

Removal of α -Picoline, β -Picoline, and γ -Picoline from Synthetic Wastewater Using Low Cost Activated Carbons Derived from Coconut Shell Fibers

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In the present study the ability of activated carbons developed from coconut shell fibers to remove α -picoline, β -picoline, and γ -picoline from aqueous solution in the broad range of concentrations (1–100 mg/L) is investigated. The derived carbons are designated as FAC (activated carbon derived from coconut shell fibers without any treatment) and ATFAC (activated carbon derived from acid treated coconut shell fibers). Systematic equilibrium and kinetic adsorption studies at different pH, temperatures, particle size, and solid-to-liquid ratio were carried out to determine various parameters necessary to establish the fixed bed reactors. The Langmuir and Freundlich models were applied and the data are not fitted well by the Freundlich and Langmuir equations, but the Langmuir model has an edge over Freundlich model. The monolayer adsorption capacity (Q^0) as calculated using Langmuir adsorption isotherm of the activated carbons viz., FAC and ATFAC is found to increase with an increase in temperature confirming the endothermic process. The ATFAC has a higher sorption capacity than FAC. Overall the adsorption of α -picoline, β -picoline, and γ -picoline on FAC and ATFAC follow the order $\text{FAC}_{\alpha\text{-picoline}} < \text{ATFAC}_{\alpha\text{-picoline}} < \text{FAC}_{\gamma\text{-picoline}} < \text{ATFAC}_{\beta\text{-picoline}} < \text{FAC}_{\beta\text{-picoline}} < \text{ATFAC}_{\gamma\text{-picoline}}$. The adsorption of α -, β -, and γ -picoline followed the pseudo-second-order rate kinetics. On the basis of these studies, various parameters such as effective diffusion coefficients, activation energy, and entropy of activation were evaluated to establish the mechanisms. It was concluded that the adsorption occurred through particle diffusion at low temperatures viz., 10 °C and 25 °C (except α -picoline where it was film diffusion), while at 40 °C it occurred through film diffusion. Similarly at concentrations of 25 and 50 mg/L the adsorption was particle diffusion controlled (except for α -picoline where it was film diffusion), while at > 50 mg/L it was film diffusion controlled.

Introduction

The α -picoline, β -picoline, and γ -picoline compounds are pyridine derivatives and structural isomers. Pyridine is the

parent of a series of compounds that is widely used as a solvent and intermediate in the production of pipridine, agricultural chemicals, drugs, dyestuffs and paints, rubber products, polycarbonate resins, and textile water-repellents (1). Picolines are useful as solvents and as raw materials for various chemical products used in the industry of polymers, textiles, fuels, agrochemical, pharmaceuticals and colorants. Various pyridine derivatives serve as antitubercular, respiratory stimulants, local anaesthetic, and analgesics. The synonyms of α -picoline, β -picoline, and γ -picoline are 2-methylpyridine, 3-methylpyridine, and 4-methylpyridine, respectively. The increasing amount of pyridine and its derivatives such as α -, β -, and γ -picoline containing wastewater is let out as effluents by various industries. Many of the pyridine derivative compounds are hazardous in nature and persist for a longer duration in the environment, as they are poor substrates to indigenous microorganisms. The removal of pyridine derivatives from a water stream is therefore of great importance.

During the past few years, new and/or stringent regulations coupled with strict enforcement concerning wastewater discharges have been imposed. Therefore, there is a definite need to have a technology, which may work suitably under the above circumstances and should be cost-effective. Various treatment technologies have been developed from time to time for the removal of pyridine and its derivatives from water/wastewater. These include adsorption (2–5), biodegradation (6–9), ion exchange (3), ozonation (10), electrochemical oxidation (11), and so on and so forth. Despite the prolific use of activated carbon for the wastewater treatment, carbon adsorption remains an expensive process, and this fact over recent years has prompted a growing research interest into the production of low cost alternatives to activated carbons.

Many investigators have studied the feasibility of less expensive materials such as rundle-spent shale (12–14), clay minerals (4, 15), activated kaolinite (16), carbons (2), and zeolite (17). This work built upon our earlier publications (2, 18–21) in which we have described other novel adsorbents for the removal and recovery of organic/inorganic substances from water/wastewater. Continuing our activities in the same direction agricultural wastes were used as a feedstock in the present investigation for the production of activated carbons. Two types of activated carbons were developed from locally available coconut shell fibers, characterized, and utilized for the removal of α -picoline, β -picoline, and γ -picoline from water/wastewater successfully.

Materials and Methods

All reagents were AR-grade chemicals. Stock solutions of the test reagents were made by dissolving α -picoline, β -picoline, and γ -picoline in double distilled water. The pH of the test solutions was adjusted using dilute H_2SO_4 (0.1 N) and NaOH (0.1 N).

Equipment. The carbons have been characterized in terms of chemical composition by carrying out the proximate and elemental analyses and also texturally by gas adsorption, mercury porosimetry, and helium and mercury density measurements. The adsorption isotherms for N_2 at -196°C were determined using a Quantachrome surface area analyzer model Autosorb-1. The mercury porosimetries have been carried out with a Quantachrome model Autoscan-60porosimeter. The mercury density has been determined as usual, when carrying out the mercury porosimetry experiments. The helium density was measured using a Quantachrome stereopycnometer. The chemical constituents of activated

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TABLE 1: Characteristics (S_{BET} , Microporosities (N_2 at 77 K), Pore Volumes, and Densities of Activated Carbons Derived from Agricultural Waste Materials^a

| sample | S_{BET} (m^2g^{-1}) | V_{mi} (cm^3g^{-1}) | W_0 (cm^3g^{-1}) | V_{me} (cm^3g^{-1}) | V_{ma} (cm^3g^{-1}) | ρ_{Hg} (gcm^{-3}) | ρ_{He} (gcm^{-3}) | V_T (cm^3g^{-1}) | V_T (cm^3g^{-1}) |
|--------|---|---|---|---|---|---|---|---|---|
| FAC | 343 | 0.10 | 0.11 | 0.03 | 0.89 | 1.58 | 0.49 | 1.41 | 1.02 |
| ATFAC | 512 | 0.17 | 0.18 | 0.07 | 0.29 | 1.65 | 0.84 | 0.58 | 0.53 |

^a $V_{\text{me}} = V_{\text{cu}}$ (at $r=10 \text{ \AA}$) - V_{mar} , $V_{\text{ma}} = V_{\text{cu}}$ (at $r=250 \text{ \AA}$), V_{cu} = cumulative pore volume (mercury porosimetry), $V_T = 1/\rho_{\text{Hg}} - 1/\rho_{\text{He}}$, ρ_{Hgr} , $V_T = V_{\text{mi}} + V_{\text{me}} + V_{\text{ma}}$.

carbons were analyzed following the standard methods of chemical analysis (2, 22, 23). Information on chemical structure was obtained by recording the infrared spectrum of the carbons in potassium bromide in the range of 500–4000 cm^{-1} using a Perkin-Elmer spectrophotometer. The carbon sample (1–3 mg) is dispersed homogeneously in 250 mg of a solid infrared transparent matrix (potassium bromide) and pressed into a disk. The cutout frequency of potassium bromide was 310 cm^{-1} .

The pH measurements were made using a pH meter (model 744, Metrohm). Absorbance measurements were made on UV–visible spectrophotometer model GBC Cintra 40. The spectrophotometer response time was 0.1 s, and the instrument had a resolution of 0.1 nm. Absorbance values were recorded at the wavelength for maximum absorbance i.e., 262, 263, and 255 nm (λ_{max}), corresponding α -picoline, β -picoline, and δ -picoline, respectively. The absorbance was measured with a 1-cm path length cell, with an accuracy of ± 0.004 . Absorbance was found to vary linearly in the concentration range of 10^{-5} – 10^{-6} M. Dilutions were made when the absorbance of unknown samples exceeded 0.8. Biodegradation of α -picoline, β -picoline, and γ -picoline was also taken into account by running the blank. Agitation of the system under investigation was carried out on a thermostat-cum-shaking assembly (model MSW 275).

Linear and nonlinear regression analysis was applied to each set of data points. A correlation coefficient (R^2) and a probability value (p) represent the “goodness of fit” of the Freundlich and Langmuir model to the data obtained by the linear and nonlinear regression program using Sigma Plot V6.0 for windows, SPSS Inc., Chicago, IL.

Adsorbent Development. The raw material i.e., coconut shell fibers (agricultural waste materials) that often present a serious disposal problem for the local environment, were collected locally from Lucknow, India. Two different types of activated carbons were developed. Class I carbon was prepared by treating one part of coconut shell fibers with two parts (by weight) of commercially available concentrated sulfuric acid (36 N) and keeping the mixture in an oven maintained at 150–165 $^{\circ}\text{C}$ for a period of 24 h. The carbonized material was washed well with double distilled water to remove the free acid and dried at 105–110 $^{\circ}\text{C}$ for 24 h. Dried coconut shell fibers were subjected to thermal activation at different temperatures viz., 200, 400, 600, and 800 $^{\circ}\text{C}$ for 1 h in an inert atmosphere. Class II carbon was prepared by simply activating the coconut shell fibers without any chemical treatment at different temperatures (200, 400, 600, and 800 $^{\circ}\text{C}$) in an inert atmosphere. The temperature and time were optimized by observing the surface properties of the activated products obtained. In both cases (with and without chemical treatment) the products obtained at temperatures higher or lower than 600 $^{\circ}\text{C}$ exhibited less adsorption capacities. The activation was carried out under closely controlled conditions to obtain optimum properties. The products so obtained were sieved to the desired particle sizes such as 30–200, 200–250, and 250–300 mesh. Finally, the product was stored in a vacuum desiccator until required. The developed carbons are designated as FAC (activated carbon derived from coconut shells) and ATFAC (activated

TABLE 2: Compositions and pH's of Activated Carbons Derived from Agricultural Waste Material

| characteristics | FAC | ATFAC |
|-----------------|--------|--------|
| ash | 7.12% | 7.22% |
| pH | 7.80 | 5.80 |
| C | 71.54% | 76.38% |
| N | 0.32% | 0.38% |
| H | 1.83% | 1.95% |

carbon derived from acid treated coconut shells). The carbon having 30–200 mesh size was used in both the sorption and kinetic studies unless otherwise stated.

For characterization of the prepared activated carbons, 1.0 g of each was stirred with deionized water (100 mL, pH 6.8) for 2 h and left for 24 h in an airtight stoppered conical flask. After the equilibration time of 24 h, the change in the pH was recorded (Table 2).

Sorption Procedure. Sorption studies were performed by the batch technique to obtain rate and equilibrium data. The batch technique was selected because its simplicity. Batch sorption studies were performed at different temperatures, particle sizes, and adsorbent doses to obtain equilibrium isotherms and data required in the design and operation of column reactors for the treatment of α -, β -, and γ -picolines bearing wastewater. For isotherm studies, a series of 100 mL conical flasks were employed. Each conical flask was filled with 50 mL of each α -picoline, β -picoline, and γ -picoline solution of varying concentrations (1 – 100 mg L^{-1}) separately and adjusted to the desired pH and temperature. The concentration range of 1 – 100 mg/L was chosen on the basis of a good deal of preliminary investigations and in accordance with the levels of pyridine derivatives generally present in wastewater/industrial effluents. A known amount of adsorbent was added to each conical flask and agitated intermittently for the desired time periods, up to a maximum of about 48 h. The contact time and other conditions were selected on the basis of preliminary experiments, which demonstrated that the equilibrium was established in 48 h. Equilibration for longer times between 48 and 72 h gave practically the same uptake. Therefore, a contact period of 48 h was finally selected for all the equilibrium tests. After this period the solution was filtered using Whatman no. 42 filter paper and analyzed for the concentration of α -picoline, β -picoline, and γ -picoline remaining in the solution by using spectrophotometer at the corresponding λ_{max} . The effect of pH was observed by studying the adsorption of α -picoline, β -picoline, and γ -picoline over a broad pH range of 2–10. The sorption studies were also carried out at different temperatures i.e., 10, 25, and 40 $^{\circ}\text{C}$ to delineate the effect of temperature and to evaluate the sorption thermodynamic parameters. Adsorption of α -picoline, β -picoline, and γ -picoline was also studied at different doses and particle sizes of adsorbents. The picolines concentrations retained in the adsorbent phase were calculated by using eq 1

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

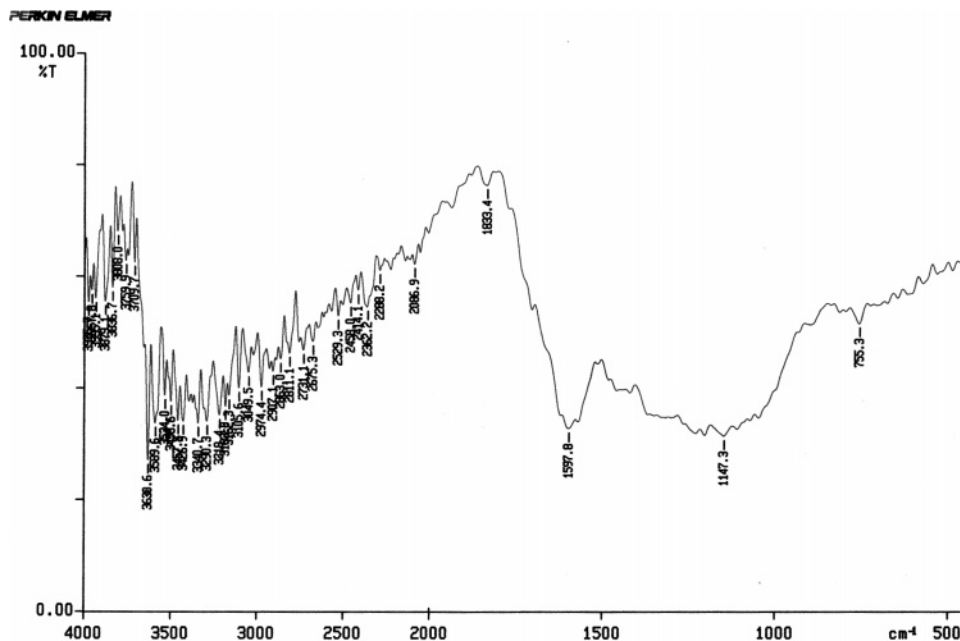


FIGURE 1. IR spectrum of ATFAC.

where q_e is the amount (mg/g) of pyridine derivatives adsorbed, C_0 and C_e are the initial and equilibrium concentrations (mg/L) of pyridine derivatives in solution, V is the volume (L) of adsorbate solution, and W is the weight (g) of the adsorbent.

Kinetic Studies. Successful application of the adsorption technique demands development of cheap nontoxic, readily available adsorbents of known kinetic parameters and sorption characteristics. Foreknowledge of optimal conditions would enable a better design and modeling of the process. Thus the effect of some major parameters, viz., contact time, amount, and particle size of adsorbent and concentration of adsorbate were studied using the batch technique. A number of stoppered flasks (100-mL capacity), containing a 50-mL solution of α -picoline, β -picoline, and γ -picoline, were placed in a thermostat-cum-shaking assembly. When the desired temperature was reached, a predetermined amount of activated carbon was added into each flask, and the solutions were agitated by mechanical shaking. At predetermined intervals of time, the solutions of the specified flasks were separated from the activated carbon and analyzed for the uptake of α -picoline, β -picoline, and γ -picoline remaining in the solution by using spectrophotometer at their corresponding λ_{\max} . The amount of α -picoline, β -picoline, or γ -picoline adsorbed was calculated using eq 1.

Quality Assurance/Quality Control. To establish the accuracy, reliability, and reproducibility of the collected data all the batch isotherm tests were replicated twice, and the experimental blanks were run in parallel. Check standards and blanks were run. National Institute of Standard and Technology (NIST) traceable standards were used for instrument calibration and standard verification. All jars, conical flasks, and containers used in the study were prepared by being soaked in a 5% HNO_3 solution for a period of 3 days before being double rinsed with distilled, deionized water and oven dried. In different experiments blanks were run and corrections were applied if necessary. All the observations were recorded in triplicate and average values are reported.

Result and Discussions

Characterization. The various characteristics of activated carbons derived from agricultural waste materials are given in Tables 1 and 2.

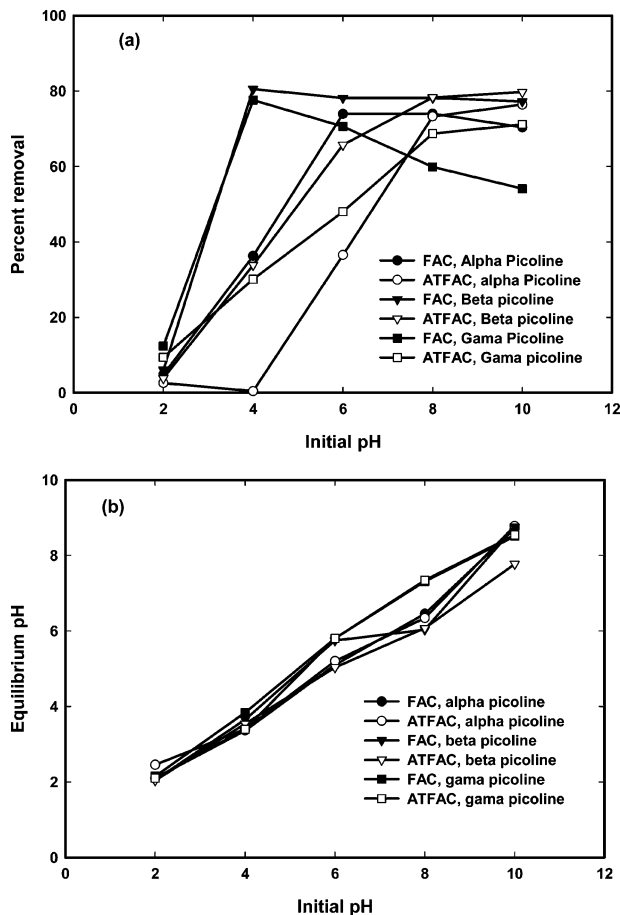


FIGURE 2. Effect of pH on the (a) adsorption of α -, β -, and γ -picoline and (b) equilibrium pH on FAC and ATFAC.

The carbons are quite stable in water, salt solutions, dilute acids, dilute bases, and organic solvents (2). The values of ash contents were found to be on higher side, and the reason for that could not be established.

The specific surface area of the carbons was evaluated from the N_2 isotherms by applying the Brunauer, Emmett, and Teller (BET) equation (23) at a relative pressure (p/p_0)

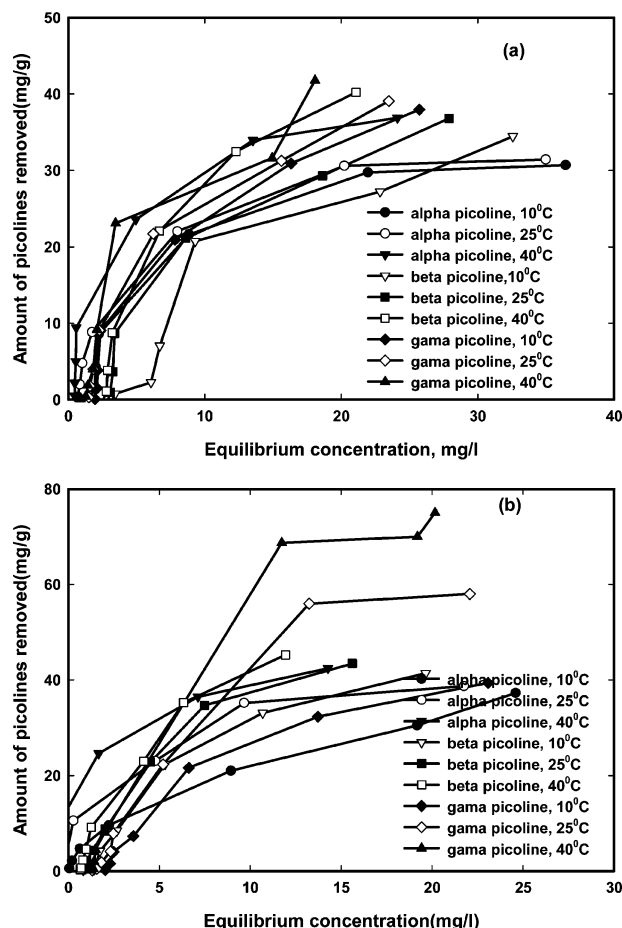


FIGURE 3. Adsorption of α -, β -, and γ -picoline on (a) FAC and (b) ATFAC at different temperatures.

of 0.35 and a_m equal to 16.2 \AA^2 (a_m is the average area covered by a molecule of N_2 in completed monolayer). The micropore volume (W_0) was obtained from the aforementioned isotherms as well by taking it as being equal to the volume of N_2 adsorbed at $p/p_0 = 0.10$ (V_{mi}) and also by applying the Dubinin–Radushkevich equation as given by eq 2

$$\log q_e = K_1 - K_2 \left[\log \left(\frac{P_s}{P} \right) \right]^2 \quad (2)$$

where

$$K_1 = \log \frac{W_0}{V_{mol}} \quad (3)$$

and

$$K_2 = 2.3K_p(RT)^2 \quad (4)$$

where q_e is the solid-phase concentration (mol/g); V_{mol} is the molecular volume (m^3/mol); and K_p is the micropore characteristics constant (mol^2/J^2).

Further, V_{mi} and W_0 are expressed as liquid volumes. The volumes of mesopores (V_{me}) and macropores (V_{ma}) were derived from plots of the cumulative pore volume (V_{cu}) against the pore radius (r) (mercury porosimetry): $V_{me} = V_{cu}$ (at $r=10$) – V_{ma} and $V_{ma} = V_{cu}$ (at $r = 250 \text{ \AA}$). The total pore volume was calculated by making use of the expression $V_T = 1/\rho_{Hg} - 1/\rho_{He}$, ρ_{Hg} and ρ_{He} are the mercury and helium densities, respectively, and also by summing up V_{mi} , V_{me} , and V_{ma} . The values of S_{BET} , V_{mi} , W_0 , V_{me} , ρ_{Hg} , ρ_{He} , V_T , and V_T are listed in Table 1. The different chemical constituents of activated

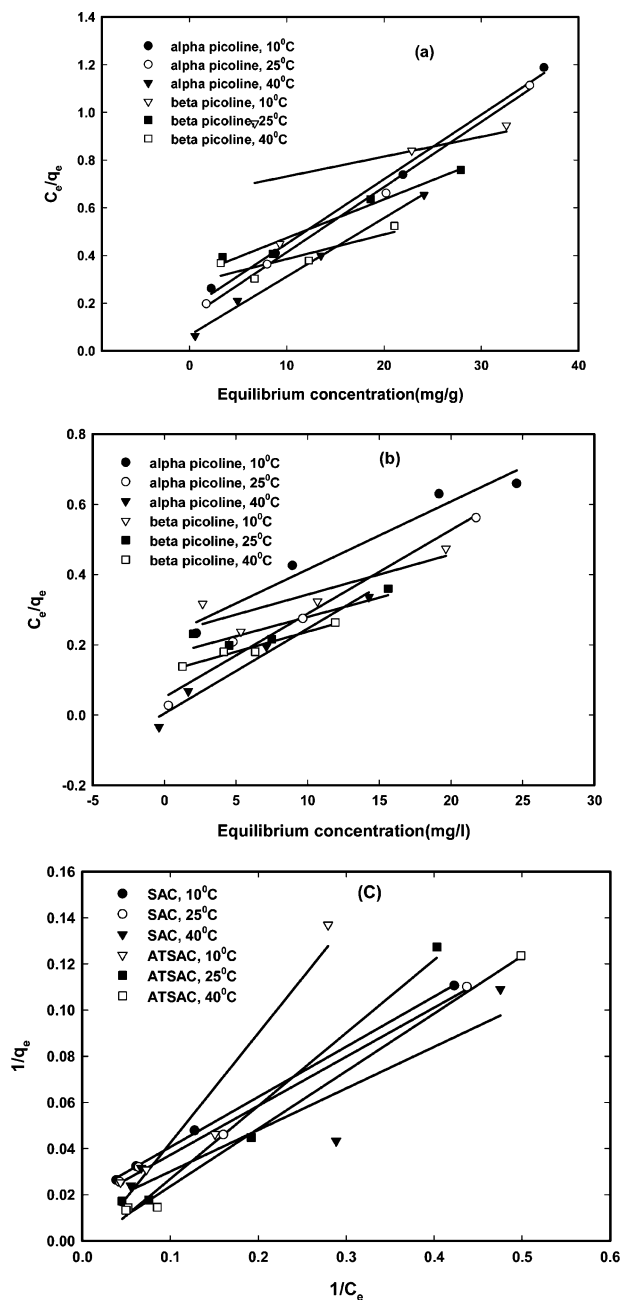


FIGURE 4. Langmuir adsorption isotherms of α -, β -, and γ -picoline on (a) FAC- α - β -picoline, (b) ATFAC- α - β -picolines, and (c) FAC-ATFAC- γ -picoline at different temperatures.

carbons are given in Table 2 along with some other characteristics.

The identification of various forms of different constituents in activated carbon viz., FAC and ATFAC has been done with the help of IR spectra. The IR spectrum (Figure 1) of the activated carbons (only the spectrum for ATFAC is given) showed weak and broad peaks in the region of $3853\text{--}453 \text{ cm}^{-1}$. Approximate FT-IR band assignment indicated the presence of carbonyl, carboxyls, lactones, phenols, olefinic, and aromatic structures. The $1800\text{--}1540 \text{ cm}^{-1}$ band is associated with $C=O$ stretching mode in carbonyls, carboxylic acids, and lactones and $C=C$ bonds in olefinic and aromatic structures, whereas the $1440\text{--}1000 \text{ cm}^{-1}$ band was assigned to the $C-O$ stretching and $O-H$ bending modes in phenols and carboxylic acids. The assignments of a specific wave-number to a given functional group was not possible because the absorption bands of various functional groups overlap

TABLE 3: Freundlich Isotherm Constants

| type of adsorbent | 10 °C | | | 25 °C | | | 40 °C | | |
|-------------------------------------|--------------|------|--------|--------------|------|--------|--------------|------|--------|
| | K_F (mg/g) | n | R^2 | K_F (mg/g) | n | R^2 | K_F (mg/g) | n | R^2 |
| α-Picoline | | | | | | | | | |
| FAC | 2.22 | 1.13 | 0.7655 | 2.26 | 1.22 | 0.7550 | 4.48 | 1.29 | 0.6983 |
| ATFAC | 4.96 | 1.52 | 0.9953 | 15.45 | 3.22 | 0.9872 | 21.69 | 3.89 | 0.9975 |
| β-Picoline | | | | | | | | | |
| FAC | 0.19 | 0.62 | 0.8098 | 0.79 | 0.70 | 0.7309 | 0.80 | 0.80 | 0.7539 |
| ATFAC | 2.07 | 0.76 | 0.9992 | 3.16 | 0.91 | 0.9624 | 4.59 | 0.96 | 0.9965 |
| γ-Picoline | | | | | | | | | |
| FAC | 5.58 | 1.65 | 0.9918 | 6.01 | 1.64 | 0.9675 | 0.22 | 0.24 | 0.9256 |
| ATFAC | 2.25 | 0.62 | 0.9866 | 3.05 | 1.15 | 0.9788 | 5.11 | 1.42 | 0.9159 |

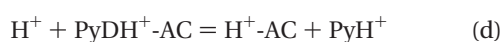
TABLE 4: Langmuir Isotherm Constants

| type of adsorbent | 10 °C | | | 25 °C | | | 40 °C | | |
|-------------------------------------|--------------|-----------------|--------|--------------|-----------------|--------|--------------|-----------------|--------|
| | Q^0 (mg/g) | $b \times 10^2$ | R^2 | Q^0 (mg/g) | $b \times 10^2$ | R^2 | Q^0 (mg/g) | $b \times 10^2$ | R^2 |
| α-Picoline | | | | | | | | | |
| FAC | 36.90 | 15.15 | 0.9955 | 37.59 | 16.77 | 0.9951 | 40.65 | 37.10 | 0.9957 |
| ATFAC | 42.01 | 16.92 | 0.9554 | 42.37 | 46.85 | 0.9781 | 47.16 | 57.76 | 0.9976 |
| β-Picoline | | | | | | | | | |
| FAC | 61.72 | 1.28 | 0.1778 | 96.15 | 3.69 | 0.9675 | 120.48 | 5.19 | 0.7471 |
| ATFAC | 86.95 | 5.04 | 0.7546 | 87.72 | 6.49 | 0.7795 | 90.90 | 11.39 | 0.9567 |
| γ-Picoline | | | | | | | | | |
| FAC | 52.91 | 8.68 | 0.9955 | 62.50 | 7.51 | 0.9948 | 82.64 | 6.71 | 0.9788 |
| ATFAC | 196.07 | 1.07 | 0.9265 | 172.41 | 2.02 | 0.8881 | 400.0 | 11.97 | 0.8995 |

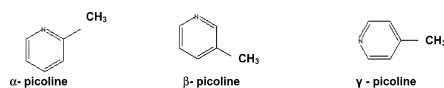
and shift, depending on their molecular structure and environment. Shifts in absorption positions can be caused by the factors such as intramolecular and intermolecular hydrogen bonding, steric effects, and degrees of conjugation.

Sorption Studies. The pyridine derivatives i.e., α -picoline, β -picoline, and γ -picoline, expected to behave as a base where nitrogen atom carries a lone pair which is completely available for protonation. The removal of α -picoline, β -picoline, and γ -picoline as a function of pH is presented in Figure 2. These studies were carried out at the initial concentration of 50 mg/L.

It is observed (Figure 2) that the removal increases sharply in case of FAC as the pH_{int} increases from 2.0 to 4.0 in the case of α -picoline, β -picoline, and γ -picoline. In the case of α -picoline the percent removal further increases up to pH 6.0 and thereafter it becomes more or less constant. On the other hand, there is no further increase in adsorption β -picoline beyond 4.0 and it attains a constant value while the removal of γ -picoline decreases beyond 4.0. Therefore in the case of FAC all the sorption and kinetic studies were carried out at the pH of 6.0. In the case of ATFAC the removal of α -picoline, β -picoline, and γ -picoline is found to increase as the pH increases beyond 2 (Figure 2) and at pH > 8.0 the uptake becomes constant and no further increase was observed at pH 10.0. Therefore all subsequent studies were carried out at pH 8.0. At pH 2.0 the pH_{equ} increases with the increasing pH_{in} , i.e., neutralization and sorption processes are parallel processes and after pH_{in} 2.0, the pH_{fin} decreases in all the cases. The chemical interaction of pyridine derivatives with activated carbons can be summarized by the following equilibria as given by Weber (5) and further utilized by others (2, 12–14).



The M^+ represents the exchangeable cations on the adsorbents, while H^+ refers to the hydronium ions. PyD denotes the pyridine derivatives viz., α -picoline, β -picoline, and γ -picoline. The structures of pyridine derivatives are given below.



The basic difference in α -picoline, β -picoline, and γ -picoline is in the substitution of CH_3 group. The surface chemistry of the activated carbons essentially depends on their heteroatom content, mainly on their surface oxygen complex content as outlined by Radovic et al. (25). They concluded that the surface charge would depend on the solution pH and the surface characteristics of the carbon. A negative charge will result from the dissociation of surface oxygen complexes of acid character such as carboxyl and phenolic groups, and these surface sites are known to be Bronsted type. The positive surface charge is due to surface oxygen complexes of basic character like pyrones or chromenes or due to the existence of electron-rich regions within the graphene layers acting as Lewis basic centers, which accept protons from the aqueous solution (26). At low pH the α -picoline, β -picoline, and γ -picoline molecules are mostly converted to $PyDH^+$ resulting in the low adsorption of protonated picolines on the positively charged carbon surface. At higher pH α -picoline, β -picoline, and γ -picoline molecules are unprotonated resulting in the higher uptake on the charged activated carbons due to dispersion interaction. These observations suggest that with a significant proportion of the pyridine derivatives being adsorbed through van der Waals forces, it is also possible that a small amount is adsorbed through formation of protonated picolines on the carbon surface at low pH. Thus

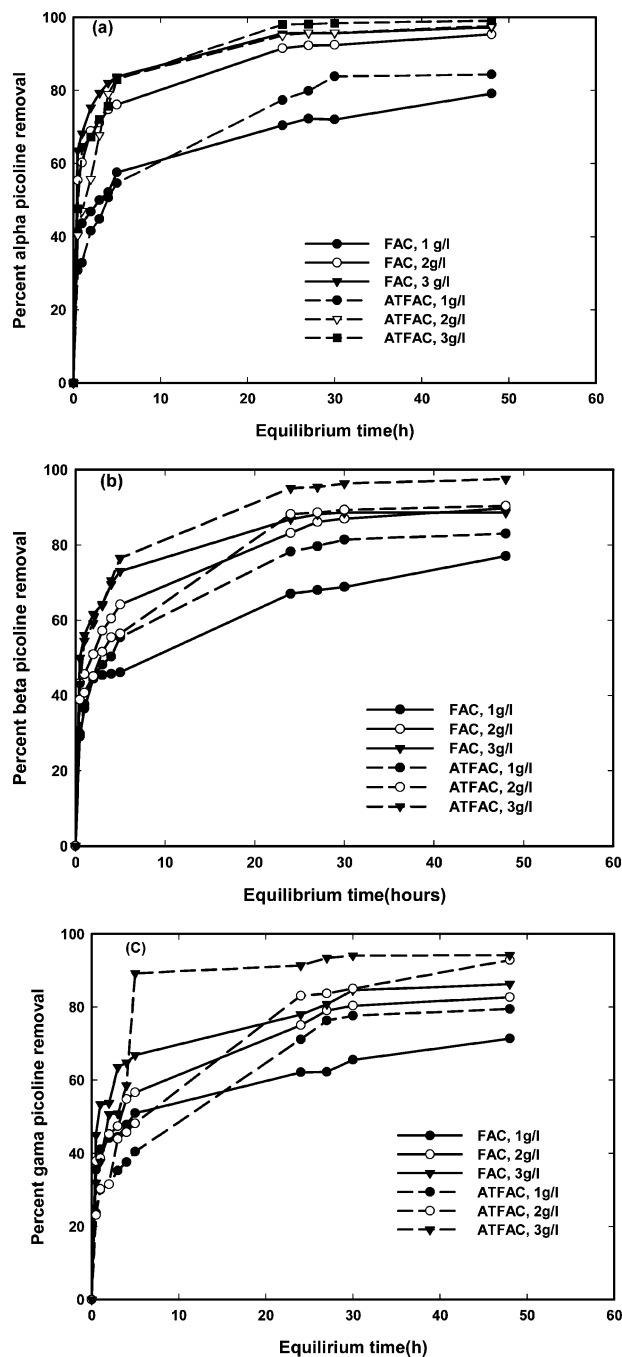


FIGURE 5. Effect of contact time on rate of adsorption of (a) α -picoline, (b) β -picoline, and (c) γ -picoline on FAC and ATFAC at different adsorbent doses, optimum pH, temperature 25 °C, and adsorbate concentration of 50 mg/L.

it may be concluded that at higher pH while electrostatic interactions are important, π - π dispersion interactions are dominant as outlined by Radovic et al. (25, 27). Thus the dominant sorption reaction is probably given by eq b. The α -picoline, β -picoline, and γ -picoline could also get adsorbed in the form of protonated molecules and can be given by eq c. Other equations also play a very small role in the adsorption mechanisms. Similar types of observations were reported earlier for pyridine adsorption on different carbon (2).

The adsorption isotherms of α -picoline, β -picoline, and γ -picoline at different temperatures and optimum pH are shown in Figure 3(a,b). All the isotherms are more or less positive, regular, and concave to the concentration axis. In all the cases the uptake of α -picoline, β -picoline, and

TABLE 5. First-Order Rate Constants (k_1) of Adsorption

| adsorbents | 10 °C | | 25 °C | | 40 °C | |
|-------------------------------------|---|----------------|---|----------------|---|----------------|
| | $k_1 \times 10^2$ (h ⁻¹) | R ² | $k_1 \times 10^2$ (h ⁻¹) | R ² | $k_1 \times 10^2$ (h ⁻¹) | R ² |
| α-Picoline | | | | | | |
| FAC | 8.24 | 0.9329 | 8.70 | 0.9852 | 9.18 | 0.9522 |
| ATFAC | 4.39 | 0.9742 | 11.30 | 0.9555 | 16.67 | 0.9915 |
| β-Picoline | | | | | | |
| FAC | 4.97 | 0.8915 | 7.83 | 0.9898 | 9.02 | 0.8263 |
| ATFAC | 5.66 | 0.8655 | 13.40 | 0.9985 | 18.75 | 0.9686 |
| γ-Picoline | | | | | | |
| FAC | 6.97 | 0.9170 | 9.09 | 0.9752 | 10.31 | 0.9831 |
| ATFAC | 5.85 | 0.9246 | 7.46 | 0.9930 | 10.34 | 0.7811 |

TABLE 6. Pseudo-Second-Order Rate Constants (k_2) of Adsorption

| adsorbents | 10 °C | | 25 °C | | 40 °C | |
|-------------------------------------|---|----------------|---|----------------|---|----------------|
| | $k_2 \times 10^2$ (gmg ⁻¹ h ⁻¹) | R ² | $k_2 \times 10^2$ (gmg ⁻¹ h ⁻¹) | R ² | $k_2 \times 10^2$ (gmg ⁻¹ h ⁻¹) | R ² |
| α-Picoline | | | | | | |
| FAC | 2.57 | 0.9967 | 4.29 | 0.9996 | 5.27 | 0.9997 |
| ATFAC | 1.52 | 0.9847 | 3.39 | 0.9998 | 0.61 | 1.00 |
| β-Picoline | | | | | | |
| FAC | 1.08 | 0.9736 | 2.70 | 0.9988 | 6.28 | 0.9997 |
| ATFAC | 1.08 | 0.9755 | 2.03 | 0.9979 | 3.17 | 0.9993 |
| γ-Picoline | | | | | | |
| FAC | 4.55 | 0.9477 | 2.57 | 0.9981 | 4.72 | 0.9998 |
| ATFAC | 1.02 | 0.8848 | 1.13 | 0.9950 | 1.34 | 0.9999 |

γ -picoline increases with increase in temperature thereby confirming the endothermic process. The uptake of pyridine derivatives on FAC and ATFAC is almost 100% at low adsorbate concentrations, while the same decreases with an increase in concentrations. The adsorption data were modeled using linear and nonlinear Langmuir (28) and Freundlich (29) isotherms as given by eqs 5–8.

Langmuir Isotherm. The Langmuir adsorption isotherm sheds no light on the mechanistic aspects of adsorption; it provides information on uptake capabilities and also reflects the usual equilibrium process behaviors. The Langmuir equation can be written as

$$q_e = \frac{Q^0 b C_e}{1 + b C_e} \quad (\text{nonlinear form}) \quad (5)$$

$$\frac{C_e}{q_e} = \left(\frac{1}{Q^0 b} \right) + \left(\frac{1}{Q^0} \right) \cdot C_e \quad (\text{linear form}) \quad (6)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of solute in the bulk solution (mg/L), Q^0 is the monolayer adsorption capacity (mg/g), and b is the constant related to the free energy or net enthalpy of adsorption ($b \propto e^{-\Delta H/RT}$).

Freundlich Isotherm. The Freundlich model does not indicate a finite uptake capacity of the sorbent and thus can only reasonably be applied in the low to intermediate concentration range. The Freundlich equation can be written as (eqs 7 and 8)

$$q_e = K_F C_e^{1/n} \quad (\text{nonlinear form}) \quad (7)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (\text{linear form}) \quad (8)$$

where q_e is the amount of solute adsorbed per unit weight

TABLE 7. Comparative Evaluation of q_e as Calculated Experimentally and by Using First- and Second-Order Rate Equations with Half-Life at Different Temperatures

| adsorbents | q_e (experimental) | | | q_e , calculated (using first-order kinetic model) | | | q_e , calculated (using second-order kinetic model) | | | $t_{1/2}$ (h) | | |
|------------|-------------------------------------|-------|-------|---|-------|-------|--|-------|-------|---------------|-------|-------|
| | 10 °C | 25 °C | 40 °C | 10 °C | 25 °C | 40 °C | 10 °C | 25 °C | 40 °C | 10 °C | 25 °C | 40 °C |
| | α-Picoline | | | | | | | | | | | |
| FAC | 23.37 | 24.81 | 24.95 | 11.52 | 8.69 | 7.75 | 23.69 | 24.94 | 25.06 | 8.41 | 7.96 | 7.55 |
| ATFAC | 25.17 | 25.45 | 25.68 | 14.26 | 10.88 | 14.78 | 24.57 | 25.38 | 25.64 | 15.79 | 6.13 | 4.16 |
| | β-Picoline | | | | | | | | | | | |
| FAC | 20.85 | 22.78 | 25.13 | 14.95 | 11.45 | 6.26 | 20.87 | 23.25 | 25.19 | 13.94 | 8.85 | 7.68 |
| ATFAC | 21.26 | 22.66 | 24.13 | 10.54 | 14.74 | 15.36 | 21.55 | 23.75 | 24.51 | 12.25 | 7.92 | 5.17 |
| | γ-Picoline | | | | | | | | | | | |
| FAC | 17.46 | 20.52 | 24.46 | 8.65 | 11.24 | 20.40 | 21.05 | 21.09 | 24.75 | 9.94 | 7.63 | 6.72 |
| ATFAC | 21.03 | 23.13 | 24.55 | 3.73 | 16.56 | 19.60 | 19.41 | 24.27 | 24.57 | 11.85 | 9.29 | 6.70 |

TABLE 8. Comparative Evaluation of q_e as Calculated Experimentally and by Using First- and Second-Order Rate Equations with Half-Life at Different Adsorbate Concentrations

| adsorbents | q_e (experimental) | | | q_e , calculated (using first-order kinetic model) | | | q_e , calculated (using second-order kinetic model) | | | $t_{1/2}$ (h) | | |
|------------|-------------------------------------|-----------------------------|------------------------------|---|-----------------------------|------------------------------|--|-----------------------------|------------------------------|-----------------------------|-----------------------------|------------------------------|
| | 10 (mg L ⁻¹) | 50 (mg L ⁻¹) | 100 (mg L ⁻¹) | 10 (mg L ⁻¹) | 50 (mg L ⁻¹) | 100 (mg L ⁻¹) | 10 (mg L ⁻¹) | 50 (mg L ⁻¹) | 100 (mg L ⁻¹) | 10 (mg L ⁻¹) | 50 (mg L ⁻¹) | 100 (mg L ⁻¹) |
| | α-Picoline | | | | | | | | | | | |
| FAC | 4.84 | 24.81 | 41.25 | 2.71 | 8.69 | 17.35 | 4.99 | 25.06 | 46.94 | 6.34 | 7.97 | 8.71 |
| ATFAC | 5.14 | 24.84 | 46.85 | 3.33 | 10.88 | 22.87 | 5.14 | 25.38 | 47.84 | 6.13 | 9.53 | 17.41 |
| | β-Picoline | | | | | | | | | | | |
| FAC | 5.68 | 22.78 | 49.82 | 2.86 | 11.45 | 21.85 | 5.79 | 23.25 | 50.50 | 7.68 | 8.36 | 9.62 |
| ATFAC | 4.57 | 22.66 | 46.39 | 3.86 | 14.84 | 28.19 | 5.06 | 23.75 | 47.85 | 5.15 | 7.52 | 9.72 |
| | γ-Picoline | | | | | | | | | | | |
| FAC | 3.95 | 20.53 | 50.03 | 3.19 | 11.24 | 18.60 | 4.28 | 21.05 | 50.50 | 6.53 | 6.82 | 7.63 |
| ATFAC | 4.49 | 23.23 | 47.69 | 3.63 | 16.56 | 18.94 | 4.73 | 24.27 | 46.95 | 9.29 | 10.83 | 14.41 |

of adsorbent (mg/g), C_e is the equilibrium concentration of solute in the bulk solution (mg/L), and K_F is the constant indicative of the relative adsorption capacity of the adsorbent.

The linear Freundlich and Langmuir isotherms for the adsorption of pyridine derivatives on FAC and ATFAC at different temperatures were plotted, and only Langmuir isotherms are presented in Figure 4. The corresponding Freundlich and Langmuir parameters along with correlation coefficients are given in Tables 3 and 4. The correlation coefficients showed that in general Freundlich and Langmuir equations do not fit the experimental data quite well. The monolayer adsorption capacity (Q^0), as calculated from linear Langmuir isotherms, for α -picoline, β -picoline, and γ -picoline was found to be relatively higher for the activated carbon prepared after chemical treatment in comparison to the one obtained without chemical treatment except for a few cases. This can be explained on the basis that the surface area of the carbon developed after chemical treatment was found to be higher than that of the carbon prepared without any chemical treatment. Also ATFAC has a high carbon content which preferentially adsorbs α -picoline, β -picoline, and γ -picoline molecules. The large surface area and pore volume of ATFAC give it excellent adsorption properties.

Further the sorption followed the order α -picoline < γ -picoline < β -picoline in the case of FAC and α -picoline < β -picoline < γ -picoline in the case of ATFAC. This may be a result of steric hindrance between the nitrogen group and the CH_3 group in the case of α -picoline and, to some extent, in β -picoline. No steric hindrance is observed in γ -picoline. Perhaps, the chemical structure plays a more important role as the adsorptives, which have two free electrons in an orbital sp^2 , are able to interact chemically with acidic functional

groups of the carbons. It appears that steric effects associated with the methyl group decrease the electronic effect (or, in other words, the basic character) owing the such electrons, in particular for α -picoline. In this connection it should be noted that the couple of free electrons are located in the same plane as the benzene ring, which is bound to the carbon atom of the methyl group. In this group, the four substitutes (i.e., the benzene ring and three hydrogen atoms) are found in a tetrahedron whose center is occupied by the carbon atom. This atomic arrangement would explain the steric effect due to the methyl group. The overall adsorption follows the sequence

$$\text{FAC}_{\alpha\text{-picoline}} < \text{ATFAC}_{\alpha\text{-picoline}} < \text{FAC}_{\gamma\text{-picoline}} < \text{ATFAC}_{\beta\text{-picoline}} < \text{FAC}_{\beta\text{-picoline}} < \text{ATFAC}_{\gamma\text{-picoline}}$$

The essential characteristic of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, R_L , which is defined by Weber and Chakravorti (30) and was applied earlier by us (2, 18–21). The R_L factor can be defined by eq 9

$$R_L = \frac{1}{1 + bC_0} \quad (9)$$

where b is the Langmuir constant, C_0 is the initial concentration, and R_L indicates the shape of the isotherm ($R_L > 1$ unfavorable; $R_L = 1$ linear; $0 < R < 1$ favorable, and $R_L < 0$ irreversible).

The dimensionless separation factor, R_L , was determined at different temperatures, particle sizes, and adsorbent doses in the broad concentration range. The values of R_L at different particle sizes, adsorbent doses, and temperatures were found to be less than 1 and greater than 0 indicating the favorable

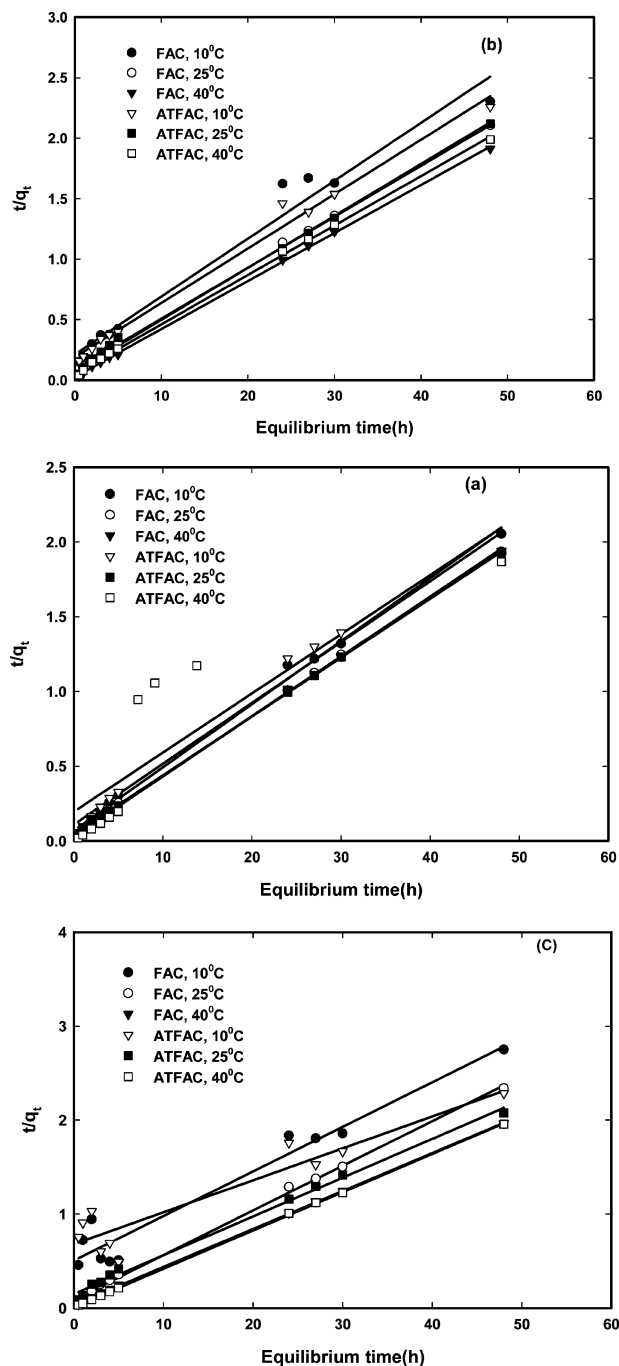


FIGURE 6. Pseudo-second-order kinetic plots for the adsorption of (a) α -picoline, (b) β -picoline, and (c) γ -picoline on FAC and ATFAC.

adsorption of α -picoline, β -picoline, and γ -picoline on FAC and ATFAC.

Kinetic Studies. The effect of the amount of the adsorbent on the rate of uptake of α -picoline, β -picoline, and γ -picoline is shown in Figure 5. It is clear from the figure that the uptake increases with an increase in the amount of the adsorbent. There is a substantial increase in the adsorption when the carbon dosage increases from 1 to 2 g/L, while the increase on introducing an additional 1 g/L of carbon is not so significant. Keeping this in mind, the amount of carbon has been kept at 2 g/L in all the subsequent kinetic studies. Further the half-life of the process (t_{50}) decreases with an increasing amount of adsorbent, confirming that the rate of adsorption is dependent on the amount of carbon. Prelimi-

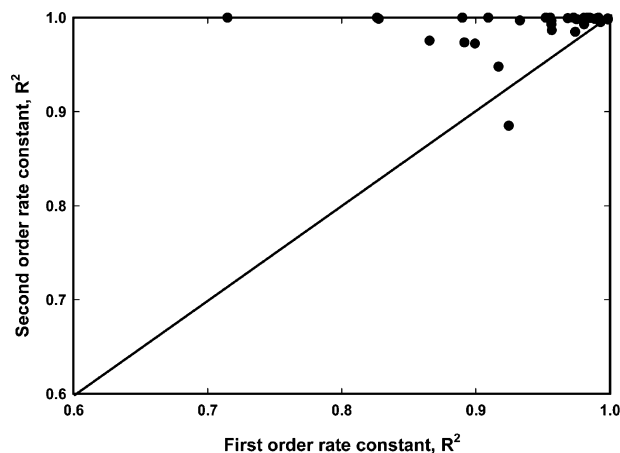


FIGURE 7. Comparative evaluation of pseudo-first-order and pseudo-second-order regression coefficients for the adsorption of α -, β -, and γ -picoline.

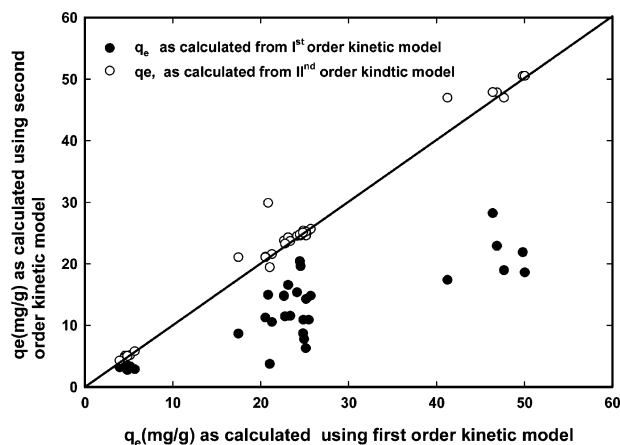


FIGURE 8. Correlation between experiment q_e and calculated q_e using first- and pseudo-second-order kinetic model.

nary investigations on the rate of uptake of α -picoline, β -picoline, and γ -picoline on activated carbons indicated that the processes are quite rapid, and typically 40–50% of the ultimate adsorption occurs within the first hour of contact (Figure 5). This adsorption subsequently gives way to a very slow approach to equilibrium, and in 48 h saturation is reached.

The rate of removal of pyridine derivatives on FAC and ATFAC are found to increase with an increase in temperature, confirming the process to be endothermic in nature. The half-life of the adsorption process (t_{50}) decreases with an increase in temperature (Table 7).

The kinetic studies were also carried out at different adsorbate concentrations viz., 10, 50, and 100 mg L⁻¹ (the figures were omitted for brevity). The amount of adsorbate removed in the first hour of contact increases with an increasing concentration of pyridine derivatives, and an increase in the initial concentration of α -picoline, β -picoline, and γ -picoline enhances the sorption rate. Further, the time required for 50% of the ultimate adsorption is very much dependent on the initial concentration (Table 8). It is clear from Table 8 that with an increase in the initial concentration of an adsorbate the half-life also increases. The kinetic studies were also studied at different particle sizes of FAC and ATFAC to see the effect of the surface area. An inverse relationship was obtained i.e., the adsorption of the pyridine derivative increases with a decrease in the particle size of activated carbons.

To elucidate the adsorption mechanism, the first-order and second-order kinetic models were tested to fit the experimental data obtained from batch experiments.

(a) Pseudo-First-Order Kinetic Model. A simple kinetic model that describes the process of adsorption is the pseudo-first-order (10 and 11) equation as suggested by Lagergren (31) and further cited by Ho et al. (32)

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (\text{linear form}) \quad (10)$$

$$q_t = q_e(1 - e^{-k_1 t}) \quad (\text{nonlinear form}) \quad (11)$$

where $k_1(\text{h}^{-1})$ is the first-order rate constant of adsorption, q_e is the amount adsorbed at equilibrium, and q_t is the amount of picolines adsorbed at time “ t ”.

In most of the cases, the first-order equation of Lagergren did not apply throughout the complete range of contact time (Figures are not provided in the manuscript.). The slopes and intercepts as calculated from the plots were used to determine k_1 (first-order rate constant) and equilibrium capacity (q_e). The values of the rate constant, k_1 , together with regression coefficients are provided in Table 5. As can be seen from Table 5, the regression coefficients are not very good; therefore, it may be concluded that picoline-adsorbent systems do not follow a first-order rate equation perfectly and higher orders rate equations may be applied to check their applicability. Also, the q_e values as calculated from the plots are lower than the experimental one at different temperatures and concentrations further corroborating the above findings (Tables 7 and 8).

(b) Pseudo-Second-Order Kinetic Model. The pseudo-second-order kinetic equation was developed by Ho and McKay (33) and can be written as (eq 12)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (12)$$

The product $k_2 q_e^2$ actually represents the initial sorption rate represented as

$$\text{rate} = k_2 q_e^2 \quad (13)$$

Using eq 12, t/q_t was plotted against “ t ” at different adsorbate concentrations at different temperatures. The second-order sorption rate constant (k_2) and q_e values were determined from slopes and intercepts of the plots (Figure 6(a)–(c)). The values of R^2 and k_2 are presented in Table 6. It is clear from Table 6, the correlation coefficients (R^2) for the linear plots are superior (in most cases ≥ 0.9990). This is further corroborated by plotting the R^2 between first- and second-order rate equations (Figure 7). The q_e values as calculated experimentally and by using the second-order rate equations are presented in Tables 7 and 8 at different temperatures and concentrations together with the half-life of the sorption processes. It is clear from Tables 7 and 8 that the theoretical q_e values agree perfectly with the experimental q_e value (Figure 8). This suggests that the sorption system is not a first-order reaction and that a pseudo-second-order predominates. It provides the best correlation of the data.

To determine the effective diffusion coefficient (D_i), energy of activation (E_a), entropy of activation (ΔS^\ddagger), and pre-exponential factor (D_0) and to interpret the experimental data, it is necessary to identify the step that governs the overall removal rate in the adsorption process. The mathematical treatments of Boyd et al. (34), Reichenberg (35), and Helfferich (36) were applied to distinguish between the particle and

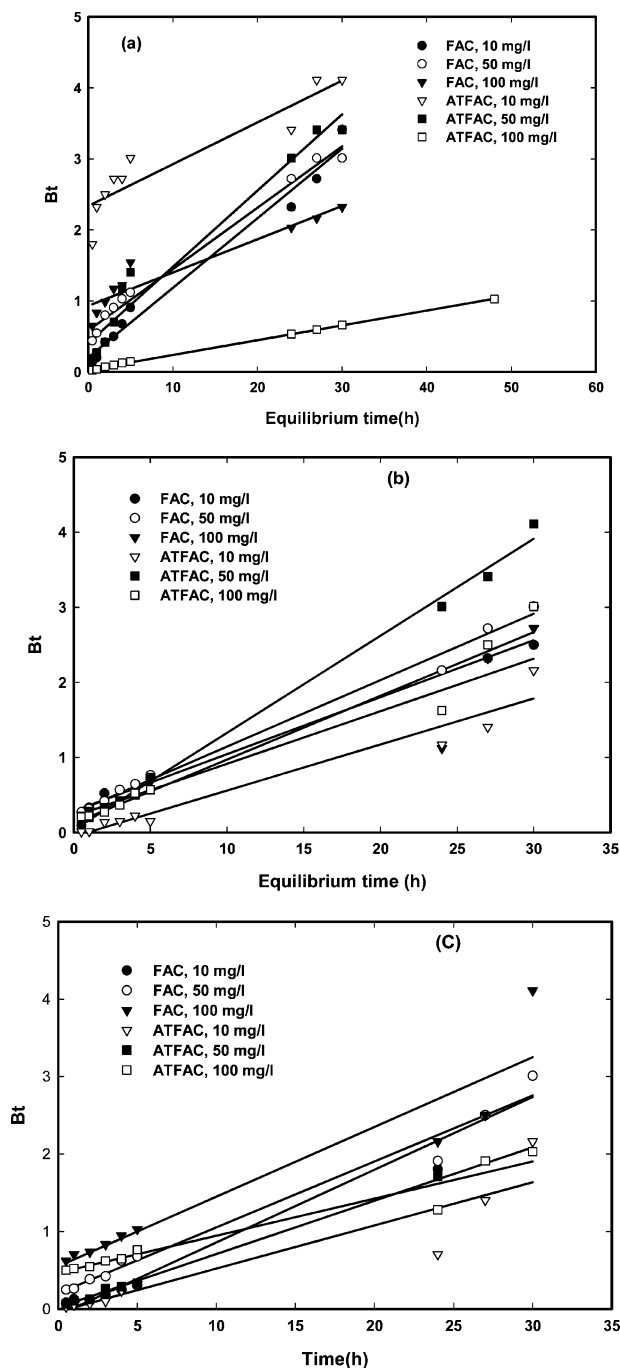


FIGURE 9. Bt vs time plots for the adsorption of α -, β -, and γ -picoline.

film diffusion and mass action controlled mechanism. The following equations (26–29) were used

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left[\frac{-D_i t \pi^2 n^2}{r_0^2} \right] \quad (14)$$

or

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp[-n^2 Bt] \quad (15)$$

where F is the fractional attainment of equilibrium at time “ t ” and is obtained by the expression

TABLE 9. Thermodynamic Parameters of Activation

| adsorbents | effective diffusion coefficient, D_i (m ² s ⁻¹) | | | pre-exponential factor (D_0) (m ² ·s ⁻¹) | energy of activation (E_a) (kJ·mol ⁻¹) | entropy of activation (ΔS^\ddagger) (JK ⁻¹ ·mol ⁻¹) |
|-------------------------------------|--|-------------------------|--------------------------|---|--|--|
| | 10 °C | 25 °C | 40 °C | | | |
| α-Picoline | | | | | | |
| FAC | 77.12×10^{-16} | 179.9×10^{-16} | 218.04×10^{-16} | 7.0×10^{-9} | 9.25 | 6.54 |
| ATFAC | 84.07×10^{-16} | 98.97×10^{-16} | 130.96×10^{-16} | 4.02×10^{-3} | 22.59 | 10.25 |
| β-Picoline | | | | | | |
| FAC | 58.99×10^{-16} | 291.0×10^{-16} | 856.16×10^{-16} | 7.8×10^{-13} | 4.65 | 3.94 |
| ATFAC | 125.4×10^{-16} | 216.7×10^{-16} | 331.7×10^{-16} | 5.95×10^{-11} | 6.07 | 4.51 |
| γ-Picoline | | | | | | |
| FAC | 65.27×10^{-16} | 151.1×10^{-16} | 238.4×10^{-16} | 5.38×10^{-9} | 13.86 | 6.48 |
| ATFAC | 116.2×10^{-16} | 168.4×10^{-16} | 201.1×10^{-16} | 3.75×10^{-12} | 5.88 | 4.38 |

TABLE 10. Sorption Capacities of Pyridine and Its Derivatives on Various Adsorbents

| s. no | adsorbent | adsorbate | sorption capacity | ref |
|-------|---------------------------|--------------------|---------------------------------------|------------|
| 1 | rundle spent shale | quinoline | 0.540 mg/g | (12) |
| 2 | rundle oil shale | pyridine | 0.260 mg/g | (13) |
| 3 | cobalt ferrocyanide | 2-aminopyridine | 4.2 mg/g | (41) |
| | | 3-aminopyridine | 26.6 mg/g | |
| | | 4-aminopyridine | 11.8 mg/g | |
| | nickel ferrocyanide | 2-aminopyridine | 5.1 mg/g | |
| | | 3-aminopyridine | 32.1 mg/g | |
| | | 4-aminopyridine | 14.4 mg/g | |
| 4 | activated carbon | pyridine | 0.014 mg/g | (42) |
| 5 | activated carbon (FAC) | pyridine | 40.52 mg/g | (2) |
| | activated carbon (SAC) | pyridine | 20.49 mg/g | |
| | activated carbon (ATFAC) | pyridine | 111.08 mg/g | |
| | activated carbons (ATSAC) | pyridine | 51.99 mg/g | |
| | activated carbons (ACF) | pyridine | 53.69 mg/g | |
| 6 | sepiolite | 2-aminopyridine | $1.96 \times 10^{-6} \text{ mol/m}^2$ | (15) |
| | | 2,2'-bipyridyl | $1.47 \times 10^{-7} \text{ mol/m}^2$ | |
| 7 | activated carbon (FAC) | α -picoline | 37.59 mg/g | this study |
| | activated carbon (FAC) | β -picoline | 96.15 mg/g | |
| | activated carbon (FAC) | γ -picoline | 62.50 mg/g | |
| | activated carbon (ATFAC) | α -picoline | 42.37 mg/g | |
| | activated carbon (ATFAC) | β -picoline | 87.72 mg/g | |
| | activated carbon (ATFAC) | γ -picoline | 172.41 mg/g | |

$$F = \frac{Q_t}{Q^0} \quad (16)$$

where Q_t is the amount of adsorbate taken up at time “ t ” and Q^0 is the maximum equilibrium uptake and

$$B = \frac{\pi^2 D_i}{r_o^2} = \text{time constant} \quad (17)$$

where D_i is the effective diffusion coefficient of ion in the adsorbent phase, r_o is the radius of the adsorbent particle, assumed to be spherical, and n is an integer that defines the infinite series solution. Bt values were obtained for each observed value of F from Reichenberg's table (34) at different temperatures and concentrations. Basically Bt is the product obtained by multiplying “ B ” with time. It is estimated by using the Reichenberg's table (34). The linearity test of Bt versus time plots was employed to distinguish between the film diffusion and particle diffusion controlled adsorption. If the plot of Bt vs time (having slope B) is a straight line passing through the origin, then the adsorption rate is governed by a particle diffusion mechanism otherwise it is governed by film diffusion. The results of FAC and ATFAC at different concentrations are plotted in Figure 9. It can be seen that at concentrations $\leq 50 \text{ mg L}^{-1}$, the Bt vs time plots are linear passing through the origin except for α -picoline (Figure 9), indicating the rate controlling step to be particle diffusion, while at concentrations $> 50 \text{ mg L}^{-1}$ the Bt vs time

plots do not pass through the origin, indicating the rate controlling step to be the film diffusion. Further, it is interesting to note that at temperatures of 10 and 25 °C, Bt vs time plots were linear and pass through the origin except for α -picoline, indicating the particle diffusion mechanism is the rate controlling step, while at 40 °C, the film diffusion was the rate controlling step (figures omitted for brevity). It is interesting to note that α -picoline behaves differently where in most of the cases the mechanism is controlled by film diffusion at different concentrations as well as temperature.

The effective diffusion coefficients as estimated at different temperatures from the slopes of the Bt plots are given in Table 9. The increased mobility of adsorbate molecules and a decrease in retarding forces acting on the diffusing adsorbate molecules results in the increase of D_i with temperature. Although the values of the diffusion coefficient are low but are quite enough to have the adsorbate transport from bulk to solid phase. Similar types of values were reported in the literature (2, 17, 37). The energy of activation, E_a , the entropy of activation, ΔS^\ddagger , and the pre-exponential factor, D_0 , analogous to the Arrhenius frequency factor were also evaluated using eqs 18 and 19

$$D_i = D_0 \exp \left[-\frac{E_a}{RT} \right] \quad (18)$$

$$D_0 = 2.72 d^2 \frac{kT}{h} \exp \left[\frac{\Delta S}{R} \right] \quad (19)$$

where k = Boltzmann constant, h = Planck constant, R = gas

constant, d = distance between two active sites of the adsorbent which is conventionally taken as 5 Å in inorganic ion exchangers minerals and other adsorbents similar to carbon. As can be seen from Table 9, the formation process of the “activated species” through which the adsorption goes by is as expected endothermic. The positive values of (ΔS^\ddagger) indicates that during the adsorption process an increase in the degree of freedom occurs; this fact suggests that retention of pyridine derivatives present in solution take place together with a partial desolvation of these molecules as well as of the active sites at the solid surface (38, 39, 40).

Further as can be seen from Table 10, the sorption capacity of the developed activated carbons is on the higher side as compared to other adsorbents/carbons applied for the removal of pyridine derivatives from water/wastewater.

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