Water Practice & Technology

IWA PUBLISHING

Water Practice & Technology Vol 17 No 11, 2386 doi: 10.2166/wpt.2022.128

4-picoline adsorption from aqueous solution by using baggage fly ash (BFA): Parametric, kinetic and thermodynamic aspects

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ABSTRACT

Numerous harmful characteristics of wastewater containing pyridine chemical have a significant negative impact on human health. Therefore, it is preferred to remove it from effluent. The derivatives of pyridine are 2- and 4-picoline. In this work, an adsorption technique was used to remove 4-picoline from the effluent. Wastewater was treated to remove 4-picoline using the natural adsorbent baggage fly ash (BFA). 4-picoline adsorption rate of 82% was reported at pH 6.22, BFA adsorbent dosage of 4 g/L, and contact time of 6 h. The current investigation found that 85.83% of 4-picoline could be removed at its maximum with BFA at a temperature of 333 K. Investigations were also carried out into how the starting concentration and temperature affected the elimination of 4-picoline. According to the kinetic analysis, the process uses pseudo-second-order rate kinetics. The thermodynamics study also demonstrated that all temperatures could be predicted using the Freundlich and Langmuir equilibrium adsorption isotherm models. It further demonstrated that 4-picoline adsorption on BFA is an endothermic process.

Key words: 4-picoline, adsorption, adsorption equilibrium, adsorption isotherm, pyridine

HIGHLIGHTS

- This study confirmed that 4-picoline can effectively be removed from wastewater by using baggage fly ash as an adsorbent.
- The adsorption kinetics of 4-picoline on baggage fly ash follow the pseudo-second order rate expression.
- The Freundlich and Langmuir adsorption isotherm models are best suited for elimination of 4-picoline from wastewater using BFA.
- The maximum removal of 4-picoline was found up to 85.83%.

INTRODUCTION

One of the largest problems the world is currently experiencing is wastewater treatment. Industrial wastewater effluents discharge a variety of toxins into water bodies, and organic pollutants are drawing a lot of attention due to the environmental risk associated with their release. Organic molecules are crucially needed in industrial products like pesticides, detergents, plastics, petroleum hydrocarbons, organic solvents, and colors (Ali *et al.* 2012; Dehkordi *et al.* 2022). With one C-H group substituted by a nitrogen atom, pyridine is a basic heterocyclic organic molecule that shares structural similarities with benzene. Thomas Anderson, a Scottish scientist, first identified it as a component of bone oil in 1849. Pyridine and its derivatives are very hazardous compounds. They are harmful to human health and effects on kidney, liver, eye contact, immune system, inhalation and reproductive system (Yates 1984; Kirk & Othmer 1996; Lewis 2004; Wu *et al.* 2021). Between 20 and 200 mg/L of pyridine derivatives are present in industrial effluents (Lataye *et al.* 2008a). However, the concentration of pyridine contaminants in wastewater must be <1 mg/L (Stern *et al.* 1997). The 4-picoline, commonly referred to as γ-picoline, is a pyridine derivative (Dilip *et al.* 2011).

The colorless liquid 4-picoline has an unpleasant odor and produces NOx fumes that are extremely hazardous. Acetone, diethyl ether, and water are all soluble in 4-picoline. 4-Picoline is generally found in industrial effluent that produced 4-vinyl pyridine and subsequent polymers. It is also found in the wastewaters of pyridine manufacturing and pharmaceutical units (Stern *et al.* 1997; Dilip *et al.* 2011). Therefore, from an environmental

perspective, eliminating 4-picoline from wastewater is quite crucial. Numerous researchers looked into a variety of treatment techniques, including biodegradation (Lee *et al.* 1994), adsorption (Mohan *et al.* 2004, 2005; Xia *et al.* 2018), ion exchange (Akita & Takeuchi 1993), electrochemical oxidation (Niu & Conway 2002), and ozonation (Stern *et al.* 1997), to remove pyridine derivatives from wastewater. Each treatment method has its advantages and disadvantages. Among various techniques the adsorption process is economical and cost-effective for wastewater treatment (Zhu *et al.* 2014; Smedt *et al.* 2015; Xia *et al.* 2018).

Many organic and inorganic chemicals from wastewater can be effectively adsorbed using natural materials derived from agricultural wastes. The sugar industry produces bagasse fly ash (BFA), an agricultural waste, which is gathered from flue gases discharged from furnaces or boilers. Since the BFA is practically free to use, it is utilized in this work as a natural adsorbent to remove 4-picoline from effluent.

MATERIALS AND METHODS

Adsorbate

4–picoline, i.e. 4-Methylpyridine (Chemical formula, $CH_3C_5H_4N$), is an organic compound collected from the Modern Science Laboratory located in Nashik city in India. It is one of the three isomers of methyl pyridine. This colorless, pungent liquid is a building block for synthesizing other heterocyclic compounds. The 4-picoline stock solution was prepared by dissolution of 1 mL 4-picoline in 999 mL distilled water. By combining the stock solution with distilled water, the desired concentration of 4-picoline needed for the experiment was created.

Adsorbent

The BFA is a natural adsorbent that was gathered from the Indian district of Ahmednagar's sugar industry. The gathered BFA was properly cleaned in hot water heated to 70 °C before being left to dry outside. Then it was sieved by using standard sieves and BFA particle size was analyzed. Using a MAC bulk density meter, the bulk density of BFA was determined. The proximate analysis of BFA was conducted using the I.S. approach (I.S. method 1984). Additionally, using the Micrometrics software, the Brunauer-Emmett-Teller (BET) method was utilized to calculate the surface area of BFA particles.

Analytical measurements

The highest absorbance of 4-picoline was discovered at 262 nm wavelength when its concentration in the water was measured using a UV spectrophotometer. Its concentration is determined by the linear portion of the curve produced by the absorbance and 4-picoline concentration plot. High concentration samples were diluted with distilled water at a distance from the linear region of a calibration curve. The precise concentration was then determined using the calibration curve's linear section.

Batch adsorption study

Various starting concentrations between 5 and 600 mg/L and temperatures between 303 and 333 K were used in the adsorption tests. 0.1 N NaOH or 0.1 N H_2S0_4 was used to change the pH of the mixture. The desired concentration of 4-picoline from 50 to 600 mg/L was added to 100 mL of each bottle. The 4-picoline solution was then mixed with an equivalent amount of BFA adsorbent, and this mixture was shaken at 150–200 RPM for 6 hours. The sample was promptly filtered, and a UV spectrophotometer was used to analyze the filtrate.

The amount of 4-picoline adsorbed (q_e) by BFA in mg/g was evaluated by using Equation (1) as (Lataye *et al.* 2008b):

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

where C_0 and C_e are the initial and equilibrium concentration measured in mg/L respectively, v and m are the volume (L) and mass (g) of adsorbent respectively.

RESULTS AND DISCUSSION

Characterization of BFA adsorbents

Table 1 lists the physicochemical characteristics of BFA, including its bulk density, particle size, surface area, fixed carbon content, moisture volatile matter and ash. The fractional sieve analysis of BFA particles was performed and 32% particles in the size range of −600 to +425 μm and 68% particles of −425 and +180 μm

Table 1 | Properties of BFA adsorbent

Properties	BFA
Bulk density (kg/m^3)	139.7
Fixed carbon content (%)	46.32
BET surface area (m^2/g)	83.11
Ash content (%)	43.6
Moisture volatile matter (%)	7.52
Average particle size (μm)	304.64

were reported. Also, the CHNSO compositions of BFA were found as follows: C (59.12%); H (0.98%); N (0.00%); S (0.00%) and O (39.90%).

Influence of starting pH of solution

Generally, when we talk about alkaline hydrolysis, we are talking about nucleophilic substitution processes where the attacking nucleophile is a hydroxide ion. For easier disposal, solid organic debris is frequently converted to liquid form using the hydrolysis reaction. Any contaminant's degradation is impacted by the pH, making it a crucial attribute to investigate. The high rate of hydroxyl radical formation during sonochemical degradation affects the final degree of degradation. It has been observed that it is influenced by the pH of the solution at first (Bai *et al.* 2009; Daware & Gogate 2020).

The molecular formula of 4Pi is C_6H_7N. The 4-picoline behaves like a base and the conversion to 4PiH+ is pH-dependent. The pH range of 2–11 has the greatest amount of 4PiH+ transformation. The 4-picoline solution's pH has an impact on the adsorbents' surface charge. Adsorption hence actually occurs on the active sites of the adsorbent via the dispersion of functional groups. The carboxyl and phenolic groups are acid characters, and pyrones or chromes are basic characters (Dilip *et al.* 2011). The structural stability of 4-picoline can be affected by the pH and also the elimination of 4-picoline was affected by the initial pH, which can range from 2 to 11, as illustrated in Figure 1. The starting concentration (*Co*), temperature (303 K), and BFA adsorbent dosage (*m*) were all held constant at 100 mg/L and 4 g/L, respectively. At pH 6.22, it was found that equilibrium was reached in 6 hours and that 82% of 4-picoline elimination was accomplished. When the solution's initial pH dropped ($pH_0 < 5$), the rate of adsorption was dramatically reduced. The minimum 4-picoline removal was almost 4.2% found at $pH_0 = 3$. Hence the maximum adsorption of 4-picoline on BFA was found at $pH_o \sim 6.22$, which was considered for further investigation.

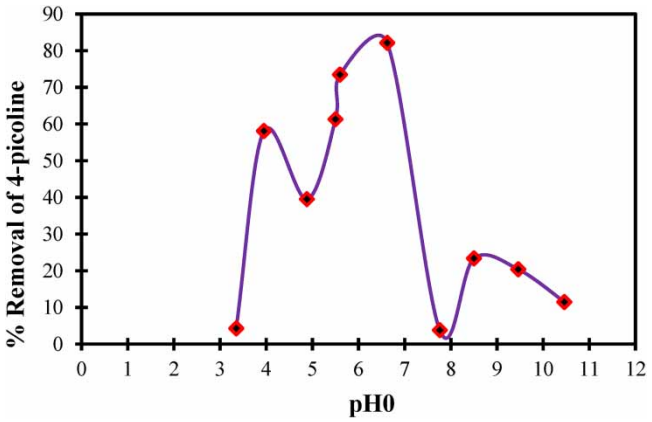

Figure 1 | Influence of pH_0 on the removal of 4-picoline ($t = 6$ h, $C_0 = 100$ mg/L, $T = 303$ K and $m = 4$ g/L).

Influence of BFA adsorbent dose

One of the most important factors in determining an adsorbent's adsorption capability is the adsorbent dose (m) during the adsorption process. Figure 2 depicts how the adsorbent dosage affected the removal of 4-picoline by

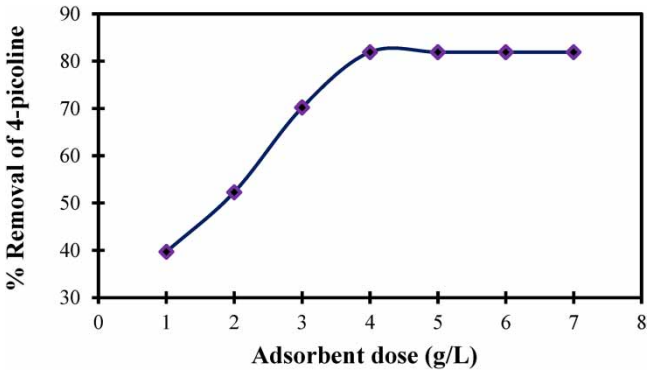

Figure 2 | Influence of quantity of BFA adsorbent on the elimination of 4-picoline at $t = 6$ h.

BFA. At a temperature of 303K, the solution's starting concentration was held constant at 100 mg/L. The results showed that as the adsorbent quantity increases from 1 to 4 g/L, the elimination of 4-picoline increases quickly. Additionally, it was shown that for $m > 4$ mg/L, an essentially constant escalation led to the elimination of 4-picoline. Adsorption rates rise as adsorbent dosage is increased because there is greater surface area available for interaction and, as a result, more adsorption sites. Therefore, at $C_0 = 100$ mg/L and temperature of 303 K, the optimal BFA adsorbent dose was 4 g/L, and it was maintained for subsequent tests.

Influence of starting concentration and temperature

The removal of 4-picoline and sorptive absorption (q_e) by BFA are affected by the starting concentration (Co) of the aqueous solution and temperature, as illustrated in Figures 3 and 4. The initial concentration varied between 50 and 600 mg/L and temperature between 283 and 333 K. The BFA adsorbent dose and contact time were kept constant at 4 g/L and 6 h, respectively. It was discovered that the starting concentration and temperature increase the amount of 4-picoline that adsorbs. The increase in starting concentration, but not the rise in temperature, has a significant impact on the 4-picoline adsorption efficiency of the BFA adsorbent. The given mass of adsorbent does in reality absorb a specific amount of adsorbate. With an increase in initial concentration, there was an increase in the amount of 4-picoline adsorbed per unit mass of BFA as a result of a decrease in the resistance to the solute's mass transfer from the solution.

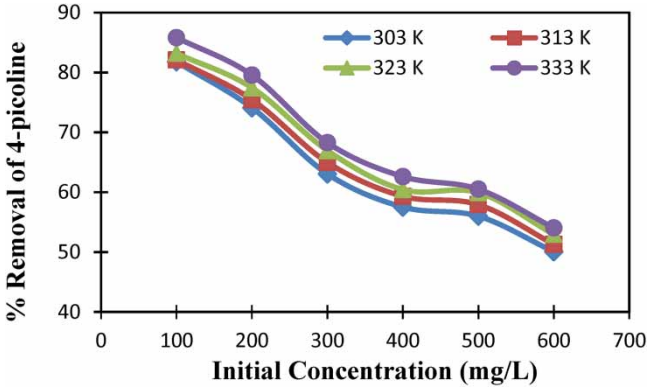

Figure 3 | Influence of starting concentration and temperature on the elimination of 4-picoline ($t = 6$ h, $pH_0 = 6.22$ and $m = 4$ g/L).

Influence of contact time

The contact time is very important to the adsorption process. Figure 5 shows how adsorption contact time influences the BFA-mediated elimination of 4-picoline. The starting concentrations of 4-picoline and BFA were held constant at 100 mg/L and 4 g/L, respectively. The first rise in 4-picoline adsorption was caused by the availability of greater adsorbent surface, or more adsorbent active sites. Due to the solute's saturation of the adsorbent

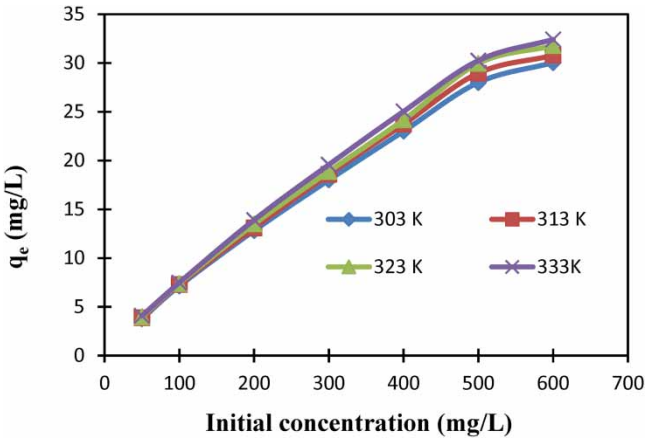

Figure 4 | Influence of a starting concentration and temperature on 4-picoline adsorption at an equilibrium ($t = 6$ h, $pH_0 = 6.22$ and $m = 4$ g/L).

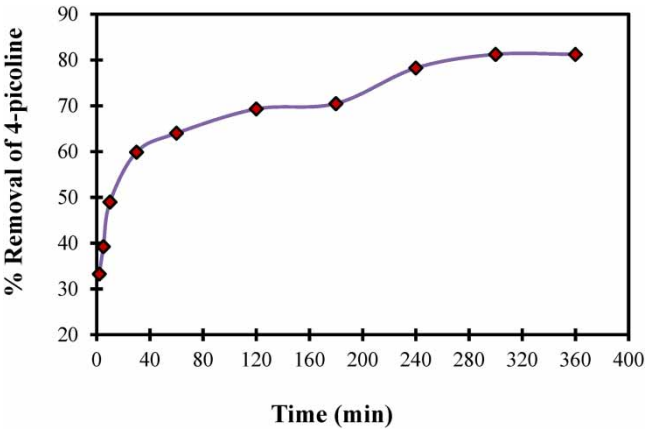

Figure 5 | Influence time on the removal of 4-picoline ($pH_0 = 6.22$, $m = 4$ g/L and $T = 303$ K).

surface after 6 hours, the adsorption rate was determined to be constant. Therefore, the contact time for the following experiment was maintained at 6 hours.

Kinetic study of 4-picoline adsorption on BFA

In order to measure the concentration of 4-picoline (C_1) in the solution at the time (t) for various beginning concentrations, a series of experimental runs were carried out during the initial adsorption period, which was for 1 h. In Figure 5 for $t = 30$ min, the removal of 4-picoline was 59.8% at $m = 4$ g/L, $T = 303$ K and $C_0 = 100$ mg/L. The rate of adsorption reduces as the amount of 4-picoline molecules on the surface of BFA increases over time due to an increase in diffusion resistance. Pore diffusion is thus the process that regulates the rate of 4-picoline adsorption.

To build industrial adsorption columns, a kinetic study of adsorption is required. Therefore, to fit the experimental results, the pseudo-first and second order kinetic models were adopted.

For fitting the experimental data, Equation (2) is employed as a pseudo-first order kinetic model (Ho & McKay 1999; Srivastav *et al.* 2005).

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

where q_e and q_t are the quantity of 4-picoline adsorbed on BFA (mg/L) at an equilibrium and time t respectively, k_f is first order rate constant (min^{-1}).

The slope and intercept of the ln $(q_e - q_t)$ vs. time (t) plot, which is depicted in Figure 6, were used to determine the constant of Equation (2). However, the outcome demonstrated the pseudo-first-order kinetic model's graph's non-linearity. Therefore, this experimental data is not suitable for pseudo-first-order rate expression.

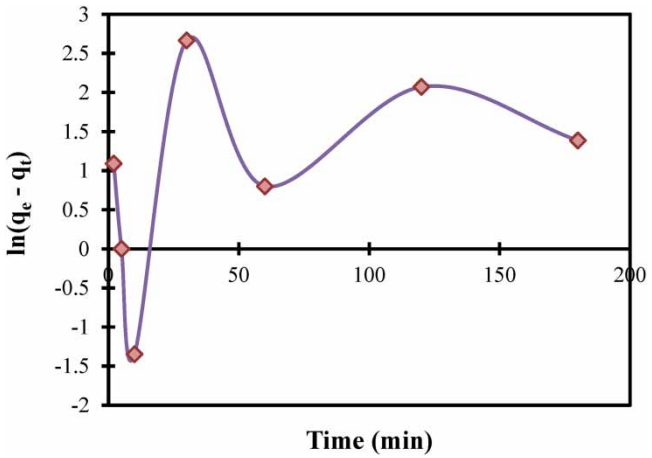

Figure 6 | 4-picoline adsorption pseudo-first order kinetic model at $C_0 = 100$ mg/L and $T = 303$ K.

Hence, Equation (3) was used for fitting pseudo-second-order kinetic model (Smith & VanNess 2004):

$$t/q_t = (1/k_s q_e^2) + (1/q_e)t \tag{3}$$

where k_s is the rate constant (g/mg.min)

The values of k_s and q_e were calculated by the slope and intercept of the plot of t, as shown in Figure 7. The result reveals the graph's linearity and successfully proves a pseudo-second-order kinetic model. The kinetic parameters k_s and q_e were computed and are shown in Table 2 at the starting concentration of 100 mg/L and temperature of 303 K.

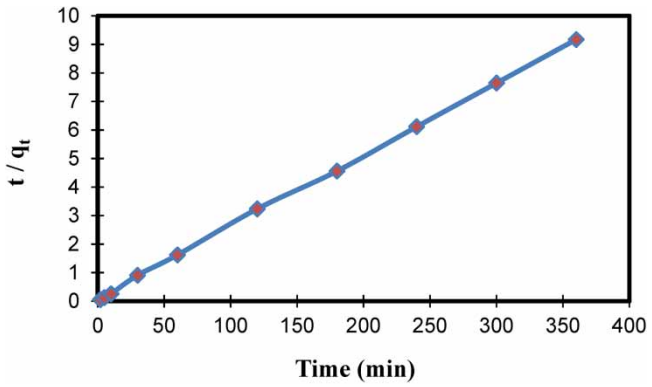

Figure 7 | 4-picoline adsorption pseudo second order kinetic model.

Table 2 | 4-picoline adsorption kinetic parameters of pseudo-second order model ($C_0 = 100$ mg/L.)

Kinetic parameters of pseudo-second order	
k_s (g/L. min)	q_e (mg/L)
1.47×10^4	38.46

4-picoline Adsorption equilibrium study

The Langmuir adsorption isotherm empirical isotherm equation makes the assumption that a monolayer will adsorb onto an adsorbent surface with a finite number of homogenous identical active sites. Equation (4) displays

the Langmuir adsorption isotherm as (Ho & McKay 1999; Smith & VanNess 2004):

$$q_e = [q_m K_L C_e/(1 + K_L C_e)] \quad (4)$$

Or

$$1/q_e = (1/K_L q_m C_e) + (1/q_m) \quad (5)$$

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

As shown in Figure 8, the slope and intercept of the plot of $1/q_e$ vs $1/C_e$ at 303 K were used to determine the constant parameters K_L and q_m. As indicated in Table 3, the values of K_L and q_m were also calculated for all other temperatures, including 303, 313, 323, and 333. With an increase in temperature, the parameter K_L rises while q_m falls. It means the affinity of the adsorbent, i.e. 4-picoline, to the BFA adsorbate, increases with temperature. The higher affinity of the 4-picoline to BFA means a high K_L value at a higher temperature of 333 K. The more adsorption capacity (q_m) of BFA is the monolayer saturation of 4-picoline at equilibrium.

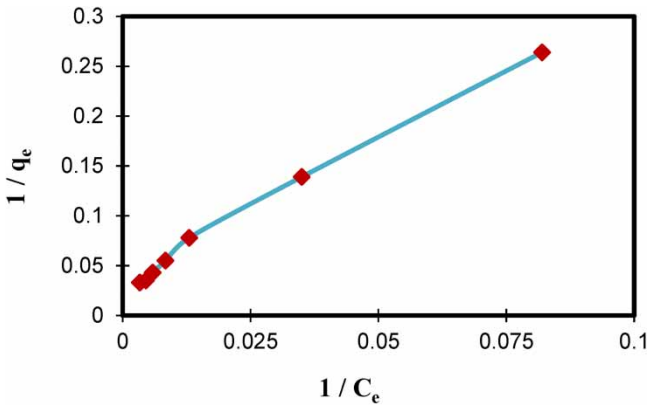

Figure 8 | Langmuir adsorption isotherm plot at $T = 303$ K.

Table 3 | 4-picoline Adsorption isotherm parameters

Isotherm equations	Constants	Temperatures (K) 303	313	323	333
Langmuir $q_e = q_m K_L C_e/(1 + K_L C_e)$	K_L (L/mg)	0.021	0.028	0.034	0.045
	q_m (mg/g)	18.51	16.12	15.14	13.51
	R^2	0.994	0.992	0.991	0.994
Freundlich $q_e = K_F C^{1/n}$	K_F (L/mg)	1.112	1.141	1.153	1.062
	N	1.38	1.68	1.79	1.51
	$1/n$	0.724	0.59	0.55	0.65
	R^2	0.997	0.997	0.998	0.998

At low pressure, the adsorption rate follows the Freundlich adsorption isotherm, which is independent of high pressure. The adsorption rate is directly proportional to pressure raised to power $1/n$ at an intermediate pressure, as is shown by Equation (6) (Ho & McKay 1999):

$$q_e = k_f c_e^{(1/n)} \quad (6)$$

Or

$$ln\ q_e = ln\ k_f + (1/n)\ ln\ C_e \quad (7)$$

where $1/n$ is a constant, which gives the intensity of the adsorption ($n > 1$), k_f is an adsorption constant (mg/g), which gives the adsorption capacity of the adsorbent

When plotted as ln q_e vs ln C_e at 303 K, the Freundlich adsorption isotherm Equation (7) is presented. The plot in Figure 9 was used to determine the slope and intercept. In Table 3, the isotherm parameters k_f and $1/n$ are calculated and displayed. The $1/n$ value reveals the variability of the active adsorbent sites as well as the affinity between 4-picoline and BFA. At 303 K, the value of $1/n$ was higher; as the temperature rose, it became lower. The K_f value demonstrates the endothermic character of the adsorption process by providing a relative measure of the adsorption capability and increased adsorption at higher temperatures. The Freundlich adsorption isotherm does not anticipate the saturation of the adsorbent on the surface of the adsorbate.

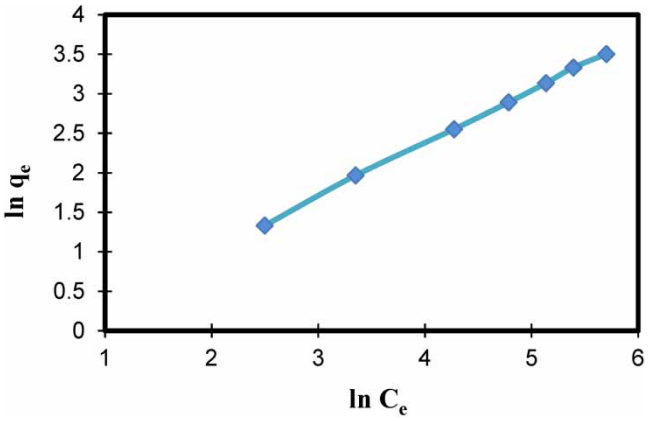

Figure 9 | Freundlich adsorption isotherm plot at $T = 303$ K.

As can be seen from Table 3, the adsorption coefficients for linearity (R^2) for both isotherms are determined to be $R^2 > 0.99$. As a result, the equilibrium adsorption at all temperatures may be described by both the Freundlich and Langmuir adsorption isotherms.

Thermodynamic study of adsorption

Investigation of the adsorption process's viability is also necessary. It is connected to the adsorption equilibrium constant, which was calculated using the following Van't Hoff Equation (8) (Smith & VanNess 2004):

$$\Delta G^{\circ}_{\text{ads}} = -RT\ ln\ K_{\text{ads}} \tag{8}$$

Also, Equation (9) was used for determining the heat of adsorption at a constant process:

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{9}$$

The above two equations are given as:

$$ln\ K_{ads} = -(\Delta G^{\circ}_{ads}/RT) = (\Delta S^{\circ}/R) - (\Delta H^{\circ}/R)\,(1/T) \tag{10}$$

where $\Delta G^{\circ}_{\text{ads}}$ is the Gibb's free energy change (kJ/mol), K_{ads} is adsorption equilibrium constant, ΔH° is the change in enthalpy (kJ/mol), S° is an Entropy change (kJ/mol K, T is the absolute temperature (K), and R is the universal gas constant (8.314 J/mol K).

Equation (11) can be used to calculate the heat of adsorption, ΔH°, from the slope of the linear Van't Hoff plot of ln K vs $(1/T)$ as follows:

$$\Delta H^{\circ} = \text{R}[(d\ ln\ K)/d(1/T)] \tag{11}$$

Figure 10 displays Van't Hoff's plot for both isotherms of Langmuir and Freundlich adsorption. The values of ΔH^0 and ΔS^0 have been determined and are displayed in Table 4. In both isotherms, the heat of adsorption values indicates that the adsorption process was endothermic. Additionally, Table 4 shows the changes in Gibb's free

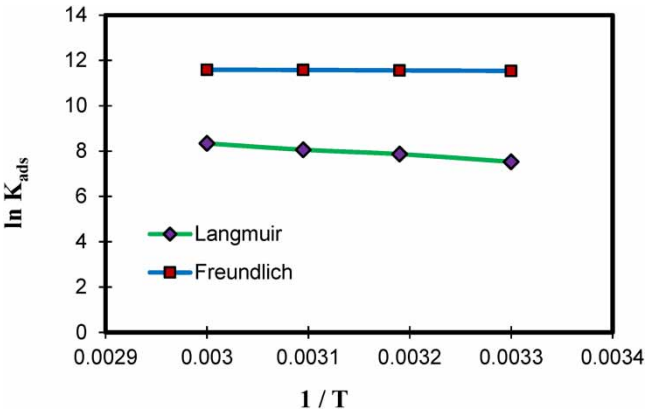

Figure 10 | Van't Hoff's plot ($pH_0 = 6.22$, $C_0 = 100$ mg/L and $m = 4$ g/L).

Table 4 | Thermodynamics parameters for an elimination of 4-picoline

			ΔG° (kJ/mol)			
Isotherm	**ΔH° (kJ/mol)**	**ΔS° (kJ/mol K)**	**303**	**313**	**323**	**333**
Langmuir	22.47	0.085	−18.96	−20.47	−21.64	−23.09
Freundlich	1.385	0.097	−29.07	−30.08	−31.09	−32.08

energy from 303 to 333 K at various temperatures. All of the ΔG°_{abs} readings were negative, demonstrating the viability and spontaneity of the adsorption process.

CONCLUSIONS

4-picoline is a hazardous compound to human health that needs to be removed from wastewater. For the adsorption of 4-picoline, a natural adsorbent is available called BFA. The current investigation discovered that 85.83% of 4-picoline could be removed at its maximum with BFA. Because the active adsorption sites were present, the adsorption rate could be improved by increasing the dose of BFA adsorbent. At 4 g/L adsorption dose and 6 h of contact duration, the highest adsorption of 82% was discovered. The ideal initial pH for removing 4-picoline was discovered to be close to 6.22, and an adsorption rate of 82.11% was discovered. The experimental results were fit with pseudo second order adsorption kinetics. The isotherm models such as Freundlich and Langmuir was used to fit the equilibrium adsorption isotherm. The thermodynamic analysis validated the endothermic nature and showed that the adsorption technique works. BFA is a preferred adsorbent for an elimination of 4-picoline from industrial wastewater.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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First received 17 July 2022; accepted in revised form 12 October 2022. Available online 20 October 2022