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Adsorption of 2-picoline onto bagasse fly ash from aqueous solution

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Abstract

The adsorption of 2-picoline from aqueous solutions onto bagasse fly ash (BFA), a solid waste collected from the particulate collection equipment attached to the stacks of bagasse fired boilers, is presented in this paper. The influence of various parameters like initial pH (pH_0), adsorbent dose (m), contact time (t), initial concentration (C_0) and temperature (T) on the adsorption of 2-picoline from the aqueous solutions were studied using batch adsorption experiments. Equilibrium adsorption and kinetic studies for 2-picoline adsorption onto BFA were also carried out. Various adsorption isotherm equations, viz. Langmuir, Freundlich, Redlich–Peterson and Temkin equilibrium equations were used to test their suitability in describing experimental isotherm data. The adsorption of 2-picoline on bagasse fly ash follows second order kinetics and the equilibrium adsorption increases with increasing initial concentration. The equilibrium sorption isotherm data could be well represented by the Langmuir and Redlich–Peterson isotherm equations. The maximum removal of 2-picoline is found to be 98% at lower concentrations ($<50\,\mathrm{mg\,dm^{-3}}$) and 49% at higher concentrations ($600\,\mathrm{mg\,dm^{-3}}$) using $5\,\mathrm{kg\,m^{-3}}$ of BFA dosage at normal temperature and natural pH_0 ($\sim$6.5). Thermodynamic studies revealed that the adsorption of 2-picoline on BFA is endothermic in nature and that the isosteric heat of adsorption decreases with the increase in the equilibrium uptake of 2-picoline on the BFA surface. Desorption of 2-picoline from the loaded BFA using water at different pH, and various other solvents showed that 2-picoline could be recovered by using acidic water and 0.1N H_2SO_4. Comparative assessment of BFA and activated carbon showed the superiority of BFA in terms of 2-picoline uptake, the rate of adsorption and the eventual cost of operation.

Keywords: 2-Picoline; Bagasse fly ash (BFA); Adsorption isotherms; Kinetics; Isosteric heat of adsorption

1. Introduction

2-Picoline (2Pi), also known as α-picoline, is a derivative of pyridine. It is a colourless liquid with a strong unpleasant odour and is used as a precursor of 2-vinylpyridine. It is used in a variety of agrochemicals and pharmaceuticals, such as nitrapyrin to prevent loss of ammonia from fertilizers; picloram, a herbicide; and amprolium, a coccidiostat. It is also used as a solvent and a raw material for various chemicals used in the manufacture of various polymers, textiles, fuels, agrochemicals, pharmaceuticals and colorants. Various pyridine derivatives serve as antitubercular, respiratory stimulants, local anaesthetic and analgesics. It is soluble in water and miscible in alcohol and ether. Its vapour is a fire and explosion hazard, when exposed to flame or spark. When heated to decomposition, it emits highly toxic fumes of NO_x in an oxidative atmosphere. It is hazardous in case of skin contact (permeator), eye contact (irritant), ingestion and inhalation [1–3].

2-Picoline-bearing wastewaters emanate from industrial units manufacturing pyridine and its derivatives, pharmaceutical units, etc. The typical concentration of 2-picoline in wastewaters produced in a multidrug intermediates-product plant manufacturing α-picoline, β-picoline, 4-aminopyridine and other pyridine derivatives is in the range of 20–200 $\mathrm{mg\,dm^{-3}}$. During spill-episodes, the concentration can increase considerably. These plants are the source of odour nuisance; intense odour emanating either from the wastewater sources and sewer lines or from the handling and storage facilities [4].

Various treatment techniques like adsorption [5] and biodegradation [6] can be used for the treatment of α-picoline bearing wastewater. Adsorption can be a preferred treatment technique, provided that the adsorption process is cost-effective. Agri-solid wastes generally exhibit excellent adsorption characteristics for many organic and inorganic solutes in the aqueous solutions. Because of the very high affinity of these solutes on the surface of the agri-wastes and high stability of the sorbates on the solid surfaces, their recovery from the adsorbents is not economical. However, the solute loaded spent sorbent, can be separated from the aqueous solution, dewatered, dried and fired in the

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Nomenclature

a_R	R–P isotherm constant ($dm^3 mg^{-1}$)
b	Temkin isotherm energy constant ($J mol^{-1}$)
B_1	constnat constant in Temkin equation
C_e	equilibrium concentration ($mg dm^{-3}$)
C_0	initial concentration of 2-picolineridine ($mg dm^{-3}$)
ΔG°_{ads}	free energy change ($kJ mol^{-1}$)
h	initial adsorption rate ($mg g^{-1} min^{-1}$)
ΔH°	change in enthalpy of 2-picoline ($kJ mol^{-1}$)
$\Delta H_{st,a}$	isosteric heat of adsorption ($kJ kg^{-1}$)
k_f	pseudo-first order kinetic equation constant (min^{-1})
k_S	pseudo-second order kinetic equation constant (g $mg^{-1} min^{-1}$)
K_F	Freumdlich constant ($dm^3 g^{-1}$)
K_L	Langmuir constant ($dm^3 g^{-1}$)
K_R	Redlich–Peterson constant ($dm^3 g^{-1}$)
K_T	constant in Temkin equation ($dm^3 g^{-1}$)
m	adsorbent dose (g)
q	amount of 2-picoline adsorbed ($mg g^{-1}$)
q_e	amount of 2-picoline adsorbed at equilibrium ($mg g^{-1}$)
q_m	monolayer adsorption capacity ($mg g^{-1}$)
q_t	amount of 2-picoline adsorbed at any time, t
R	universal gas constant ($J mol^{-1} K^{-1}$)
ΔS°	entropy change ($kJ mol^{-1} K^{-1}$)
t	contact time (min)
T	temperature (K)
V	volume (dm^3)
W	weight of adsorbent (g)

Greek letters

β	exponent in R–P equation, lies between 0 and 1
λ_{max}	wavelength (nm)

furnaces/incinerators to chemically transform the adsorbates into innoccuous combustion products with simultaneous energy recovery. Bagasse fly ash (BFA) is a waste material obtained from the particulate collection equipment attached downstream to the boilers/furnaces using bagasse as the fuel. BFA entails no cost, excepting its collection and transportation to the utility point. Because of its excellent sorption characteristics, BFA has been used by several investigators [4,7–15] as an adsorbent for the removal of organics, dyes, phenols, etc.

The sorption characteristics of 2-picoline from synthetic aqueous solutions onto BFA is reported in the present paper. The effect of initial pH of the solution ($2 \leq pH_0 \leq 12$), adsorbent dose ($2 g dm^{-3} \leq m \leq 30 g dm^{-3}$), contact time ($0 d \leq t \leq 3 d$), initial 2-picoline concentration ($50 mg dm^{-3} \leq C_0 \leq 600 mg dm^{-3}$) and temperature ($283 K \leq T \leq 323 K$) on the adsorption of 2-picoline onto BFA has been investigated. Adsorption kinetics and equilibrium characteristics have also been studied. Various equilibrium isotherm equations, viz. Freundlich, Langmuir, Redlich–Peterson (R–P) and Temkin equations have been used to test their applicability to describe the experimental equilibrium sorption data. Error analysis has also been carried out to test the adequacy and the accuracy of the isotherm equations. Thermodynamic studies have been made to understand the effect of 2-picoline concentration on isosteric heat of adsorption. Desorption studies have been carried out to determine the recovery of 2-picoline and the stability of the spent BFA.

2. Materials and methods

2.1. Adsorbent

BFA, obtained from Deoband Sugar Mills, Deoband, U.P. (India) was washed with hot water (70 °C), dried and sieved using IS sieves (IS 437-1979). The mass fraction between −600 and +180 μm was used for the sorption of 2-picoline from the aqueous solution. The physico-chemical characteristics of BFA were determined using standard methods. Proximate analysis of BFA was carried out using the standard procedure (IS: 1350-1984, part-I). Bulk density was determined using a MAC bulk density meter. Scanning electron microscopy (SEM) micrographs of BFA samples were obtained using scanning electron microscope (LEO 435 VP). The specific surface area and the pore diameter of the BFA particles were measured by nitrogen adsorption isotherm using an ASAP 2010 Micromeritics instrument and by the Brunaer–Emmett–Teller (BET) method, using the software of Micromeritics. Nitrogen was used as cold bath (77.15 K). The Barrett–Joyner–Halenda (BJH) method was used to calculate the mesopore distribution [16]. Fourier transform infrared (FTIR) spectra of blank and 2-picoline loaded BFA was obtained with a Nicolet Avatar 370 CsI spectrometer (Thermo Electron Corporation, USA) using KBr pellet (pressed disk) technique over a spectral range of 4000 to 400 cm^{-1}.

The zero surface charge characteristics of the BFA were determined by using the solid addition method [17]. To a series of 0.1 dm^3 conical flasks, 0.045 dm^3 of KNO_3 solution of known strength was transferred. The pH_0 values of the solution were roughly adjusted from 2 to 12 by adding either 0.1N HCl or 0.1N NaOH. The total volume of the solution in each flask was made exactly to 0.05 dm^3 by adding the KNO_3 solution of the same strength. The pH_0 of the solutions were then accurately noted. One gram of BFA was added to each flask, which were securely capped immediately. The suspensions were then manually shaken and allowed to equilibrate for 48 h with intermittent manual shaking. The pH values of the supernatant liquid were noted. The difference between the initial and final pH (pH_f) values ($\Delta pH = pH_0 - pH_f$) was plotted against the pH_0. The point of intersection of the resulting curve at which $\Delta pH = 0$ gave the pH_{PZC}. The procedure was repeated for different concentrations of KNO_3.

2.2. Adsorbate

All the chemicals used in the study were of analytical reagent grade. The adsorbate, 2-picoline (synonym: 2-methylpyridine, chemical formula = C_6H_7N, formula weight = 93.13 and $\lambda_{max} = 262$ nm) was supplied by Acros Organics (USA). An accurate volume of aqueous 2-picoline solution was taken and mixed well with double-distilled water to prepare a 2-picoline stock solution of 1000 mg dm^{-3} concentration. The stock solution was successively diluted with double-distilled water to obtain the desired test concentration of 2-picoline.

2.3. Analytical measurements

The 2-picoline dissolved in water has been found to be stable over the concentration range of 50–600 mg dm^{-3} used in the study. No change in the 2-picoline concentration was observed over a time period of 12 h. The experiments were carried out in the stoppered/capped glass containers and no loss of 2-picoline due to its vaporization has been observed during the experiments and the analysis. The concentrations of 2-picoline in the aqueous solutions were determined by using a Perkin Elmer Lambda 35 double beam spectrophotometer. The wavelength corresponding to maximum absorbance (λ_{max}) of 2-picoline was found out by scanning a standard solution of known concentration at different wavelengths. The λ_{max} as determined from this plot was 262 nm. This wavelength was used for preparing a calibration curve between absorbance and 2-picoline concentration (mg dm^{-3}) in aqueous solution. The linear region of this curve was further used for the determination of 2-picoline concentration of the unknown aqueous sample. Samples of higher concentrations of 2-picoline beyond the linear region of the calibration curve, were diluted with double-distilled water, whenever necessary, for the accurate determination of its concentration from the linear portion of the calibration curve.

2.4. Batch adsorption study

All the batch experiments were conducted at 30 ± 1 °C. For each experimental run, 0.05 dm^3 of 2-picoline solution of known initial concentration (C_0), pH$_0$ and m, taken in a 0.25 dm^3 stoppered conical flask was agitated in a temperature-controlled orbital shaker at a constant speed of 150 ± 5 rpm. Samples were withdrawn at appropriate time intervals and centrifuged using a research centrifuge (Remi Instruments, Mumbai, India). The residual 2-picoline concentration (C_e) of the centrifuged supernatant was then determined. Effect of pH$_0$ on 2-picoline removal was studied over a pH$_0$ range of 2–12. pH$_0$ was adjusted by the addition of either 0.1N H_2SO_4 or 0.1N NaOH solutions. For the determination of the optimum m, a 0.05 dm^3 2-picoline solution was contacted with different amounts of adsorbents (m) till equilibrium was attained. Kinetics of adsorption was determined by analyzing adsorptive uptake of 2-picoline from the aqueous solution at different time intervals. For adsorption isotherms, 2-picoline solutions of $C_0 = 50$–600 mg dm^{-3} were agitated with a known amount of adsorbent m till equilibrium was achieved. The effect of temperature on equilibrium adsorption was studied in the temperature range of 283 K $\leq T \leq$ 323 K. Blank runs with only the adsorbent in 0.05 dm^3 of double-distilled water were conducted simultaneously at similar conditions to account for any leaching of 2-picoline by the BFA and the adsorption by glass containers. Similarly, blank runs with 2-picoline solution ($C_0 = 50$ mg dm^{-3}) and without the adsorbent were also conducted. No change in the 2-picoline concentration was observed over a time period of 12 h. For desorption studies, 0.5 g of 2-picoline loaded BFA ($q_e = 17.9$ mg g^{-1}) was contacted with 0.05 dm^3 of the eluting solvent, mixed and agitated for 6 h. The mixture was centrifuged and the supernatant was analyzed for 2-picoline. The amount of 2-picoline adsorbed by the adsorbent at equilibrium was calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

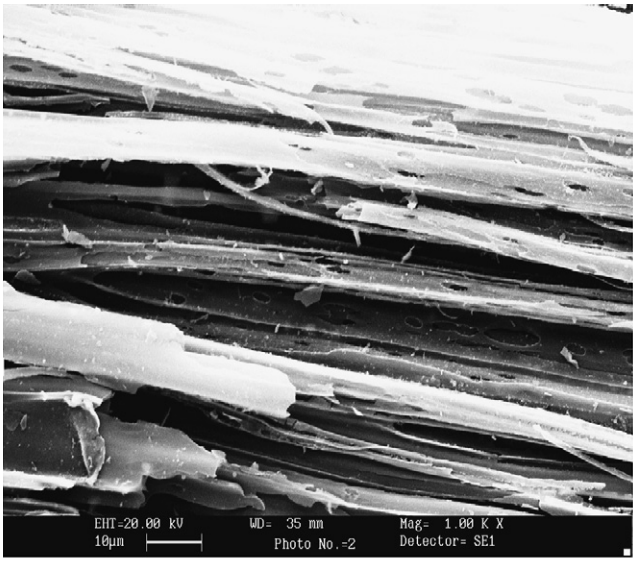
where C_0 and C_e are initial and equilibrium concentrations (mg dm^{-3}) of 2-picoline in the solution, V the volume (dm^3), W the weight (g) of the adsorbent and q_e is the amount of 2-picoline adsorbed by the adsorbent at equilibrium (mg g^{-1}).

3. Results and discussion

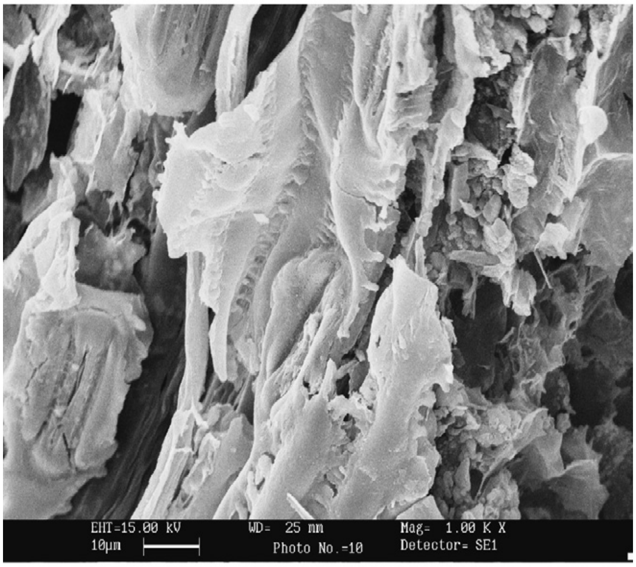
3.1. Characterization of adsorbent

The physico-chemical properties of BFA like, bulk density (mass per unit bed volume), BET surface area, moisture content, volatile matter, ash content, fixed carbon and heating value are found to be 133.33 kg m^3, 168.83 m^2 g^{-1}, 7.64%, 17.37%, 26.43%, 48.56% and 28.73 MJ kg^{-1}, respectively. The fractional sieve analysis of the particles is as follows: $-600 + 425$ μm: 31.42%; $-425 + 180$ μm: 68.43%. The average particle diameter was found to be 381.45 μm. The BET surface area is 168.8 m^2 g^{-1} whereas BJH adsorption/desorption surface area of pores is 54.2/49.9 m^2 g^{-1}. The single point total pore volume of pores (<1042.3 Å) is 0.101 cm^3 g^{-1} whereas cumulative pore volume of pores (17 Å < d < 3000 Å) is 0.053 cm^3 g^{-1}. The average BET pore diameter is 23.97 Å whereas the BJH adsorption/desorption average pore diameter is 39.36/33.9 Å. The SEM micrographs as given in Fig. 1(a) show that the BFA has fibrous structure having large pore size with strands in each fiber. Fig. 1(b) shows the SEM micrographs of the BFA loaded with 2-picoline.

The surface structures of the carbon–oxygen (functional groups) are very important in influencing the surface characteristics and surface behaviour of the adsorbents. The FTIR spectrum is generally used to identify some of the characteristic functional groups capable of adsorbing organics. Fig. 2 shows the FTIR spectra of blank and 2-picoline-loaded BFA. Three clear peaks around 1400, 1640 and 2340 cm^{-1} are identifiable which are affected due to 2-picoline-adsorption onto BFA. The peak around 1400 cm^{-1} is attributed to CH_3 bending vibration and some interaction between C–O stretching and in plane C–O–H bending. This peak also corresponds to bound water coordinated to cations. This may also be attributed to single C–N bond (not to hydrogen). The peak around 1640 cm^{-1} is attributed to hydrogen bending vibrations reflecting the presence of bound water. It may also be due to conjugated hydrocarbon bonded carboxyl groups. The peak at 1634 cm^{-1} may also be due to NH deformation and CO group stretching. The broad band between 3000 and 4000 cm^{-1} indicates the presence of both free and hydro-



(a) Virgin BFA



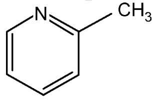
(b) 2-picoline loaded BFA

Fig. 1. SEM of BFA at 1000×.

gen bonded OH groups on the BFA surface. Upon 2-picoline adsorption, these peaks get slightly shifted with the increase in transmittance. The peak shift from about 1634–1650 cm^{-1} may be due to NH deformation and R–N–H bending vibrations. The increase in transmittance is attributed to the effects of adsorption of 2-picoline resulting in the decline of the effectiveness of the functional groups in adsorption [4].

3.2. *Effect of initial pH (pH_0) of the solution*

The structure of 2-picoline (α-picoline) [2] is given below



α- picoline

2-Picoline behaves like a base ($pK_a \sim 5.96$) [18], and the transition of 2-picoline to $2PiH^+$ is pH dependent, with a maximum amount of $2PiH^+$ occurring in the pH range of 4.5–12.0. The solution pH affects the surface charge of the adsorbents and, therefore, the adsorption process through dissociation of functional groups, viz. surface oxygen complexes of acid character such as carboxyl and phenolic groups or of basic character such as pyrones or chromens, on the active sites of the adsorbent [19]. pH may affect the structural stability of 2-picoline. Effect of pH_0 on the 2-picoline removal by BFA is shown in Fig. 3 for $C_0 = 100\,\mathrm{mg\,dm^{-3}}$ at $30 \pm 1\,^\circ\mathrm{C}$ after 6 h of contact with $m = 5\,\mathrm{g\,dm^{-3}}$. Equilibrium was found to have been attained in $t = 6$ h. Further increase in contact time upto 1 day and 3 day showed a deviation of 0.2% and 0.6%, respectively. A maximum 2-picoline adsorption of ∼97% was found to occur at the natural pH_0 ($pH_0 \approx 6.45$) of the aqueous solution. More than 90% adsorption seems to occur at $pH_0 \geq 4$. However, as the pH_0 decreases ($pH_0 < 4$), the adsorption decreases drastically with a minimum 2-picoline removal of 15% at pH_0 2. The zero charge of BFA, ΔpH_{zpc} has been found to occur at $pH \sim 9$.

BFA contains oxides of aluminium, calcium and silicon on its surface. The presence of the metal oxides in contact with water leads to the development of surface charge according to the pH of the solution [4]:

$$H_2O \rightleftharpoons H^+ + OH^- \tag{a}$$

$$M + OH^- \rightarrow MOH \tag{b}$$

$$M{-}OH + H^+ \rightarrow M{-}OH_2{}^+ \tag{c}$$

$$M{-}OH + OH^- \rightarrow M{-}O^- + H_2O \tag{d}$$

where M stands for Al, Ca and Si. The chemical interaction of 2-picoline with BFA may be explained on the basis of the explanation put forth by Weber [20], and Zhu et al. [21] for adsorbent–pyridine interaction

$$2Pi + H \rightleftharpoons 2PiH^+ \tag{e}$$

$$2Pi + BFA \rightleftharpoons 2Pi - BFA \tag{f}$$

$$2PiH^+ + M^+ - BFA \rightleftharpoons 2PiH^+ - BFA + M^+ \tag{g}$$

$$H^+ + 2PiH^+ - BFA \rightleftharpoons H^+ - BFA + 2PiH^+ \tag{h}$$

$$H^+ + BFA \rightleftharpoons H^+ - BFA \tag{i}$$

$$2Pi - H^+ - BFA \rightleftharpoons 2PiH^+ - BFA \tag{j}$$

Since 2-picoline contains nitrogen atom, which is more electronegative than a SP^2 hybridized C, 2-picoline gets preferentially adsorbed on a positively charged surface [22]. At low pH ($pH_0 \leq 4$), the 2-picoline is converted to $2PiH^+$ through protonation via reaction Eq. (e) resulting in the low adsorption of protonated 2-picoline on the positively charged BFA surface as shown by reaction Eq. (g). At higher pH ($pH \geq 4$), π–π dispersion interactions also takes place as given by Radovic et al. [23,24] and electrostatic interactions become important and 2-picoline molecule is sorbed onto BFA. It may, however, be noted that BFA has a maximum affinity to 2-picoline and $2PiH^+$ at $pH_0 \sim 6.45$. $2PiH^+$ adsorption is at a lower rate than

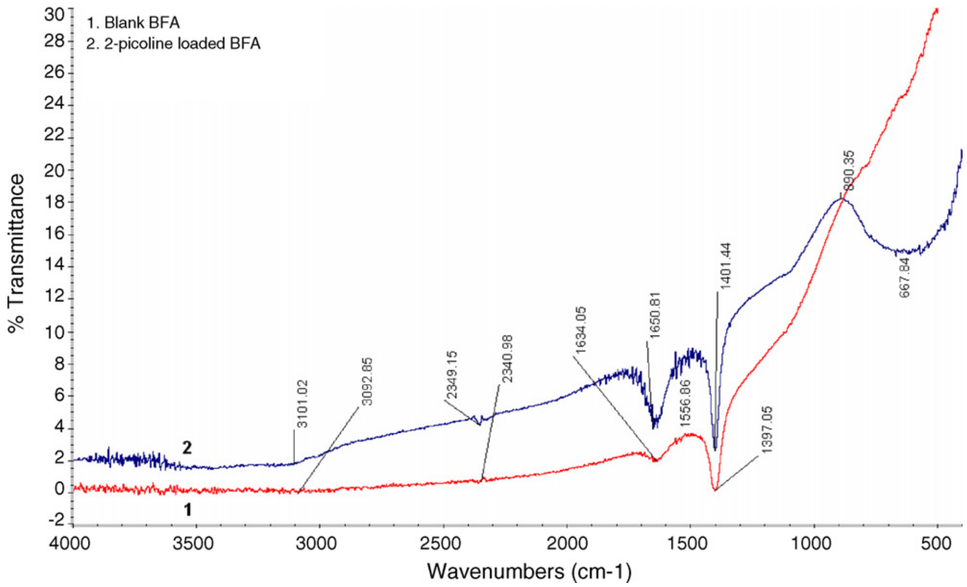


Fig. 2. FTIR spectra of blank and 2-picoline loaded BFA.

that of 2-picoline molecules. Therefore, the dominant sorption reaction (at $pH_0 \approx 6.45$) is perhaps given by Eq. (f). Other reactions given by Eqs. (e), (g)–(j) play insignificant role in the overall adsorption of 2-picoline onto BFA. Similar results were observed earlier for the adsorptive removal of pyridine by using BFA [4].

It may be noted that the solution pH varies with contact time on the addition of BFA. It is found that the solution pH (pH_0 6.45) increases instantaneously to about 8.25 after the addition of the optimum amount of BFA, rises to about 8.75 (i.e. nearer $\Delta pH_{zpc} \sim 9$) after 6 h and remains constant thereafter. In view of these observations, further experiments were performed at pH_0 6.45.

3.3. *Effect of adsorbent dose (m)*

The effect of m on the uptake of 2-picoline by BFA for $C_0 = 100\,mg\,dm^{-3}$ is shown in Fig. 4. The 2-picoline removal is observed to increase with an increase in m upto about $5\,g\,dm^{-3}$. The incremental 2-picoline removal between 5 and $8\,g\,dm^{-3}$ of BFA dosage is only marginal and beyond $8\,g\,dm^{-3}$, the 2-picoline removal remains almost unaffected by the BFA dosage. 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 $m > 5\,g\,dm^{-3}$, the incremental 2-picoline uptake is very small, as the 2-picoline surface concentration and the 2-picoline bulk solution concentration come to equilibrium to each other [13]. Thus, the optimum m for C_0 of $100\,mg\,dm^{-3}$ may be taken as $5\,g\,dm^{-3}$.

3.4. *Effect of initial concentration (C_0) and temperature*

The effect of C_0 ($50\,mg\,dm^{-3} \leq C_0 \leq 600\,mg\,dm^{-3}$) and temperature ($283\,K \leq T \leq 323\,K$) on the equilibrium uptake of 2-picoline by the BFA at $m = 5\,g\,dm^{-3}$ and $t = 6\,h$ was studied and a plot of the removal of 2-picoline and the sorptive uptake of 2-picoline by BFA versus C_0 with temperature as a parameter is given in Fig. 5. 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. It may, however, be noted that as C_0 and/or temperature increases, the 2-picoline loading onto BFA (i.e. q_e) increases. This means that the 2-picoline sorption capacity of the BFA increases significantly with an increase in C_0, but only weakly with an increase in temperature of the solution. This is because of the fact that a given mass of adsorbent adsorbs only a fixed amount of adsorbate. From the figure, it is evident 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.

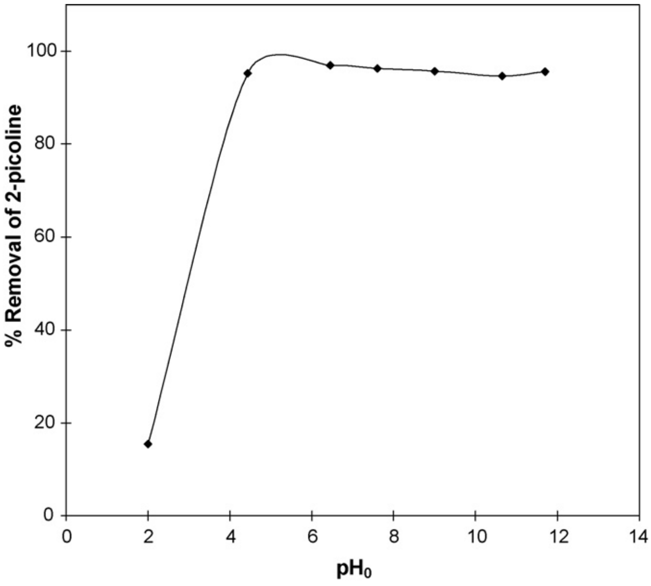


Fig. 3. Effect of initial pH_0 of the aqueous solution on the removal of 2-picoline by BFA ($C_0 = 100\,mg\,dm^{-3}$, $m = 5\,g\,dm^{-3}$, $T = 303\,K$, $t = 6\,h$).

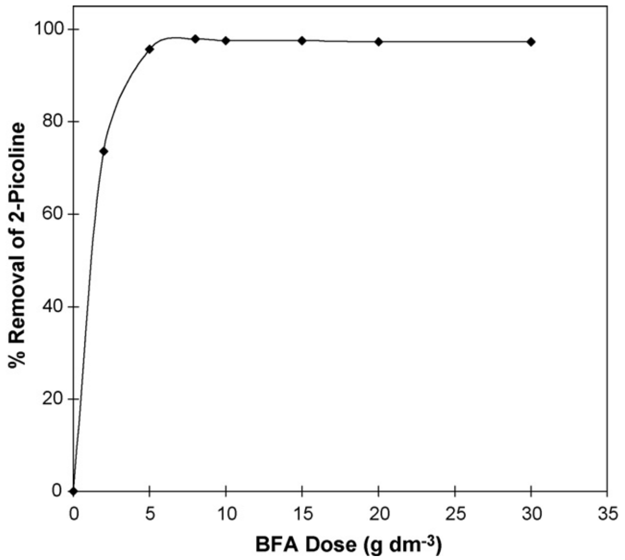


Fig. 4. Effect of m on the removal of 2-picoline by BFA ($C_0 = 100\,\mathrm{mg\,dm^{-3}}$, pH_0 6.45, $T = 303$ K, $t = 6$ h).

3.5. Effect of contact time

The effect of contact time on the removal of 2-picoline by BFA for $m = 5\,\mathrm{g\,dm^{-3}}$ and $C_0 = 100$, 200 and $300\,\mathrm{mg\,dm^{-3}}$ is shown in Fig. 6. Rapid adsorption of 2-picoline during the initial period of 5 min is observed. The adsorption rate decreased substantially and rapidly with time beyond 5 min. The adsorptive uptake of 2-picoline by BFA is thus almost instantaneous: About 90% of 2-picoline from an aqueous solution of $C_0 = 100\,\mathrm{mg\,dm^{-3}}$ is adsorbed in 5 min of contact. The residual 2-picoline concentration is 5.38% after 1 h, 3.77% after 6 h, 3.16% after 24 h and 3.15% after 72 h contact time. Since the difference in 2-picoline removal at 6 and 72 h is less than 0.6% of the 72 h removal, a steady-state approximation was assumed and a quasi-equilibrium situation was accepted at $t = 6$ h and further experiments were conducted at $t = 6$ h only.

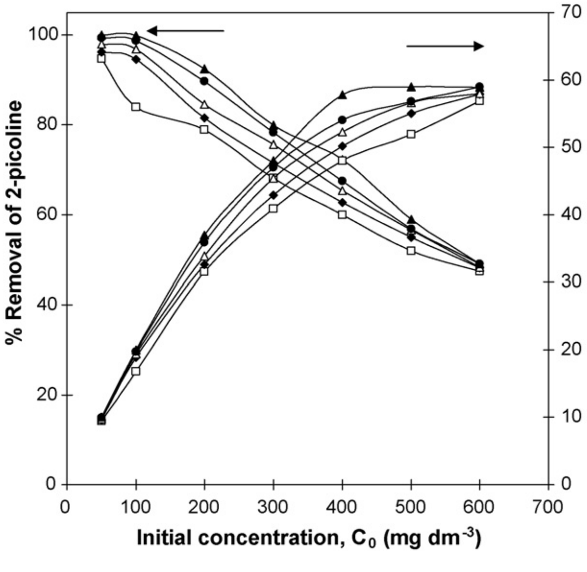


Fig. 5. Effect of C_0 and temperature on the removal and uptake of 2-picoline by BFA ($m = 5\,\mathrm{g\,dm^{-3}}$, pH_0 6.45, $t = 6$ h). (□) 283 K; (♦) 293 K; (△) 303 K; (●) 313 K; (▲) 323 K.

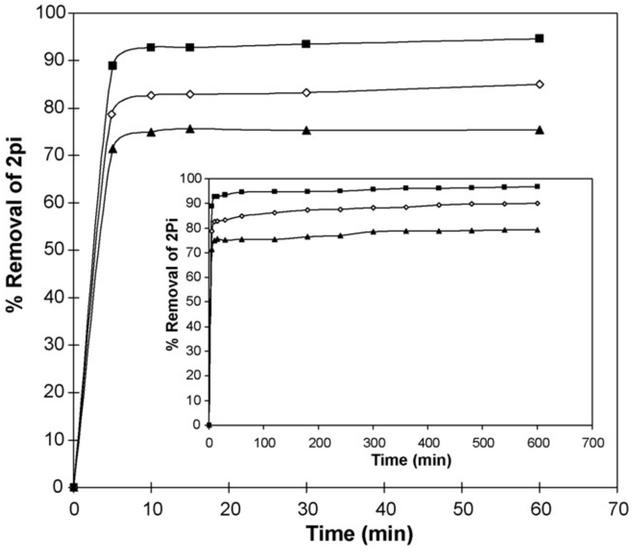


Fig. 6. Effect of contact time on the removal of 2-picoline by BFA at various C_0 values, $\mathrm{mg\,dm^{-3}}$ ($m = 5\,\mathrm{g\,dm^{-3}}$, pH 6.45, $T = 303$ K). (■) $100\,\mathrm{mg\,dm^{-3}}$; (◇) $200\,\mathrm{mg\,dm^{-3}}$; (▲) $300\,\mathrm{mg\,dm^{-3}}$.

3.6. Kinetics of adsorption

The adsorption rate of 2-picoline onto BFA is found to be very fast initially. Almost instantaneous adsorption takes place. 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. With $m = 5\,\mathrm{g\,dm^{-3}}$, $C_0 = 100\,\mathrm{mg\,dm^{-3}}$, and $T = 30\,^{\circ}\mathrm{C}$, almost 90% 2-picoline removal takes place during the initial 5 min of contact between the BFA and the 2-picoline solution. At $t = 15$ min, 92.71% 2-picoline removal is obtained. The data for q versus t during the initial 1 h of contact shows a very fast increase in q with time upto initial 5 min followed by a sharp plateau at quasi-equilibrium situation. Initial uptake is attributed to surface adsorption. When the 2-picoline adsorption at the exterior surface reached the saturation level, the 2-picoline begins to enter the pores of the BFA and is adsorbed by the interior surface of the BFA particles. The interior surface seems to be very active and have a very high affinity towards 2-picoline molecules. Hence a very high 2-picoline uptake by BFA is observed. As the surface saturates with 2-picoline molecules, the adsorption rate decreases due to an increase in the diffusion resistance. This means that the pore diffusion is the rate controlling step during 2-picoline adsorption.

The sorption kinetics was studied by using pseudo-first order kinetic and pseudo-second order kinetic models to fit the experimental kinetic data.

The pseudo-first order kinetic equation is given as [25,15]:

$$\log(q_\mathrm{e} - q_t) = \log q_\mathrm{e} - \frac{k_\mathrm{f}}{2.303}t \qquad (2)$$

Table 1
Kinetic parameters for the removal of 2-picoline by adsorption onto BFA at various initial concentrations ($T = 303$ K, pH_0 6.45, $m = 5$ m dm^{-3})

C_0 (mg dm^{-3})	Pseudo-first-order model			Pseudo-second-order model			
	k_f (min^{-1})	q_e (mg g^{-1})	R^2	h (mg g^{-1} min^{-1})	k_S (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2
100	0.006	0.981	0.94	13.245	0.035	19.342	1
200	0.006	1.677	0.88	11.587	0.009	35.971	1
300	0.006	1.662	0.87	17.953	0.009	47.619	1

where k_f (min^{-1}) is the first order rate constant, q_e is the amount of 2Pi adsorbed on the adsorbent at equilibrium (mg g^{-1}) and q_t the amount adsorbed on the adsorbent at any time t (mg g^{-1}). These constants can be calculated from the slope and intercept of the plot $\ln(q_e - q_t)$ versus time t. The first order equation did not represent the kinetic data of 2Pi adsorption satisfactorily.

The pseudo-second order kinetic equation is given by [25]:

$$\frac{dq_t}{dt} = k_S(q_e - q_t)^2 \tag{3}$$

where k_S is the rate constant (g mg^{-1} min^{-1}). The integration of Eq. (3) with the boundary conditions: $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, leads to:

$$\frac{t}{q_t} = \frac{1}{k_S q_e^2} + \frac{1}{q_e}t = \frac{1}{h} + \frac{1}{q_e}t;\ \text{or}\ q_e = \frac{k_S q_e^2 t}{1 + k_S q_e t} \tag{4}$$

where h is the initial sorption rate (mg g^{-1} min^{-1}) at $t \to 0$.

The value of h and q_e can be determined experimentally from the slope and intercept of the plot of t/q_t versus t (not shown here), respectively. k_S value can then be estimated from the value of h. However, the linear regression method is not appropriate for the determination of kinetic parameters. Instead the non-linear method should be used. In the non-linear method, an "optimization" procedure using the Solver add-in function given in MS excel Spreadsheet could be applied. Table 1 shows the values of constants of pseudo-first and pseudo-second order kinetic equations.

From Table 1, it is found that the first-order kinetic equation does not represent the experimental adsorption data satisfactorily. However, the second-order kinetic model represents the adsorption data well with the correlation coefficient obtained from non-linear optimization method being almost equal to 1.

3.7. Adsorption equilibrium

Several equilibrium isotherm equations are proposed in the literature to describe the equilibrium adsorption characteristics. These isotherm equations and their attributes have been explained in our earlier publications [4,15]. It has been shown earlier that the Langmuir and Redlich–Peterson equations provide better description of sorption behaviour of pyridine from the aqueous solution onto BFA than other sorption isotherm equations [4]. The Langmuir equation assumes monolayer sorption onto an adsorbent surface with a finite number of identical homogeneous sites. This equation is given by:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad \text{or} \quad \frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m} \tag{5}$$

or

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{6}$$

where q_m is the monolayer sorption capacity (mg g^{-1}) and is a constant, and K_L is a constant related to the free energy of sorption ($K_L = e^{-\Delta G/RT}$). It is the reciprocal of the concentration at which the adsorbent is half-saturated. A plot of experimental sorption data as either $1/q_e$ versus $1/C_e$ or C_e/q_e versus C_e enables the calculation of the values of the constants (Table 2).

For very small C_e values, Eq. (4) also reduces to the Henry's equation with

$$q_e = q_m K_L C_e = k_H C_e \tag{7}$$

where $k_H = q_m K_1 =$ Henry's constant

The Redlich–Peterson (R–P) [26] equation is a three-parameter model and is given as:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \tag{8}$$

where K_R is R–P constant (dm^3 g^{-1}) and a_R is also R–P isotherm constant (dm^3 mg^{-1}) and β is the exponent having values between 0 and 1. The R–P equation is a general isotherm equation which reduces to Freundlich, Langmuir and Henry's isotherm equations under different limiting situations. For $a_R \gg 1$, Eq. (8) reduces to Freundlich equation [27] with $K_F = K_R/a_R$ and $(1 - \beta) = 1/n$. For $\beta = 1$, Eq. (8) reduces to Langmuir equation, with $K_L = a_R$. For $\beta = 0$, Eq. (8) reduces to the Henry's equation [28], i.e.

$$q_e = \frac{K_R C_e}{1 + a_R} = k_H C_e \tag{9}$$

where $k_H = K_R/(1 + \alpha_R)$

Thus at low loadings, Eqs. (7) and (9) may have similar behaviour, i.e.

$$\frac{K_R}{1 + a_R} = q_m K_L \tag{10}$$

By taking logarithms of both the sides of Eq. (8), we get a non-linear equation, i.e.

$$\ln\left(K_R \frac{C_e}{q_e} - 1\right) = \ln a_R + \beta \ln C_e \tag{11}$$

Table 2
Isotherm parameters and error analyses values for the adsorption of 2-picoline onto BFA ($C_0 = 50$–$600\,\mathrm{mg\,dm^{-3}}$, $m = 5\,\mathrm{g\,dm^{-3}}$, $t = 6\,\mathrm{h}$, pH_0 6.45)

Isotherm equations	Constants	Temperatures (K)				
		283	293	303	313	323
Langmuir, $q_e = q_m K_L C_e/(1 + K_L C_e)$	K_L ($\mathrm{dm^3\,mg^{-1}}$)	0.028	0.046	0.068	0.109	0.191
	q_m ($\mathrm{mg\,g^{-1}}$)	60.976	60.241	59.880	59.524	59.880
	R^2 (linear)	0.990	0.992	0.996	0.997	0.998
	R^2 (non-linear)	0.995	0.996	0.998	0.999	0.999
Freundlich, $q_e = K_F C_e^{1/n}$	K_F ($\mathrm{dm^3\,mg^{-1}}$)	6.500	9.143	11.586	15.506	23.578
	n	2.579	2.968	3.331	3.982	5.747
	$1/n$	0.388	0.337	0.300	0.251	0.174
	R^2 (linear)	0.983	0.976	0.982	0.968	0.958
	R^2 (non-linear)	0.992	0.988	0.985	0.984	0.979
Temkin, $q_e = (RT/b)\ln K_T C_e$	B	10.316	9.444	8.592	7.294	5.129
	K_T ($\mathrm{dm^3\,mg^{-1}}$)	0.599	1.284	2.758	10.258	311.461
	R^2 (linear)	0.959	0.989	0.989	0.994	0.962
	R^2 (non-linear)	0.980	0.994	0.994	0.997	0.984
Redlich–Peterson, $q_e = K_R C_e/(1 + a_R C_e^{\beta})$	a_R ($\mathrm{dm^3\,mg^{-1}}$)	4.357	0.430	0.714	2.092	23.604
	K_R ($\mathrm{dm^3\,mg^{-1}}$)	31.921	8.958	16.745	52.854	769.723
	β	0.634	0.820	0.839	0.850	0.897
	R^2 (linear)	0.994	0.999	0.999	0.999	0.999
	R^2 (non-linear)	0.997	0.999	0.999	1.000	1.000

Eq. (11) can be fitted to experimental data by maximizing the correlation coefficient between the predicted values of q_e from Eq. (11) and the experimental data using the solver add-in function of the MS excel, using the iterative values of K_R.

The Temkin isotherm [29,30] is given as:

$$q_e = \frac{RT}{b} \ln(K_T C_e) \tag{12}$$

which can be linearized as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \tag{13}$$

where $B_1 = RT/b$, b is the Temkin energy constant ($\mathrm{J\,mol^{-1}}$).

This isotherm contains a factor, K_T that explicitly takes into account the interactions between adsorbing species and the adsorbent. A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants b, B_1 and K_T from the slope and intercept, respectively.

The Freundlich, Langmuir, R–P and Temkin isotherm equations have been used to describe the experimental data for equilibrium adsorption of 2-picoline onto BFA. The parametric values of the respective isotherms have been obtained by using linear and non-linear regression analyses using MS Excel and are given in Table 2. The testing of the isotherm equations in correlating the experimental equilibrium sorption data for 2-picoline onto BFA shows similar results as that for pyridine sorption onto BFA [4]. It is found that the Redlich–Peterson equation followed by Langmuir equation best represented the experimental equilibrium sorption data. Figs. 7 and 8 show the plots for the Langmuir and R–P isotherms fitting the experimental data at different temperatures. Fig. 9 shows the comparative fit of all the isotherms with the experimental data.

3.8. Desorption of 2-picoline

In order to check for the stability of 2-picoline sorbed onto BFA and to determine the recovery of the adsorbate and the regeneration of the spent BFA, the desorption characteristics of 2-picoline have been studied at the temperatures of 288 and 303 K. Several solvents, viz. distilled water of varying pH ($2 \le \mathrm{pH} \le 11$), 0.1N H_2SO_4, 0.1N HNO_3, and 0.1N NaOH solutions have been used as the desorbing solvents. For desorption experiments, an accurate amount (~0.5 g) of 2-picoline loaded BFA ($q_e = 17.9\,\mathrm{mg\,g^{-1}}$) was mixed with $0.05\,\mathrm{dm^3}$ of the solvent and the mixture was agitated in an orbital shaker for 6 h at

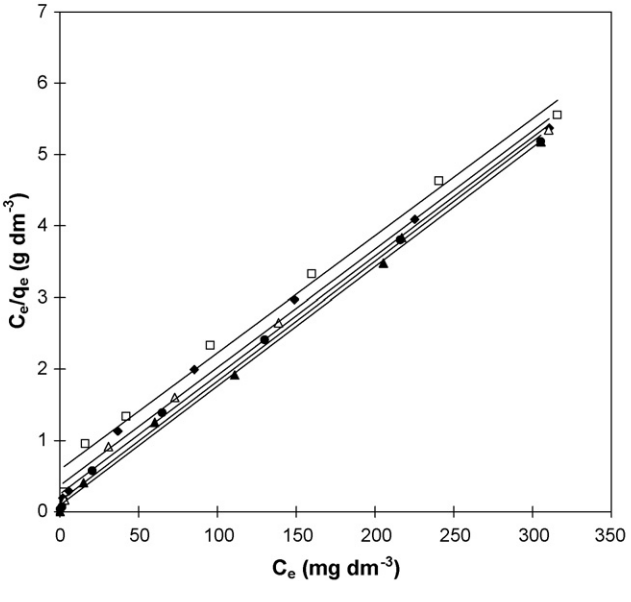


Fig. 7. Langmuir isotherm plot for the removal of 2-picoline by BFA ($m = 5\,\mathrm{g\,dm^{-3}}$, pH_0 6.45, $t = 6\,\mathrm{h}$). (□) 283 K; (◆) 293 K; (△) 303 K; (●) 313 K; (▲) 323 K.

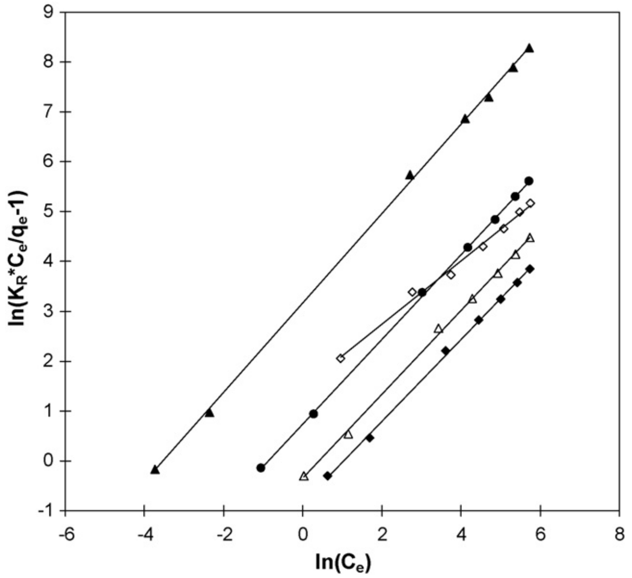


Fig. 8. Redlich–Peterson isotherm plot for the removal of 2-picoline by BFA ($m = 5\,g\,dm^{-3}$, pH_0 6.45, $t = 6\,h$). (□) 283 K; (◆) 293 K; (△) 303 K; (●) 313 K; (▲) 323 K.

a constant temperature. After 6 h, the mixture was centrifuged and the supernatant was analyzed for the 2-picoline concentration and the amount of 2-picoline desorbed was determined. The results are shown in Figs. 10 and 11. It is found that the acidic solutions perform better in eluting 2-picoline from the BFA. The soil-distilled water slurry showed poor desorption efficiency (≈7.0%). Since substantial amount of 2-picoline could not be removed even with acids, and that the BFA is available at a throw-away price, desorption and regeneration of the spent BFA are not recommended. The spent BFA can be simply separated from the mixture by filtration, dewatered and sun-dried, and then fired as a fuel into the boiler furnaces/incinerator to recover its energy value.

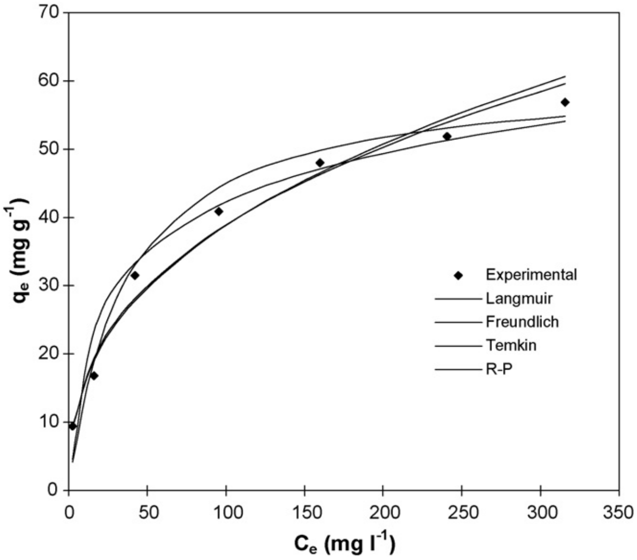


Fig. 9. Comparison of the fit of the various isotherm equations with the experimental sorption data for 2-picoline onto BFA at temperature 303 K.

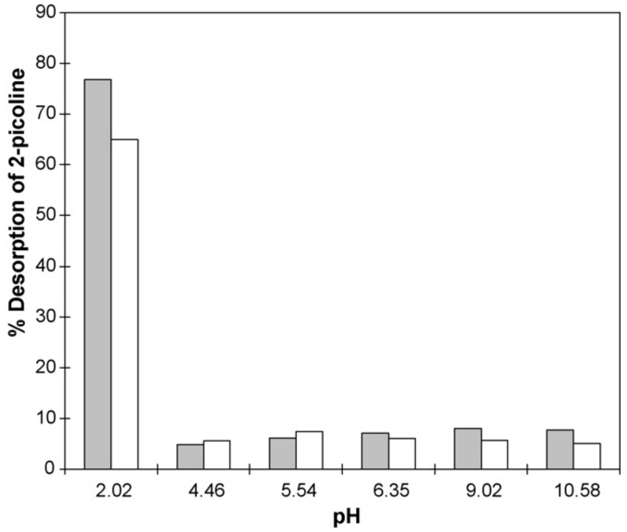


Fig. 10. Desorption of 2-picoline in water at different pH ($q_e = 17.9\,mg\,g^{-1}$), temperature (K). (□) 288; (▨) 303.

3.9. Estimation of thermodynamic parameters

The Gibbs free energy change of the adsorption process is related to the adsorption equilibrium constant by the classical Van't Hoff equation [31]:

$$\Delta G^{\circ}_{ads} = -RT \ln K_{ads} \tag{14}$$

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:

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{15}$$

The above two equations give

$$\ln K_{ads} = \frac{-\Delta G^{\circ}_{ads}}{RT} = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{R}\frac{1}{T} \tag{16}$$

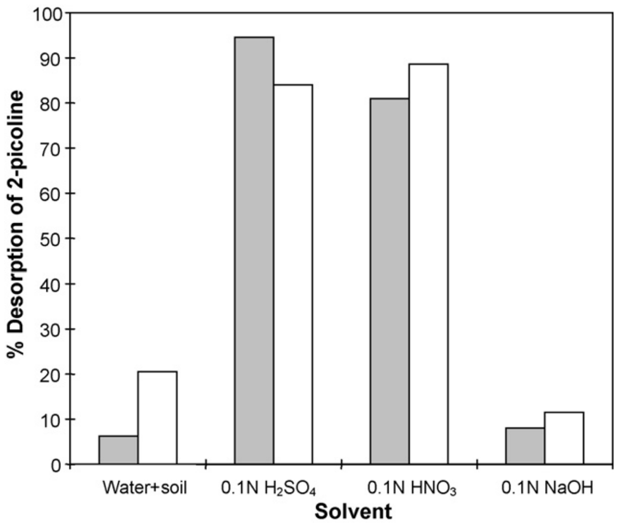


Fig. 11. Desorption of 2-picoline in different solvents ($q_e = 17.9\,mg\,g^{-1}$), temperature (K). (□) 288; (▨) 303.

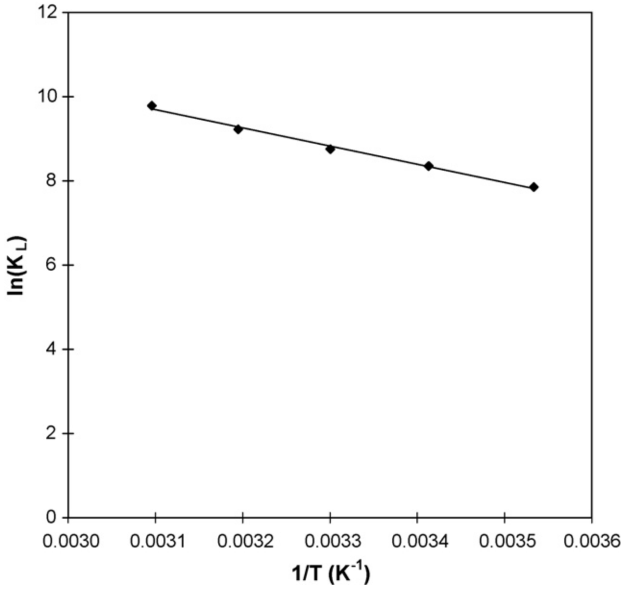


Fig. 12. Vant's Hoff Plot from Langmuir isotherm constant.

where $\Delta G^\circ_{\text{ads}}$ is the free energy change (kJ mol^{-1}), ΔH° the change in enthalpy (kJ mol^{-1}), ΔS° the entropy change (kJ mol^{-1} K^{-1}), K_{ads} the equilibrium constant of interaction between the adsorbate and the BFA surface, T the absolute temperature (K) and R is the universal gas constant (8.314 J mol^{-1} K^{-1}). Thus ΔH° can be determined by the slope of the linear Van't Hoff plot i.e. as ln(K_{ads}) versus (1/T), using the equation:

$$\Delta H^\circ = \left[R\frac{d\ \ln\ K}{d(1/T)}\right] \tag{17}$$

ΔH° as obtained here corresponds to the isosteric heat of adsorption ($\Delta H^\circ_{\text{st}}$) with zero surface coverage (i.e. $q_e = 0$). Since the Langmuir isotherm has been found to well represent the equilibrium sorption data, the Langmuir constant K_L has been used to determine the thermodynamic parameters from Eqs. (12)–(14). The Van't Hoff plot for the Langmuir isotherm is shown in Fig. 12. The values of the parameters ΔH°, ΔS° and ΔG° are given in Table 2.

Adsorption of 2-picoline from an aqueous solution onto BFA is an exothermic process, whereas the diffusion of the 2-picoline molecules into the pores of the BFA is an endothermic process. The positive ΔH° value obtained in Table 3 indicates that the overall-sorption process is endothermic in nature. $\Delta G^\circ_{\text{ads}}$ values were negative indicating that the sorption process led to a decrease in the Gibbs free energy and the adsorption process is spontaneous and feasible.

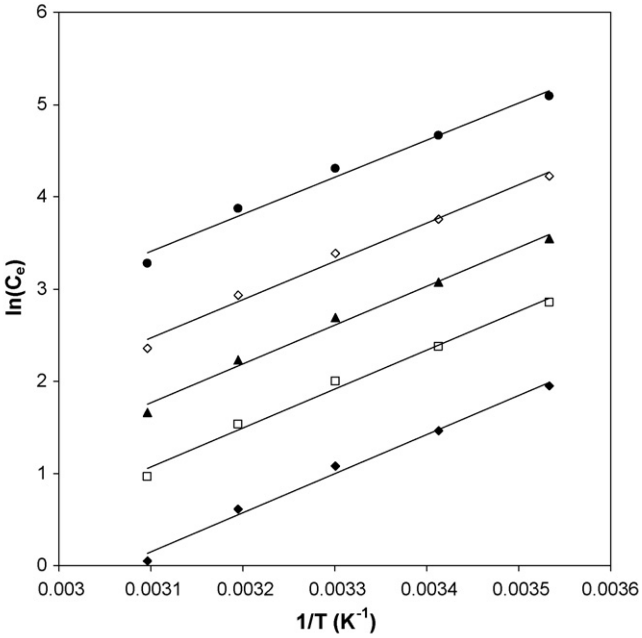


Fig. 13. Adsorption isosters for determining the isosteric heat of adsorption q_e (mg g^{-1}). (◆) 10; (□) 20; (▲) 30; (◇) 40; (●) 50.

3.9.1. Isosteric heat of adsorption

Apparent isosteric heat of adsorption ($\Delta H_{\text{st,a}}$) at constant surface coverage (q_e = 10, 20, 30, 40, 50 mg g^{-1}) was calculated using the Clausius–Clapeyron equation as [32]:

$$\frac{\mathrm{d}\ \ln\ C_e}{\mathrm{d}T} = \frac{-\Delta H_{\text{st,a}}}{RT^2} \tag{18}$$

$$\Delta H_{\text{st,a}} = \left.\frac{\mathrm{d}\ \ln\ C_e}{\mathrm{d}(1/T)}\right|_{q_e} \tag{19}$$

For this purpose, the equilibrium concentration (C_e) at a constant q_e was obtained from the Langmuir isotherm plot at different temperatures. Then the extracted C_e at a constant q_e was plotted as ln(C_e) versus (1/T). $\Delta H_{\text{st,a}}$ was calculated from the slope of the plots between ln(C_e) versus (1/T) (Fig. 13). The calculated $\Delta H_{\text{st,a}}$ was plotted against the surface sorbate loading, q_e in Fig. 14. The plot showed that $\Delta H_{\text{st,a}}$ decreased as the surface sorbate loading increased. The variation in $\Delta H_{\text{st,a}}$ with surface loading can be attributed to the possibility of having lateral interactions between adsorbed 2-picoline ions. $\Delta H_{\text{st,a}}$ as calculated from the figure was found to be 378.03, 376.86,

Table 3
Thermodynamic parameters for the adsorption of 2-picoline onto BFA (C_0 = 50–600 mg dm^{-3}, m = 5 g dm^{-3}, t = 6 h, pH$_0$ 6.45)

Isotherm (s)	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})	ΔG° (kJ mol^{-1})				
			283 K	293 K	303 K	313 K	323 K
Langmuir	35.86	0.192	−18.40	−20.32	−22.24	−24.16	−26.08
Freundlich	17.37	0.173	−46.75	−48.47	−50.20	−51.92	−53.65
Temkin	109.3	0.471	−24.08	−28.80	−33.51	−38.22	−42.94
R–P	35.13	0.218	−26.65	−28.83	−31.01	−33.20	−35.38

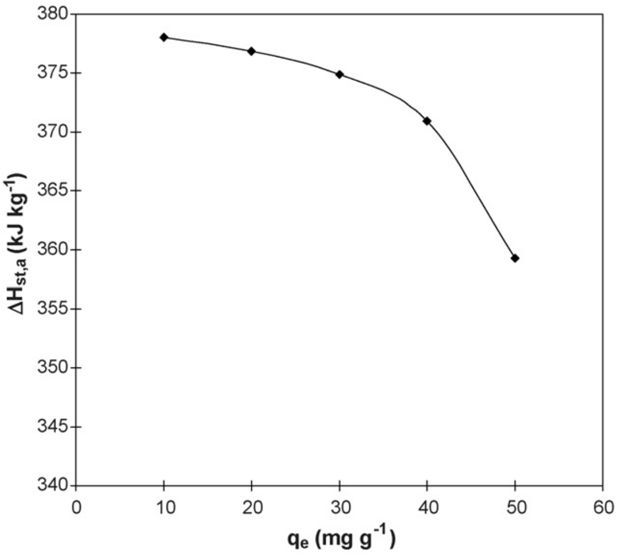


Fig. 14. Variation of $\Delta H_{st,a}$ with respect to surface loading.

374.87, 370.91 and 359.253 kJ kg^{-1} for $q_e = 10$, 20, 30, 40 and 50 mg g^{-1}, respectively. The positive values of $\Delta H_{st,a}$ confirm that the adsorption of 2-picoline onto BFA is an endothermic process.

3.10. Comparative assessment of BFA as an adsorbent

Mohan et al. [5] reported the removal of 2-picoline from aqueous solution using activated carbons derived from coconut shells with and without acid treatment. They have used a very low initial picoline concentration (50 mg dm^{-3}), and consequently a low adsorbent dosage (2 g dm^{-3}) for adsorption studies. Thus, the ratio of C_0/m used by these authors is 25 mg g^{-1}. During the present study, the ratio of C_0/m varied between 10 and 120 mg g^{-1}. Further, the q_e versus C_e data indicate that the q_e can be as high as ~60 mg g^{-1}, indicating a very high adsorptive uptake of 2-picoline by BFA. It may also be noted that the removal of 2-picoline by activated carbon at $t = 6$ h is much lower than that for BFA, even though C_0/m used for BFA is very high. The adsorption by BFA is also almost spontaneous whereas it is sluggish for the activated carbon. Mohan et al. [5] have not reported on the desorption aspects of 2-picoline from activated carbon. Since the activated carbon is quite costly, its regeneration and reuse will be essential in case it is to be used for the adsorptive removal of 2-picoline. Based on these experimental data, and the fact that the BFA is available at a throw-away price and hence can be used and disposed off as a fuel in the boiler furnaces/incinerators, the BFA proves to be a very attractive adsorbent for the removal of 2-picoline from aqueous solutions, even at very high concentrations.

4. Conclusions

The present study shows that the bagasse fly ash (BFA) is an effective adsorbent for the removal of 2-picoline from aqueous solutions. The maximum removal of 2-picoline is observed upto 98% in the lower concentration range (<50 mg dm^{-3}) and 49% in the higher concentration range (50–600 mg dm^{-3}) using 5 kg m^{-3} of BFA dose at normal temperature. The sorptive uptake of 2-picoline increases with an increase in initial concentration: 9.8 mg g^{-1} at $C_0 = 50$ mg dm^{-3} to 59 mg g^{-1} at $C_0 = 600$ mg dm^{-3}. Adsorption is found to be very fast and about 90% 2-picoline removal is achieved in the initial 5 min of contact between BFA ($m = 5$ g dm^{-3}) and the 2-picoline solution ($C_0 = 100$ mg dm^{-3}) at 30 °C. The adsorption of 2-picoline on bagasse fly ash follows second order kinetics and the equilibrium adsorption increases with increasing initial concentration. The equilibrium sorption isotherm data could be well represented by the Langmuir and Redlich–Peterson isotherm equations. Thermodynamic calculations indicate that the overall adsorption process is endothermic and therefore, the 2-picoline removal increases with increasing temperature. Isosteric heat of adsorption is found to be in the range of 378.03–359.253 kJ kg^{-1} for the q_e values in the range of 10–50 mg g^{-1}. The desorption study reveals that the acidic solvents of BFA can elute upto 94% of 2-picoline from the 2-picoline-loaded BFA (0.5 g of BFA with $q_e = 17.9$ mg g^{-1}) at normal temperature. The regenerated BFA still contains 0.895 mg g^{-1} of 2-picoline. It is recommended that the spent BFA should be fired in the furnace/incinerator to recover its energy value. Comparative assessment of the adsorption characteristics of BFA with that of activated carbon prepared from coconut shell shows the superiority of the BFA in its adsorption capacity for 2-picoline, the rate of adsorption and the cost of treatment.

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