Study of equilibrium and thermodynamic adsorption of α-picoline, β-picoline, and γ-picoline by Jordanian zeolites: Phillipsite and faujasite

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ARTICLE INFO

ABSTRACT

In the present study the ability of phillipsite and faujasite to remove α-picoline, β-picoline, and γ-picoline from aqueous solution in the broad range of concentrations (1–500 mg L^{-1}) was investigated. Adsorption equilibrium was carried out at different initial concentrations, sorbent concentrations, and temperatures. Brunauer–Emmett–Teller (BET), the Harkins–Jura, the Smith, and the Halsey equations were applied to the experimental data. The data fitted the BET model best. The overall adsorption of α-, β-, and γ-picoline on phillipsite and faujasite followed the order: faujasite$_{α-picoline}$ < phillipsite$_{α-picoline}$ < faujasite$_{β-picoline}$ < phillipsite$_{β-picoline}$ < faujasite$_{γ-picoline}$ < phillipsite$_{γ-picoline}$. The values of change in Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) were calculated. Thermodynamic study revealed that the adsorption of picolines onto phillipsite and faujasite was an exothermic process. Isosteric heat of adsorption was found to decrease with the increase in surface loading.

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1. Introduction

The α-picoline, β-picoline, and γ-picoline compounds (their synonyms are 2-methylpyridine, 3-methylpyridine, and 4-methylpyridine, respectively) are pyridine derivatives and structural isomers. Picolines are useful as solvents and as raw materials for various chemical products used in the industries of polymers, textiles, fuels, agrochemicals, pharmaceuticals, and colorants [1]. Many of the pyridine derivative compounds are hazardous in nature and persist for a long time in the environment, as they are poor substrates to indigenous microorganisms. The removal of pyridine derivatives from waters is therefore of great importance. Various treatment technologies have been developed for the removal of pyridine and its derivatives from water/wastewater. These include adsorption [1,2], biodegradation [3], ion exchange [4], ozonation [5], and electrochemical oxidation [6].

Many investigators have studied the feasibility of using cheap adsorbing materials such as spent-rundle shale [7], clay minerals [8], and zeolite [9,10]. Nevertheless, none of these adsorbents has been fully explored or utilized for the removal of pyridine derivatives such as α-, β-, and γ-picoline from waste streams [1,2]. Zeolites are commonly used as cation exchangers, molecular sieves, adsorbents, and catalysts [10]. The cation exchange properties of zeolites are exploited in wastewater treatment to remove species such as heavy metals and ammonium [11,12]. Small organic or inorganic molecules may be trapped within the dehydrated internal channels of zeolites. Thus, zeolites have a wide use as molecular sieves [11]. Zeolites may permit molecules to enter their network, but only if the molecules are smaller than the diameter of their channels; large molecules will be excluded from the zeolite porous network. Zeolite-bearing tuff deposits are found in several locations in Jordan. The present study was undertaken to evaluate the ability of Jordanian zeolites (faujasite and phillipsite) to adsorb pyridine derivatives.

2. Materials and methods

2.1. Adsorbents

Samples of Jordanian zeolites were collected from two different sites in the basaltic desert in northeast and east of Jordan. The samples of zeolites were crushed and sieved to 0.6–1.0 mm particle size and stored in polyethylene containers for further use. Homo-ionic Na-zeolites were prepared using the procedure of Wingenfelder et al. [13]. The pretreated minerals were dried at 60 °C overnight and stored in polyethylene containers. External and internal cation exchange capacity (ECEC and CEC) determination followed the procedure of Ming and Dixon [14] as modified by Haggerty and Bowman [15].

Photomicrography of the exterior surface of unloaded and loaded zeolite was obtained by SEM (FEI Quanta 200, The Netherlands). XRD analysis of the natural zeolitic tuffs was carried out.

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2.2. Adsorbates

All the chemicals used in the study were of analytical reagent grade. The adsorbates α-, β-, and γ-picoline were obtained from Sigma–Aldrich. The physicochemical properties of picolines are presented in Table 1. Stock solutions of the test reagents were made by dissolving α-picoline, β-picoline, and γ-picoline in double distilled water.

2.3. Analytical measurements

The picolines dissolved in water were found to be stable over the concentration range of 1–500 mg L^{-1} used in the study. No change in the picolines concentration was observed over a time period of 24 h. The experiments were carried out in stoppered glass bottles and no loss of picolines due to their volatilization was observed during the experiments and the analysis. Absorbance measurements were made on UV–vis Spectronic 601 spectropho-tometer. The wavelengths corresponding to maximum absorbance (λ_{max}) of picolines were determined by scanning a standard solu-tion of known concentration at different wavelengths. Absorbance values were recorded at the wavelength of maximum absorbance i.e., 262, 263, and 255 nm (λ_{max}), for α-, β-, and γ-picoline, respec-tively. These wavelengths were used for preparing a calibration curves in aqueous solutions.

2.4. Batch adsorption study

Batch adsorption experiments were carried out with different initial concentrations at 298 and 328 K using a water bath shaker. The pH values were adjusted using HCl or NaOH before addition of zeolite to a value of 2. An equal amount (2.5 g) of zeolite was intro-duced into 100 mL bottles and 50 mL of α-, β-, and γ-picoline solu-tion of desired concentration (1–500 mg L^{-1}) were added to each bottle and shaken for 24 h. Immediately after shaking, each sample was filtered through 0.45-μm syringe filter. The filtrates were ana-lyzed for the concentration remaining in solution. Control samples with picoline solutions and without adsorbent were also included. No adsorption occurred on either glassware or filtration systems.

The amount of adsorbed picolines by zeolite, q_e (mg g^{-1}) was calculated using the following equation:

$$q_e = \frac{(C_o - C_e)V}{m} \qquad (1)$$

where q_e is the amount (mg g^{-1}) of picolines adsorbed, C_o and C_e are the initial and equilibrium concentrations (mg L^{-1}) of picolines in solution, V is the volume (L) of solution, and m is the mass of zeolite (g).

3. Results and discussion

3.1. Characterization of zeolite adsorbents

The total cation exchange capacities of phillipsite and faujasite were 73.0 and 70.4 cmol$_{(+)}$ kg^{-1} and the external cation exchange capacities were 15.4 and 12.0 cmol$_{(+)}$ kg^{-1}, respectively. The SEM photographs in Fig. 1 were taken to observe the surface morphol-ogy of natural zeolites and the zeolites loaded with γ-picoline. It showed possible γ-picoline clusters, on occupied surfaces. X-ray diffraction of the phillipsite and faujasite zeolitic tuffs are shown in Fig. 2.

3.2. Effect of initial concentration

The effect of the initial concentration on the adsorption of α-, β-, and γ-picoline by phillipsite and faujasite zeolites was investigated in the range 1–500 mg L^{-1}. The percent picoline adsorption de-creased with increase in initial concentration (Fig. 3). The amount of picolines adsorption depends on the position of methyl group at-tached to the organic ring and followed the order α-picoline < β-picoline < γ-picoline. This may be the result of steric hindrance be-tween the nitrogen group and the CH$_3$ group in case of α-picoline and β-picoline. The steric hindrance in γ-picoline is less than in α- and β-picolines. The steric effect associated with the methyl group decreases the electronic effect (or, in other words, the basic charac-ter), 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 ben-zene ring and three hydrogen atoms) are found in a tetrahedron whose center is occupied by the carbon atom. This atomic arrange-ment thus explains the steric effect due to the methyl group [1].

When the picoline concentration in the test solution was 1.0 mg L^{-1}, and the amount of adsorbent in the suspension was 50 g L^{-1}, 81%, 91%, and 96% of the initial picoline concentration was removed for α-, β- and γ-picoline by phillipsite at 298 K. Whereas, when the initial concentration was 500 mg L^{-1}, the amount of picolines removed dropped to 25%, 46%, and 64% in the same order.

The removal percent at low concentration (1 mg L^{-1}) for α-pic-oline, β-picoline, γ-picoline by faujasite at 298 K was 73%, 83%, and 93%, respectively. While at high concentration (500 mg L^{-1}) the re-moval percent was 20%, 37%, and 54% in the same order (Fig. 3).

3.3. Effect of sorbent mass

To evaluate the optimum dosage of the sorbent, different masses of faujasite were used to adsorb γ-picoline in solution. Fifty milliliters of solution containing 25 mg L^{-1} of picoline were placed in vials. A certain mass of sorbent (1–100 g L^{-1}) was placed in each vial. After a contact time of 24 h, the content of picoline in the fil-trates was measured using the method mentioned above. Fig. 4 shows that an increase in the faujasite dose increased the percent-age of picoline removal, R, from aqueous solution from 3% to 44%. By increasing the dose of faujasite, the number of adsorption sites available for sorbent–sorbate interaction is increased, thereby resulting in the increased percentage of picoline removal from solution.

Table 1
Physicochemical properties of picolines [16,17].

Properties	Pyridine derivatives		
	α-picoline	β-picoline	γ-picoline
Formula	C$_6$H$_7$N	C$_6$H$_7$N	C$_6$H$_7$N
Molar mass (g mol^{-1})	93.13	93.13	93.13
Density (g mL^{-1})	0.946 at 20 °C	0.957 at 25 °C	0.956 at 25 °C
Boiling point (°C)	129.5	143.9	144.9
pKa	6.00	5.63	5.98
Solubility in water	Freely soluble	Miscible	Miscible
Structure			