



Batch adsorption of *p*-nitrophenol by ZSM-11: equilibrium, kinetic, and thermodynamic studies

Mang Lu^a, Yue Cheng^{a,*}, Shun-long Pan^b, Gui-ying Wei^a

^aSchool of Materials Science and Engineering, Jingdezhen Ceramic Institute, Jingdezhen 333403, Jiangxi, China, emails: bjmanglu@163.com (M. Lu), cy_jci@163.com (Y. Cheng), 1213112961@qq.com (G.-y. Wei)

^bSchool of Environmental and Biological Engineering, Nanjing University of Science and Technology, Nanjing 210094, China, email: huanjingpanda@163.com

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ABSTRACT

In this study, ZSM-11 zeolite was successfully prepared by direct hydrothermal synthesis using silica sol as silicon source and tetrabutylammonium hydroxide as organic structure directing agent. X-ray diffraction confirmed the prepared product was well-crystalline ZSM-11 zeolite. Scanning electron microscopy showed that a single particle of the prepared product had a mean size of approximately $2.5 \mu\text{m} \times 6 \mu\text{m}$. Batch adsorption experiments exhibited that solution pH, ZSM-11 dosage, and NaCl concentration had effects on PNP (*p*-nitrophenol) removal. A high adsorption capacity of 56.3 mg/g was obtained at pH 4, 25°C, ZSM-11 dosage of 0.3 g/L, and initial PNP concentration of 20 mg/L. The addition of NaCl (5.8–580 mg/L) exerted a positive impact on PNP adsorption. Results of desorption experiments showed that a desorption percentage of 78.9% could be obtained in 120 min using 1.44% NaOH solution as desorbent. The equilibrium adsorption data of PNP onto the as-prepared samples were well fitted by the Freundlich isothermal model in the temperature range 25–45°C. The adsorption kinetics was found to obey the pseudo-second-order model. Thermodynamically, it was found that the adsorption of PNP onto ZSM-11 was spontaneous and enthalpy-driven with $\Delta H^\circ = -10.96 \text{ kJ/mol}$. The ZSM-11 samples were found to be effective adsorbent for the removal of PNP from wastewater.

Keywords: Silicalite-2; Zeolite; *p*-Nitrophenol (PNP); Adsorption isotherms; Adsorption kinetics; Adsorption thermodynamics

1. Introduction

As an important intermediate in organic synthesis, *p*-nitrophenol (also called 4-nitrophenol or paranitrophenol and abbreviated as PNP in this study) is widely used in dyes, explosives, pesticides, plasticizers, and herbicides industries [1]. Among the mononitrophenols, PNP has the highest production

worldwide, highest toxicity, and is listed as toxic pollutants by the US Environmental Protection Agency (USEPA) [2].

Currently, available methods for removing PNP from wastewater mainly consist of solvent extraction [3], chemical oxidation [4,5], biodegradation [6,7], and adsorption [8–11]. These extraction methods require multiple steps, time-consuming and consume large amounts of organic solvent, which are not practical

*Corresponding author.

for wastewater with low PNP content. Chemical oxidation involves high reagent costs and may produce secondary pollutants [4,5]. Although PNP can be decomposed by biological processes, these treatment methods are suffering from the limitation of high PNP concentration and long treatment duration because of the toxic or refractory characteristics of PNP [6,7]. Among the numerous techniques of PNP removal, adsorption using solid adsorbents is an effective separation process for treating effluents with high PNP concentration [8–11]. Recently, driven by the desire to efficiently remove PNP from aqueous solution, researchers have synthesized some novel adsorbent materials with high surface area, porous structure, and strong adsorption affinity, such as nano- α -Fe₂O₃ [8], nano-SiO₂ [9], polyamine chelating resin [10], and magnetic polymer beads [11].

Recently, many scientists have been interested in and have explored the use of various zeolites for adsorption of organic compounds [12–16]. Silicalite-2 (ZSM-11), a MEL-type high-silica zeolite composed of two intersecting straight channels ($5.3 \times 5.4 \text{ \AA}$) and highly symmetric skeleton, has attracted significant attention because of its particular catalytic and adsorptive properties [13,17]. To the authors' knowledge, no study has been conducted on the adsorption capability of ZSM-11 towards PNP.

In this study, ZSM-11 was prepared by hydrothermal synthesis method. The synthesized zeolite was characterized in detail by various techniques. The zeolite was used to adsorb PNP from aqueous solution. The adsorption characteristics including isotherms, kinetics, and thermodynamics were investigated. The effect of temperature, pH, ZSM-11 dosage, and NaCl concentration on PNP adsorption was examined. The effect of desorbent (NaOH) concentration on PNP desorption was also studied.

2. Materials and methods

2.1. Synthesis of ZSM-11

The ZSM-11 zeolite was synthesized by hydrothermal synthesis using silica sol (25% aqueous solution) as silicon source, and tetrabutylammonium hydroxide (TBAOH, 25% aqueous solution) as organic structure-directing agent. All chemicals were of analytical reagent grade and directly used without further purification. In brief, the required amount of silica sol was added dropwise to TBAOH solution under continuous stirring in a polypropylene bottle. Then deionized water was added to this solution and the mixture was stirred for another 3 h at ambient temperature, followed by aging overnight. The final gel composition

was 1SiO₂:0.35TBAOH:25H₂O. The synthesis was carried out in a Teflon reactor at 170°C for 2 d. The resulting ZSM-11 zeolite was recovered by filtration, exhaustively washed with distilled water until the filtrate was neutral, and finally dried at 100°C for 12 h. The occluded TBAOH organic cations were removed by calcination at 600°C for 3 h.

2.2. Characterization

X-ray diffraction patterns (XRD) were obtained from a Bruker D8 advance diffractometer (Bruker, Germany) with Cu K α radiation from 5° to 70° at a rate of 0.2°/s. The tube current was 100 mA with a tube voltage of 40 kV. Crystal size and morphology were investigated using a scanning electron microscopy (SEM) on a JEOL JSM-6380 field-emission SEM (Japan).

2.3. Adsorption of PNP onto ZSM-11 zeolite

A stock solution of PNP (1,000 mg/L) was prepared in deionized water and all working solutions were prepared by diluting the stock solution to the required concentrations. The solution pH was adjusted using 0.1 M HCl and 0.1 M NaOH. All chemicals used were of analytical grade.

In 250 mL stoppered Erlenmeyer flasks, desired amounts of ZSM-11 adsorbent were independently added to 100 mL of adsorbate solution (20 mg/L) of PNP. The flasks were placed in a shaker run at 150 rpm and at 25, 35, and 45°C, respectively. To investigate the effect of ionic strength on PNP adsorption by the zeolite, appropriate amounts of NaCl were added to 100 mL of 20 mg/L PNP solution (pH 4) to reach a final concentration of 5.8, 58, and 580 mg/L, respectively, and the dosage of ZSM-11 was 0.3 g/L.

Portions of each solution were taken at different periods of time and filtered through a 0.45 μ m filter. The concentrations of PNP in the solutions before and after adsorption were determined spectrophotometrically (WFZ800-D3B, Beijing Ruili Analysis Instrument Co., Ltd, China) by monitoring the absorbance at 317 nm. The losses of PNP by both photochemical decomposition and volatilization were found to be negligible during adsorption (data not shown). All the experiments were performed in batch mode taking three replicates and mean values were reported. Standard deviations were found to be within $\pm 3\%$. PNP uptake at equilibrium was calculated by Eq. (1)

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

where q_e is the adsorption capacity in mg/g, C_0 and C_e are the initial and equilibrium concentrations of PNP in mg/L, V is the volume of PNP solution in L, and m is the mass of dry adsorbent used in g.

2.4. Desorption of PNP from ZSM-11

The desorption of PNP-loaded adsorbent was performed by using various strengths of NaOH solution (50 mL, 0.8–1.76%) by taking 0.03 g of ZSM-11 pre-adsorbed with 100 mL of 20 mg/L PNP and shaken continuously at 150 rpm. Desorption efficiency was calculated using the following equation:

$$\% \text{Desorption} = \frac{C_d \times V_d}{m \times q_e} \times 100 \quad (2)$$

where C_d is the desorbed adsorbate concentration (mg/L), V_d is the volume of the desorption solution (L), m is the mass of the pre-adsorbed adsorbent (g), and q_e is the amount of the adsorbate pre-adsorbed on the adsorbent (mg/g).

3. Results and discussion

3.1. XRD and SEM

Fig. 1(A) shows the XRD pattern of ZSM-11 samples synthesized. The sample exhibits the typical single diffraction peak at $2\theta = 7.92^\circ$, 8.78° , 23.14° , 23.98° , and 45.21° , indicating well-crystalline ZSM-11 zeolite prepared by one-stage crystallization method [18]. Additionally, the sample shows some diffuse diffraction peaks with high height and high intensity.

Fig. 1(B) shows the morphology and crystal size of the zeolite sample. The obtained product exhibits regular oval shape for single particle with diameters of approximately $2.5 \mu\text{m} \times 6 \mu\text{m}$, which is in agreement with previous reports [13,17]. Moreover, many small pores are distributed onto the surface of the product, which are beneficial for absorbing compounds [17].

3.2. Effect of pH on adsorption

The solution pH value is an important controlling parameter in the adsorption process. The 20 mg/L of PNP solution used in the present study has a natural pH of 6. The effect of pH on PNP adsorption by ZSM-11 is plotted in Fig. 2. It can be seen that the adsorption of PNP increased gradually with decreasing pH from 10 to 2. After 50 min, the highest q_e (57.8 mg/g) occurred at pH 2. In contrast, the lowest q_e (35.9 mg/g) was observed at pH 10. At pH 4, a high adsorption

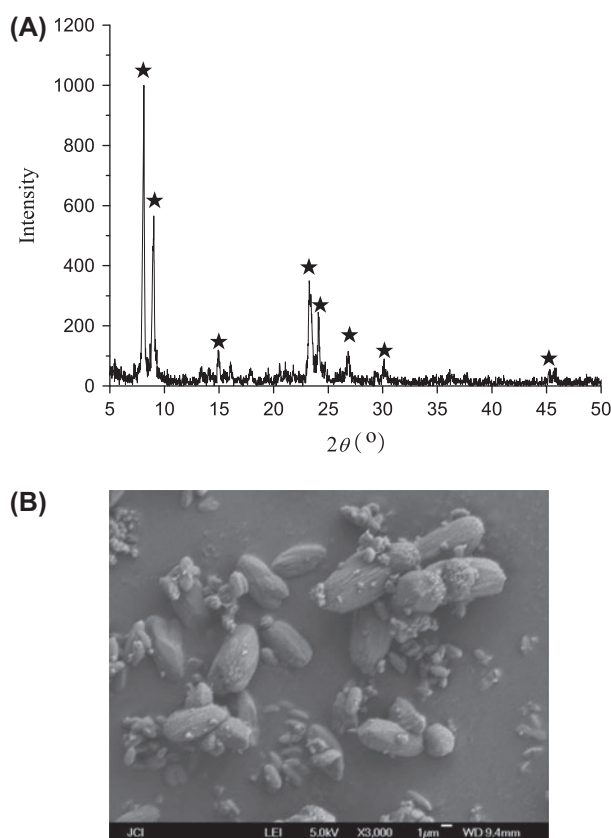


Fig. 1. XRD pattern (A) and SEM paragraph (B) of the laboratory-synthesized ZSM-11 sample.

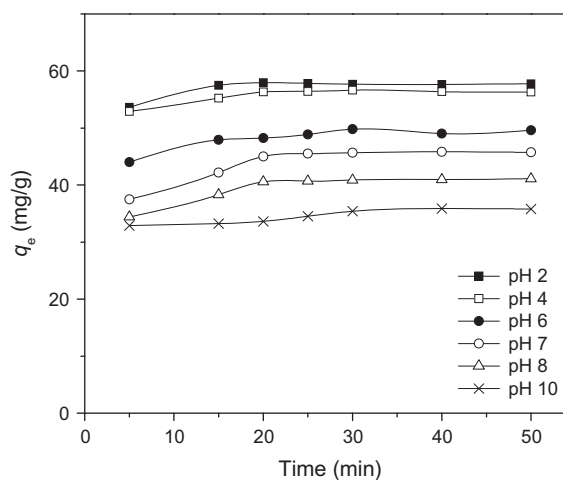


Fig. 2. Effect of initial solution pH on the adsorption of PNP onto ZSM-11 at 25°C. $[\text{PNP}]_0 = 20 \text{ mg/L}$, $[\text{ZSM-11}]_0 = 0.3 \text{ g/L}$.

capacity of 56.3 mg/g was obtained, which is close to that obtained at pH 2.

This increment in sorption due to the decrease in initial pH can be attributed both to the surface charge behavior of the ZSM-11 zeolite and the dissociation chemistry of the solute PNP. ZSM-11 contains a large number of Si–OH groups on the ribbons that are present on its external surface. These groups are subjected to protonation or deprotonation depending on pH values. Greater PNP adsorption onto ZSM-11 at lower pH may be due to neutralization of the negative charges at its surface. In contrast, the adsorbent surface becomes negatively charged at higher pH [19]. Meanwhile, molecular PNP converts to anions at $\text{pH} > 7.15$ (pK_a of PNP = 7.15) due to dissociation reaction as follows [20]:



As a result, the negative charges on the sorbent surface will cause electrostatic repel for dissociated PNP anions. Thereupon, a low solution pH benefits PNP adsorption onto ZSM-11. After comprehensive consideration, pH 4 of PNP solution was used for the subsequent experiments in the present study.

Fig. 2 also demonstrates that PNP adsorption did not decrease to zero when the solution pH was elevated to 10. This is because that: (1) nitro groups of PNP molecules have strong electron-withdrawing effect, which renders the negative charges of PNP anions adsorbed onto the zeolite surface being dispersed to a certain degree, and thus reduces the electrostatic repel between PNP anions and negative charges of zeolite surface, leading to a certain level of PNP adsorption; (2) under alkaline conditions, raising solution pH is bound to increase Na^+ concentration. Na^+ ions in the solution have a certain shielding effect on the negative charges of PNP anions and negative charges of zeolite surface, which may lessen the electrostatic repel between PNP anions and negative charges of zeolite surface, thus producing a certain level of PNP adsorption.

3.3. Effect of adsorbent dosage on adsorption

The effect of ZSM-11 dosage (varying from 0.1 to 0.7 g/L) on the PNP uptake capacity for the initial adsorbate concentration of 20 mg/L is presented in Fig. 3. Initially, the adsorption efficiency of the zeolite for PNP increased steadily with the increase in added ZSM-11, which is attributed to greater surface area and availability of more adsorption sites with the increase in adsorbent dosage. At higher amount of adsorbent, there was faster superficial adsorption onto the zeolite surface that produced a lower solute

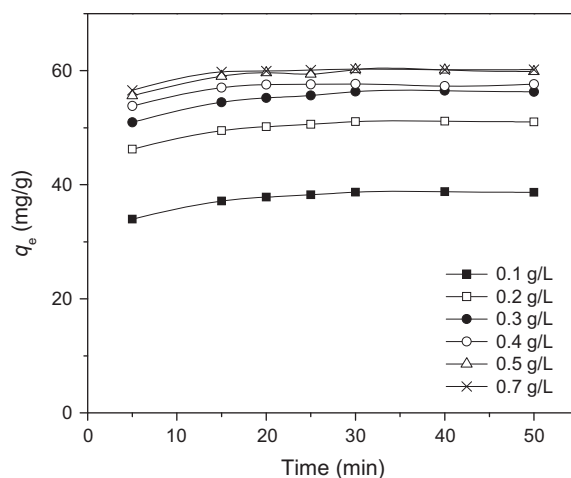


Fig. 3. Effect of adsorbent dosage on the adsorption of PNP onto ZSM-11 at 25°C. $[\text{PNP}]_0 = 20 \text{ mg/L}$, $[\text{pH}]_0 = 4$.

concentration in the solution than when zeolite dosage was lower. In the present study, however, increasing ozone dosage beyond 0.3 g/L did not result in significant enhancement of the PNP adsorption amount, which is due to the splitting effect of flux (concentration gradient) between adsorbate and adsorbent [21]. The great increase in the amount of adsorbent particles may enhance their collision probability in aqueous solution, causing overlapping of adsorption sites. In addition, the high dosage of adsorbent can increase the stickiness of solid–liquid suspension, which may thus inhibit the diffusion of adsorbate molecules onto the adsorbent surface.

3.4. Effect of NaCl concentration on adsorption

Pollutants are always present in contaminated effluents or soils together with certain amounts of soluble salts. The electrolyte concentration or ionic strength of wastewater can significantly influence the adsorption capacity of an adsorbent by altering its surface potential. Thus, it is necessary to evaluate the adsorption performance of an adsorbent under various electrolyte concentrations before its field application. The effect of NaCl concentration on the adsorption of PNP onto ZSM-11 is illustrated in Fig. 4. A remarkable increment in the amount of PNP adsorption onto ZSM-11 was observed with increase in NaCl concentration (Fig. 4), indicating a higher competitiveness of PNP anions than Cl^- ions for adsorption sites on ZSM-11. The enhancement of PNP adsorption in the presence of NaCl in solution is due to the salting out effect of electrolytes at higher ionic strength via decreasing the solubility of PNP. The favorable effect

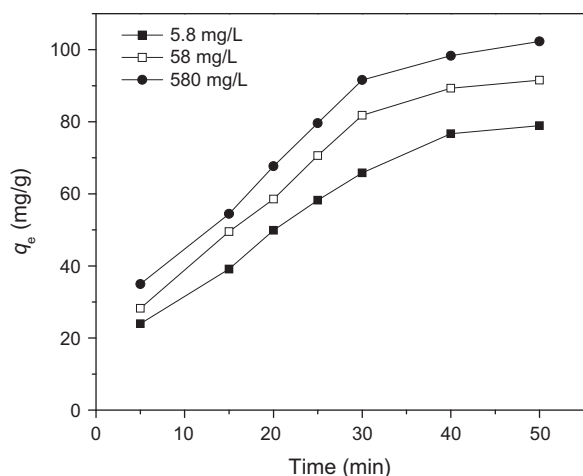


Fig. 4. Effect of NaCl concentration on the adsorption of PNP onto ZSM-11 at 25°C. $[\text{PNP}]_0 = 20 \text{ mg/L}$, $[\text{pH}]_0 = 4$, $[\text{ZSM-11}]_0 = 0.3 \text{ g/L}$.

of electrolytes on adsorption of phenolic compounds was previously reported for activated carbon [22] and zeolite [23].

3.5. Effect of NaOH concentration on PNP desorption

Desorption was carried out with different concentrations of NaOH solutions at pH 4 up to 210 min. It can be seen from Fig. 5 that the optimum desorption duration was 120 min for all the four concentrations of NaOH solutions applied. Once desorption time was prolonged to >120 min, desorption efficiency decreased remarkably. In 120 min, desorption percentages for 0.8, 1.12, 1.44, and 1.76% NaOH solutions

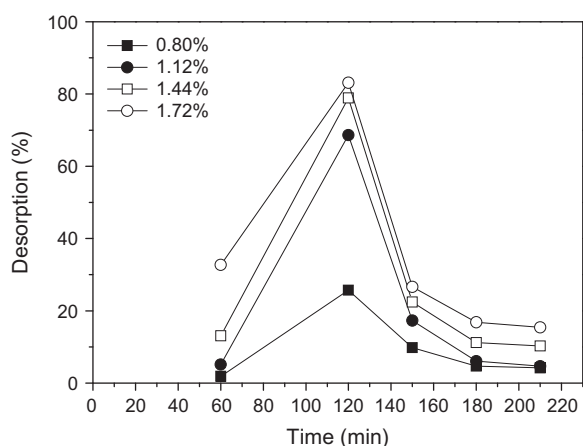


Fig. 5. Effect of NaOH concentration on the desorption of PNP from ZSM-11 at 25°C. $[\text{PNP}]_0 = 20 \text{ mg/L}$, $[\text{pH}]_0 = 4$, $[\text{ZSM-11}]_0 = 0.3 \text{ g/L}$.

were 25.7, 68.6, 78.9, and 83.1%, respectively (Fig. 5). Although the desorption of PNP showed an increasing trend with the increasing NaOH concentration, the increment in desorption efficiency was insignificant when the desorbent content was elevated from 1.44 to 1.76%. Hence, 1.44% NaOH was selected as regenerating agent.

3.6. Adsorption isotherms

Temperature has a prominent impact on the adsorption capacity of adsorbents. Table 1 lists the PNP uptake, q_e (mg/g), onto zeolite versus the solution temperature at initial concentration of 20 mg/L. In general, the PNP uptake was found to slightly decrease with increasing solution temperature from 25 to 45°C.

Adsorption isotherms reflect the relationship between the amount of a solute adsorbed at constant temperature and its concentration in the equilibrium solution, which provides essential physiochemical data for evaluating the applicability of the adsorption process as a complete unit operation [24]. In this study, two adsorption isotherms: Langmuir and Freundlich were applied to fit the equilibrium data of adsorption of PNP onto ZSM-11 zeolite (Table 1).

3.6.1. Langmuir model

The Langmuir model assumes that adsorption is monolayer and the adsorbent surface consists of active sites having a uniform energy and thus, the adsorption energy is constant. The Langmuir adsorption isotherm expression is shown in Eq. (4) [25]:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (4)$$

Table 1
Effect of temperature on the adsorption of PNP onto ZSM-11. $[\text{PNP}]_0 = 20 \text{ mg/L}$, $[\text{pH}]_0 = 4$, $[\text{ZSM-11}]_0 = 0.3 \text{ g/L}$

Time (min)	q_e (mg/g)		
	25°C	35°C	45°C
5	50.9	49.5	48.5
15	54.5	52.7	51.6
20	55.2	53.1	52.7
25	55.7	53.8	53.3
30	56.3	54.2	53.7
40	56.5	54.1	53.7
50	56.3	54.0	53.6

where q_e (mg/g) is the PNP amount adsorbed per unit mass of adsorbent, C_e is the equilibrium concentration of PNP (mg/L), q_{\max} (mg/g) and K_L (L/mg) are the Langmuir constants related to adsorption capacity and rate of adsorption, respectively.

3.6.2. Freundlich model

In contrast to Langmuir model, the Freundlich model assumes that the adsorbent surface energy is heterogeneous. It is assumed that the stronger binding sites are occupied first and that the binding strength decreases with the increasing extent of site occupation. The Freundlich adsorption isotherm expression is shown in Eq. (5) [26]:

$$q_e = K_F C_e^{1/n} \quad (5)$$

where K_F (mg/g (L/mg) $^{1/n}$) is defined as the adsorption capacity of the adsorbent. The $1/n$ value ranging between 0 and 1 is a dimensionless factor that measures the adsorption intensity or surface heterogeneity.

The Langmuir parameters (K_L and q_{\max}) and Freundlich parameters (K_F and n) for the adsorption isotherms are given in Table 2. Due to higher R^2 values listed in Table 2, the Freundlich model yielded the better fit than the Langmuir model at 25, 35, and 45°C. Thus, the Freundlich isotherms are the most suitable equations to describe the adsorption equilibrium of PNP onto ZSM-11 at 25–45°C. The values of n are greater than one indicates the favorable adsorption of PNP onto ZSM-11.

3.7. Adsorption kinetics

In this study, the kinetics of the adsorption data was analyzed using two different kinetic models: the pseudo-first-order and pseudo-second-order models.

3.7.1. Pseudo-first-order kinetic model

The pseudo-first-order kinetic model has been widely used to predict the adsorption kinetics [27]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

where q_e and q_t (mg/g) are the amounts of adsorbate adsorbed at equilibrium e and at any time t (min), respectively. The constant k_1 (1/min) is the adsorption rate constant of pseudo-first-order reaction.

3.7.2. Pseudo-second-order kinetic model

The pseudo-second-order equation based on the equilibrium adsorption is expressed as [28]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

where q_e and q_t (mg/g) are the amounts of adsorbate adsorbed at equilibrium e and at any time t (min), respectively. The constant k_2 (g/mg min) is the adsorption rate constant of pseudo-second-order adsorption.

Fitting kinetics parameters of adsorption of PNP onto ZSM-11 according to pseudo-first-order (Eq. (6)) and pseudo-second-order models (Eq. (7)) at 25, 35, and 45°C are tabulated in Table 3. The results show that pseudo-second-order model fits the experimental data quite well, indicating the applicability of second-order kinetic model to describe the adsorption of PNP onto ZSM-11.

3.8. Adsorption thermodynamics

The thermodynamic parameters, such as enthalpy (ΔH°), entropy (ΔS°), and Gibb's free energy (ΔG°), were estimated using the following relation [12]:

$$\Delta G^\circ = -RT \ln K_L \quad (8)$$

$$\ln K_L = -\frac{\Delta G^\circ}{RT} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

Table 2

Langmuir and Freundlich parameters of adsorption isotherms of PNP onto ZSM-11 (according to Eqs. (4), (5), and Table 1) at 25, 35, and 45°C

Temperature (°C)	Freundlich model			Langmuir model		
	K_F (mg/g (L/mg) $^{1/n}$)	n	R^2	q_{\max} (mg/g)	K_L (L/mg)	R^2
25	31.89	2.59	0.9538	23.291	1.0459	0.9242
35	31.69	2.43	0.9285	21.877	0.9608	0.9043
45	29.78	2.18	0.8689	19.822	0.7822	0.8383

Table 3

Kinetics rate constants (k_1 , k_2) of PNP adsorption onto ZSM-11 (according to Eqs. (6), (7), and Table 1) at 25, 35, and 45 °C

Temperature (°C)	First-order model		Second-order model	
	k_1 (1/min)	R^2	k_2 (g/mg min)	R^2
25	0.1214	0.9505	0.0180	0.9999
35	0.1239	0.6510	0.0189	0.9989
45	0.1426	0.9760	0.0190	0.9998

where R (8.314 J/mol K) is the universal gas constant, K_L (L/mg) is the Langmuir isotherm constant, and T (K) is the absolute solution temperature.

In this study, the values of $\ln K_L$ were plotted against $1/T$ (Fig. 6), where the ΔH° and ΔS° values were calculated from the slope and intercept of the plot. The obtained thermodynamic parameters are listed in Table 4. Negative ΔG° values were obtained at all temperatures, confirming that the adsorption of PNP onto ZSM-11 is spontaneous and thermodynamically favorable. The more negative values of ΔG° imply that a greater driving force is required for the adsorption process [29]. The ΔG° value decreases as the temperature increases, indicating a less driving force causing lesser adsorption capacity at higher temperatures. Negative ΔH° values demonstrate the exothermic nature of these adsorptions, which is in accordance with the results obtained by Yousef et al. [12] for the study of adsorption of phenol onto natural zeolites. Negative ΔS° values suggest that the organization of the adsorbate at the solid/solution interface becomes less random. In this study, the negative ΔS° values may reveal that ZSM-11 surface does not prefer PNP molecules over adsorbed water molecules. Thereupon, the PNP adsorption onto ZSM-11 under the

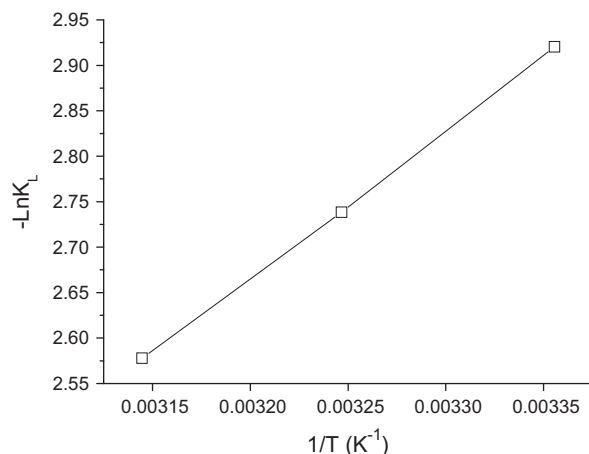


Fig. 6. Plot of $\ln K$ vs. $1/T$ for the adsorption of PNP onto ZSM-11 (according to Eqs. (8), (9), and Table 1) at 25, 35, and 45 °C.

Table 4

Thermodynamic parameters for the adsorption of PNP onto ZSM-11 (according to Eqs. (8), (9), and Table 1) at 25, 35, and 45 °C

Temperature (°C)	ΔH° (kJ/mol)	ΔG° (kJ/mol)	ΔS° (J/mol K)
25	-10.96	-7.232	-13.08
35		-6.932	-13.04
45		-6.812	-12.51

applied conditions of the present study is deemed as an enthalpy-driven process.

4. Conclusions

In this study, ZSM-11 zeolite was successfully prepared by one-stage hydrothermal synthesis. The results of adsorption experiments clearly indicate the potential of ZSM-11 as an adsorbent for the removal of PNP from wastewater. The adsorption kinetics of PNP onto the ZSM-11 samples studied followed the pseudo-second-order kinetic model. The equilibrium adsorption data were well represented by Freundlich isotherm equation at the temperature range 25–45 °C. Thermodynamic study showed that the adsorption of PNP onto ZSM-11 is spontaneous and an enthalpy-driven process with a negative enthalpy ($\Delta H^\circ = -10.96$ kJ/mol).

Acknowledgments

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