. This is because of the decrease in the resistance to mass transfer of the solute from the solution.

3.5. Effect of contact time

The effect of contact time on the removal of 2-picoline by AGCA for $m = 2\,\text{g/L}$ and $C_0 = 100$, 150 and 200 mg/L is shown in Fig. 5. Initially, the adsorption rate of 2-picoline onto AGCA was found to be instantaneous because of the availability of more adsorption sites. The steady state adsorption is assumed after 7 h and further experiments were carried out at $t = 7\,\text{h}$.

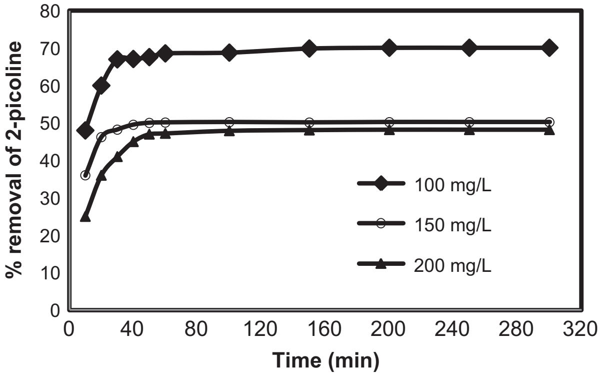

Fig. 5. Effect time on the removal of 2-picoline by using AGCL ($m = 2\,\text{mg/L}$, $\text{pH}_0 = 6$ and $T = 303\,\text{K}$).

3.6. Kinetics of adsorption

A number of experimental runs for different t were conducted at several C_0 with the optimum m to determine the residual 2-picoline concentration in the solution (C_t) with time (t) during the initial sorption period of 1 h. Fig. 5 shows that for $t = 60\,\text{min}$, 65% of 2-picoline removal was obtained at $C_0 = 100\,\text{mg/L}$, $m = 2\,\text{g/L}$ and $T = 303\,\text{K}$. Finally, the surface saturates with 2-picoline molecules, the adsorption rate decreases due to the increase in the diffusion resistance. This means that the pore diffusion is the rate controlling step during 2-picoline adsorption.

Prediction of the batch adsorption kinetics is necessary for the design of industrial adsorption columns. Hence, the sorption kinetics was studied by using the pseudo-first-order and pseudo-second-order kinetic models to fit the experimental kinetic data.

The pseudo-first-order kinetic equation is [19,20]:

$$\log(q_e - q_e) = \log q_e - (k_f/2.303)t \tag{2}$$

where k_f (min^{-1}) is the first-order rate constant, q_e is the amount of 2-picoline adsorbed on the adsorbent at equilibrium (mg /L) and q_t is the amount adsorbed on the adsorbent at respective time t (mg/L). These constants can be calculated from the slope and intercept of the plot, ln ($q_e - q_t$) vs. time, t.

Fig. 6 shows the non-linear nature of the graph for the pseudo-first-order kinetic model at 100 mg/L and 303 K. So, the pseudo-first-order rate expression is not suitable for these experimental data. Hence, we are proceeding for pseudo-second-order kinetic model.

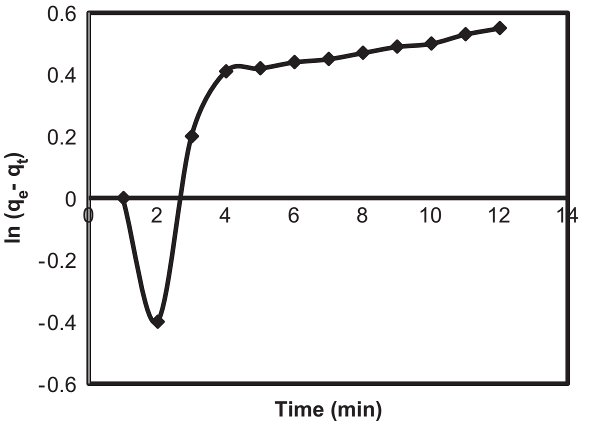

Fig. 6. Pseudo-first-order kinetic model at 100 mg/L and 303 K.

The pseudo-second-order kinetic equation is [20]:

$$dq_t/d_t = k_s(q_e - q_t)^2 \tag{3}$$

where k_s is the rate constant (g/mg min). The integration of equation with the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, leads to:

$$t/q_t = (1/k_s q_e^2) + (1/q_e) = (1/h) + (1/q_e)t \tag{4}$$

or

$$q_e = (k_s q_e^2 t) + (1 + k_s q_e t) \tag{5}$$

where h is the initial sorption rate (mg/g min) at $t \to 0$. The values of h and q_e can be determined experimentally from the slope and intercept of the plot of t/q_t vs. t. The k_s value can then be estimated from the value of h.

Fig. 7 shows the linear nature of the graph for the pseudo-second-order kinetic model at $C_0 = 100$, 150 and 200 mg/L and 303 K and hence the data are fitted with this model. The kinetic parameters, k_s and q_e are determined for 100 mg/L and are shown in Table 2.

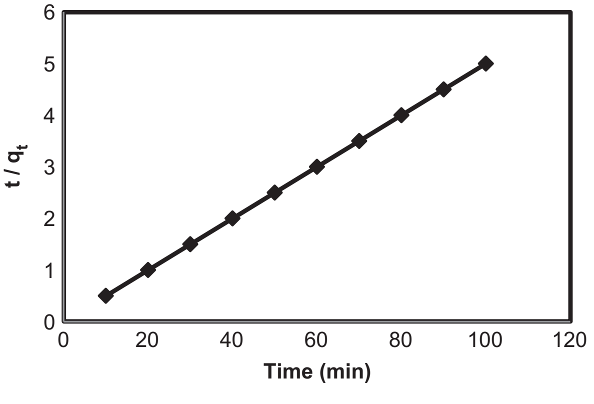

Fig. 7. Pseudo-second-order kinetic model at 100 mg/L and 303 K.

Table 2
Pseudo-second-order kinetic parameters at $C_0 = 100$ mg/L

C_0(mg/L)	Pseudo-second-order kinetic parameters		
	h (mg /L min)	k_s (g/L min)	q_e (mg/L)
100	12.45	0.0908	1.875

3.7. Adsorption equilibrium

The Langmuir isotherm is an empirical isotherm derived from a proposed kinetic mechanism. The Langmuir equation assumes monolayer sorption onto an adsorbent surface with a finite number of identical homogeneous sites. This equation is [1,2]:

$$q_e = [q_m K_L C_e / 1 + K_L C_e] \tag{6}$$

or

$$1/q_e = (1/K_L q_m C_e) + (1/q_m) \tag{7}$$

or

$$C_e/q_e = (1/K_L q_m) + (C_e/q_m) \tag{8}$$

where q_m is the monolayer sorption capacity (mg/L) and is a constant, K_L is the constant related to the free energy of sorption.

Fig. 8 shows the plot of an experimental sorption data C_e/q_e vs. C_e at 283 K. The isotherm parameters K_L and q_m were determined at 283, 293 and 303 K. All these values are shown in Table 3. The values of K_L

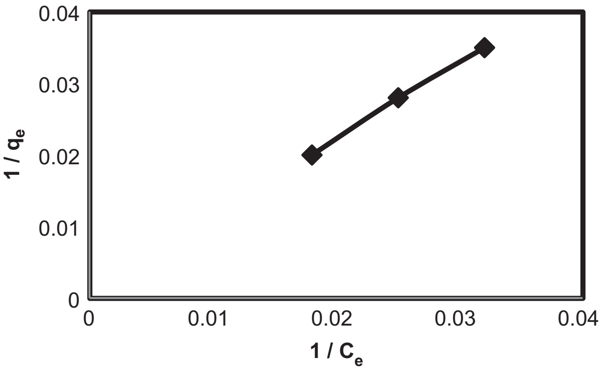

Fig. 8. Langmuir isotherm plot at $T = 283$ K.

Table 3
Adsorption isotherm parameters for the removal of 2-picoline at $C_0 = 100\,\mathrm{mg/L}$

Isotherm equations	Constants	Temperatures (K)		
		283	293	303
Langmuir $q_e = q_m K_L C_e/(1 + K_L C_e)$	K_L (L/mg)	0.0299	0.1029	0.1438
	q_m (mg/g)	3.225	2.3803	1.886
Freundlich $q_e = K_F C^{1/n}$	K_F (L/mg)	1.3535	1.4477	1.4769
	n	12.78	19.762	55.86
	$1/n$	0.0782	0.0506	0.0179

increases and q_m decreases with increasingtemperature. K_L indicates the affinity of the adsorbents to the adsorbate. High K_L indicates a higher affinity. The maximum adsorption capacity of the adsorption (q_m) is the monolayer saturation at equilibrium.

In the Freundlich adsorption isotherm, extent of adsorption is directly proportional to pressure at low pressure and it is independent at high pressure. Therefore at the intermediate value of pressure, adsorption is directly proportional to the pressure raised to power *1/n*, where *n* is a variable whose value is greater than one. The constant of proportionality *k*, also known as the adsorption constant, was used.

The Freundlich equation is [20]:

$$q_e = k_f C_e(1/n) \tag{9}$$

or

$$\ln q_e = \ln k_f + (1/n) \ln C_e \tag{10}$$

where k_f is the sorption capacity of the adsorbent (mg/g) and *1/n* is a constant which gives the intensity of the adsorption.

Fig. 9 shows the plot of ln q_e vs. ln C_e at 283 K. The isotherm parameters such as k_f and *1/n* are shown in Table 3. The higher the value of $1/n$, the higher is the affinity between the adsorbate and adsorbent and the heterogeneity of the adsorbent sites. The *1/n* values indicate the relative distribution of energy sites and depend on the nature and strength of the adsorption process. The Freundlich isotherm does not predict the saturation of the adsorbent surface by the adsorbate. The k_f value can be taken as a relative indicator of the adsorption capacity. The magnitude of k_f showed higher uptake at higher temperature indicating the endothermic nature of the adsorption process.

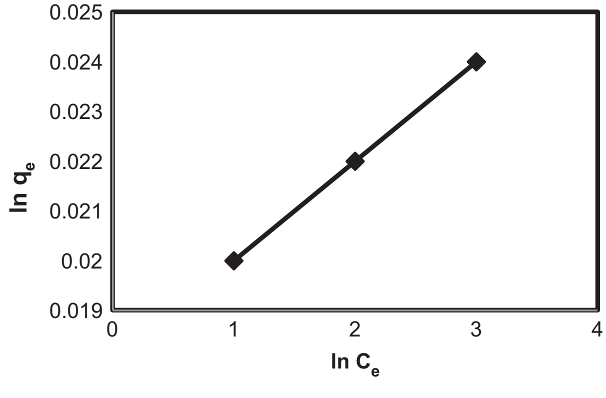

Fig. 9. Freundlich isotherm plot at $T = 283$ K.

It can be noticed from Table 3 that the Freundlich adsorption isotherm could be used to represent the equilibrium adsorption at all temperatures.

3.8. Thermodynamic study

The Gibbs free energy change of the adsorption process is related to the adsorption equilibrium constant by the classical van't Hoff equation [21]:

$$\Delta G^\circ_{\mathrm{ads}} = -RT \ln K_{\mathrm{ads}} \tag{11}$$

The Gibbs free energy change is also related to the change in the entropy and the heat of adsorption at a constant temperature as given by the equation:

$$\Delta G^\circ_{\mathrm{ads}} = \Delta H^\circ - T\Delta S^\circ \tag{12}$$

The above two equations give:

$$\ln K_{\mathrm{ads}} = (\Delta G^\circ_{\mathrm{ads}}/RT) = (\Delta S^\circ/R) - (\Delta H^\circ/R)(1/T) \tag{13}$$

where $\Delta G^\circ_{\mathrm{ads}}$ = free energy change (kJ/mol), ΔH° = change in enthalpy (kJ/mol), S° = entropy change (kJ/mol K), K_{ads} = equilibrium constant of interaction between the adsorbate and the AGCA surface, T = absolute temperature (K) and R = universal gas constant (8.314 J/mol K).

The ΔH° can be determined by the slope of the linear van't Hoff plot i.e. ln *K* vs. (*1*/*T*), using the equation:

$$\Delta H^\circ = R[(d \ln K)/d(1/T) \tag{14}$$

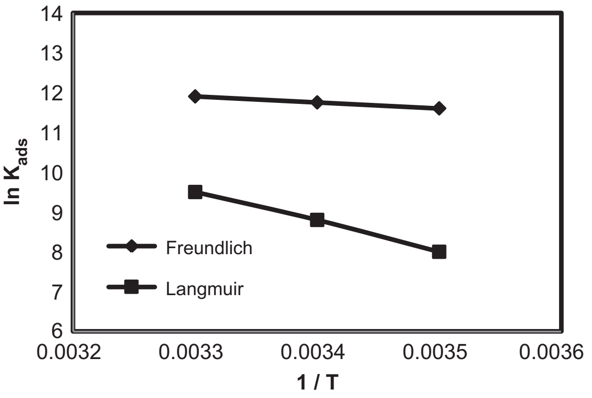

Fig. 10. Van't Hoff's plot ($C_0 = 100\,\mathrm{mg/L}$, $m = 2\,\mathrm{g/L}$ and $\mathrm{pH}_0 = 6$).

Table 4
Thermodynamics parameters for the removal of 2-picoline by using AGCA

Isotherm	ΔH° (kJ/mol)	ΔS° (kJ/mol K)	ΔG° (kJ/mol)		
			283 K	293 K	303 K
Langmuir	64.56	0.021	−19.4	−23	−24.6
Freundlich	3.54	0.02	−28.4	−29.5	−30.6

Fig. 10 shows the van't Hoff's plot for the Langmuir and Freundlich adsorption isotherm, from which ΔH° and S° values have been determined and are shown in Table 4. The positive ΔH° value indicates that the overall sorption process is endothermic in nature. $\Delta G^\circ_{\mathrm{ads}}$ values at 283, 293 and 303 K were determined and are also shown in Table 4. For significant adsorption to occur, the free energy changes of adsorption, G°, must be negative. So, from Table 4, ΔG° values were negative indicating that the sorption process led to the decrease in Gibb's free energy. It also indicates the feasibility and spontaneity of the adsorption process.

4. Conclusions

The AGCA is an attractive adsorbent for the removal of 2-picoline from synthetic wastewater. The results of the present study showed that the maximum removal of 2-picoline was observed up to 75.1% at lower concentration, 50 mg/L and 25.1% at higher concentration, 300 mg/L. The optimum AGCL dose was 2 g/L. The maximum uptake of the adsorption was observed at the natural initial pH (pH 6) of the solution. Equilibrium between the adsorbate in the solution and on the adsorbent surface was practically achieved in 7 h. The adsorption kinetics of 2-picoline on agro coal ash was found to follow the pseudo-second-order rate expression. The equilibrium adsorption isotherm data were represented by Langmuir and Freundlich adsorption isotherm models. The thermodynamic properties showed the feasibility and spontaneity of the process and also found that the adsorption of 2-picoline is favourable by anincrease in the temperature of the operation.

Thus, AGCA is found to be an attractive and low-cost adsorbent. It is an agro waste material and is easily available. Hence removal of 2-picoline from the wastewater is an environmental clean approach.

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