Adsorption kinetics and equilibrium of phenol drifts on three zeolites

Research article

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Abstract: In this study, the sorption of phenol drifts was studied by performing batch kinetic sorption experiments. The equilibrium kinetic data was analyzed using the pseudo-second-order kinetic model. Fowler-Guggenheim model gives a perfect fitting with the isotherm data. The influence of porous structure of a zeolite particle on phenol adsorption from aqueous solutions is analyzed and discussed. The adsorption for phenol drifts on zeolite was proved to be an exothermic process. Thus the solubility of the phenolic compound and the pH of the solution play also an important role in adsorption phenomena. The relative affinity of the phenolic compound toward the zeolite was related to the electron donor-acceptor complexes that were formed between the basic sites on the zeolite (oxygen) and hydrogens (acidic site) of the phenols. Finally zeolite seems to be an efficient adsorbent; it can be easily regenerated by methanol leaching.

Keywords: Phenol drifts • Adsorption • Zeolites • Batch adsorption

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1. Introduction

With the development of the industry and the intensive use of pesticides, wastewater discharges have evolved considerably in quantity and quality. Phenols and related compounds present in wastewater are toxic to humans and aquatic life [1–3]. Therefore, organizations of health and

the environment issue instructions to set the maximum allowable levels of pollutants. As a result, great research efforts on adsorption processes and adsorbent materials for separating organic pollutants from waste streams have been developed [4–6].

Activated carbon is the most widely used adsorbent for water treatment, however, regeneration is difficult and expensive [7, 8]. This has led many laboratories to focus on research of new, efficient and regenerative adsorbents [6, 9, 10].

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Zeolites have been recently noted as a practical alternative to activated carbon because of their high surface area, their high selectivity and their economic cost for regeneration after saturation [11, 12].

In this work, three kinds of zeolites are used: a Faujasite type (HFAU) partially dealuminated, Mordenite type (HMOR) and a Beta type (HBEA). HFAU consists of sodalite cages which are connected through hexagonal prisms. The pores are arranged perpendicular to each other. The pore, which is formed by a 12-membered ring, has a relatively large diameter of 7.4 Å. The inner cavity has a diameter of 12 Å and is surrounded by 10 sodalite cages. HMOR structure is a framework containing chains of five-membered rings of linked silicate and aluminate tetrahedral. These building units are linked by edge-sharing into chains along *c*, which are in turn linked together by 4-rings to form a puckered sheet perforated with 8-ring holes. These permeable sheets are oriented parallel to [010]. Linking these sheets together with 4-rings, 12-ring channels are formed parallel to [001]. The 8-ring holes of successive sheets do not align to make channels parallel to [010]. Beta type (HBEA) can be regarded as a highly internally grown hybrid of two distinct (polymorph A and B) but closely related structures that both have fully three-dimensional pore systems with 12 membered ring diameter of 5.6–6.7 Å.

The physicochemical mechanisms in these materials are complex [13]; no simple theory of adsorption could adequately describe experimental results.

Electrostatic and van Der Waals forces, H-binding, dipole–dipole interactions, ion exchange, covalent bonding, cation bridging and water bridging can be responsible for adsorption of organic compounds in zeolites [13–15].

The equilibrium adsorption isotherm is of importance in the design of adsorption systems. Several isotherm equations are available and one isotherm is selected in this study: the Fowler–Guggenheim adsorption model [16].

Batch studies were carried out to identify the rate controlling steps. Many adsorption kinetics models of single-solute were reported in the literature. For example, Mass transfer classical model [17], Intra-particular diffusion [18] and External diffusion [19]. In our study, the pseudo second order [20, 21] will be used to fit the adsorption kinetics data.

The objective of this work is to study the removal of various organic compounds (phenol, 2-chlorophenol, 2-nitrophenol and salicylic acid) in water over zeolites by comparing the influence of their physicochemical properties. Adsorption was conducted in a batch apparatus, and the effect of pH was studied. Furthermore, we have tried to highlight the influence of the structure of the zeolite on adsorption of these pollutants. The effect of temperature and the size of porous were also investigated.

On the other hand, our study was carried out to identify the Kinetic parameters of the sorption of phenol drifts and to specify the rate constants and other parameters for the application of zeolites in water treatment.

2. Experimental part

2.1. Zeolites Adsorbents

Partially dealuminated HFAU zeolite and BEA zeolite were supplied by Zeolyst International, HMOR samples were provided by Institut Regional des Matériaux Avancés (IRMA) Ploemeur-France. Si/Al ratio were determined using an X-ray fluorescence spectrometer MagiX (Philips) on pellets composed of 200 mg of compacted product (Table 1). The adsorbent structure before and after adsorption was determined by Powder X-Ray Diffraction (XRD) on Bruker D8 Advanced diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ Å}$).

The surface functional groups and adsorptive form of organic compounds were identified using IR spectroscopy. The measurements were recorded using a Bruker IFS66S with a Bruker SpectraTech Baseline DRIFT module, for doing DRIFT (Diffuse Reflectance Infrared Fourier Transform) spectra. DRIFT spectra were recorded between 4000 and 600 cm^{-1} .

The microporous and mesoporous volume and the specific surface area were determined from nitrogen adsorption isotherms at 77 K on a Micromeritics ASAP 2410 porosimetre using the BET method (on a linear P/P^0 domain between 0.01 and 0.3) and the single-point method at $P/P^0 = 0.26$. The calcined samples were placed in a glass measurement cell, and then they were degased at 350°C under vacuum prior to the measurement. Thermogravimetric and differential thermal analyses (TGA and DTA) were performed in flowing air using a Setaram Labsys thermanalyser. Powders were heated at a rate of $3^\circ\text{C} \cdot \text{min}^{-1}$ up to 700°C , and were cooled down to room temperature. The characteristics of zeolite samples are given in Table 1.

2.2. Adsorbates

Phenol, 2-chlorophenol, 2-nitrophenol and salicylic acid were purchased from Aldrich. The solutions were prepared using distilled water. The main physiochemical properties of these compounds are featured in Table 2.

2.3. Adsorption experiments

Adsorption experiments were carried out using the batch method for different initial phenol drifts concentrations. For each flask, a fixed amount of adsorbent was added to

Table 1. Characterization of the Zeolite Samples.

Adsorbent	Formula	Pore size (Å)	Si/Al	SBET (m ² /g)	Pore volume (cm ³ · g ⁻¹)	
					micropore	mesopore
HBEA ₁₉	H _{3.2} Al _{3.2} Si _{60.8} O ₁₂₈	6.6*6.7 and 5.6*5.6	19	650	0.244	0.083
HMOR ₁₈	H _{2.6} Al _{2.6} Si _{45.4} O ₉₆	6.5*7 and 2.6*5.7	18	530	0.174	0.084
HFAU ₁₉	H _{9.6} Al _{9.6} Si _{182.5} O ₃₈₄	7.4*7.4	19	740	0.245	0.11

Table 2. Physicochemical properties of Chemicals.

Molecules
Purity	99%	98%	98%	99%
IUPAC Name	Phenol	2-chlorophenol	2-nitrophenol	Salicylic Acid
Symbol	PHOH	OCP	ONP	SA
Chemical formula	C ₆ H ₆ O	C ₆ H ₅ ClO	C ₆ H ₅ NO ₃	C ₇ H ₆ O ₃
λ (nm)	270	216	276	207
Solubility Water ^a	87	28.5	1.26	2
pKa	9.95	8.49	7.17	2.97
Kinetic diameter (Å) ^b	6.7	8.1	8.1	8.4

^aMeasured at 20°C and pH = 6^bKinetic diameters for different compounds are calculated using the software "Cerius2"

100 mL phenols solution. The initial pH of the solution was adjusted using 1 mol/L HCl or NaOH solutions to pH between 2 and 10. The flasks were agitated and incubated in an incubator shaker at different temperatures until reaching equilibrium. Samples were taken from the flasks at regular time intervals for analyzing the concentration phenol drifts in the solution. The residual amount of phenol drifts in each flask was investigated using UV/VIS spectrophotometer at different λ depending on the phenol drift used (Table 2).

The amount adsorbed of the adsorbates can be calculated by the following equation:

$$m_A(Q) = V(C_0 - C) \quad (1)$$

where

m_A : mass of zeolite (g);

V : volume of solution (L);

C : concentration after adsorption (mg · L⁻¹);

C_0 : initial concentration (mg · L⁻¹);

Q : amount adsorbed (mg · g⁻¹ of zeolite).

2.4. Kinetics models

The real challenge in the adsorption field is to identify the adsorption mechanism. Therefore a study of the adsorption kinetics is important since the kinetics describe

an uptake rate of adsorbate which in turn helps to predict the adsorption mechanism.

The adsorption kinetics may be governed by different diffusion steps as: external diffusion, intra-particle diffusion, adsorption kinetics governed by the surface reaction.

2.4.1. Intra-particle diffusion

The equation of Intra-particle diffusion models derives from Weber and Morris model [18] is expressed as:

$$q_t = \left(\frac{V}{m} \right) K_w t^{1/2} \quad (2)$$

q_t : adsorption capacity of zeolite at t

m : adsorbent mass (g)

V : solution volume (L)

K_w : diffusion constant of intra-particle (from Weber and Morris)

t : time

2.4.2. Pseudo-first-order model

It was intuitively associated with the model of one-site-occupancy adsorption kinetics governed by the rate of surface reaction [22]. This model did not perfectly fit our results. It is expressed as:

$$\frac{dq_t}{dt} = K(q_e - q_t) \quad (3)$$

The integrated form of the differential equation becomes

$$\ln(q_e - q_t) = \ln q_e - Kt \quad (4)$$

2.4.3. Pseudo second order model

The pseudo-second order kinetic equation was proposed by Blanchard *et al.* [21] and is also based on the sorption capacity of the solid phase and is expressed as:

$$\frac{dq_t}{dt} = K(q_e - q_t)^2 \quad (5)$$

If second-order kinetics is applicable, the plot of t/q against t should give a linear relationship.

2.5. Adsorption isotherms model

Several mathematical models can adequately describe the adsorption isotherms, and thus obtain information on the maximum adsorption capacity or different types that take place during the adsorption. Our isotherms have been successfully described by Fowler Guggenheim following the equation [16]:

$$KC = \frac{\theta}{1 - \theta} \exp\left(\frac{2\theta W}{RT}\right) \quad (6)$$

where

K : equilibrium constant for adsorption of the adsorbate on an active site;

C : concentration at equilibrium adsorption;

W : empirical interaction energy between two molecules adsorbed on nearest neighboring sites;

R : ideal gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$);

T : thermodynamic temperature;

θ : fractional coverage of the surface.

Fowler-Guggenheim equation is taking into account the lateral interaction. This model is based on the hypothesis that interaction energy is constant and independent of fractional coverage of the surface θ , and; hence, the number and distribution of adsorbed molecules.

3. Results and discussion

3.1. Effect of initial pH on phenol drifts adsorption

The study of adsorption of phenol on HFAU zeolite was performed at room temperature and under atmospheric pressure with concentration of 1 g/L for pH values between 2 and 10. The choice of this pH range is carried out to

Figure 1. Influence of pH on phenol adsorption over HBEA (■), HFAU (◆) and HMOR (▲).

examine the evolution of the adsorption of solute associated with the different chemical forms which are presented, depending on pH.

Figure 1 shows the effect of solution pH on the adsorption of phenol on the HBEA, HFAU and HMOR zeolites at given conditions. Adsorption has been increased with increasing pH up to 4.0, then between (4 and 7) the adsorption capacities of phenol were nearly identical; finally, decreasing adsorption of phenol with increasing pH (pH 7–10). The maximum adsorption of phenol occurred normally when pH was lower than its pKa (9.89), at which phenol is present in the neutral form. Phenol is an acidic molecule, so an increasing pH results in an increasing anionic fraction in solution and; hence, a decreasing adsorption.

Dursun *et al.* [23] indicated that, phenol and its derivatives adsorb on activated carbon via a “donor–acceptor complex”. In our case this mechanism involves siloxane group Si–oxygen groups acting as electron donor, and the hydrogen bond as acceptor.

The low pH value was obtained by using an acid solution. It introduced additional protons in the solution, which competed for the Siloxan (Si–O–Si) sites. The decrease in phenol adsorption from pH = 5.3 to 2 was due to the increased H^+ adsorption on the siloxan sites, which suppresses phenol adsorption on these sites. On the other hand, the decrease in the phenol amount adsorbed from pH = 6.7 to 10 was attributed to both greater solubility of dissociated phenol at pH > pKa and increased repulsion forces between the dissociated form of the adsorbate and the zeolite surface.

On the other hand, HBEA zeolite appears more efficient than HFAU and HMOR for adsorption of phenol, the discussion is presented in part 3.5.

3.2. Phenol drifts isotherms obtained over HFAU and HBEA

We then studied the adsorption of various derivatives of phenol over different types of zeolites at various pH values and compared it with the results obtained for phenol ad-

Figure 2. Influence of pH on phenol drifts adsorption (◆) ONP, (■) OCP and (▲) SA over HBEA.

Figure 3. Effect of particles size on phenol adsorption over HBEA zeolite of 0.05–0.07 mm (◆), 0.2–0.4 mm (▲) and 0.6–0.7 mm (□).

sorption. In Figure 2, the results obtained over HBEA are presented, we can show that the lowest adsorbed quantity is observed at pH 10 ($\text{pH} \sim \text{pK}_a$) where nitrophenol molecules are in the dissociated form. Then, the adsorption capacity has increased with decreasing pH and have become very important at pH 4 and 5.3 (Q_{ads} around 235 mg/g). Same results as that obtained for phenol at $\text{pH} < 4$ was also obtained. Similar results were obtained for ortho-chlorophenol as in the case of ortho-nitrophenol. On the other hand, SA adsorbs strongly over HBEA zeolite only at very acidic pH. This is due to its physicochemical properties (pK_a 2.97). Therefore, at $\text{pH} \sim 4$, the salicylic acid molecules are in the dissociated form, which create electrostatic repulsion forces with the basic oxygen of the zeolite.

The influence of the substituent group nature on the evolution of the adsorption capacity of HFAU zeolite is visible in Figure 1 and Figure 2. It is observed that the adsorption capacity varies according to the following order:

Ortho-nitrophenol > Ortho-chlorophenol > Phenol > Salicylic acid

If we trace the evolution of solubility based on adsorption capacity (Figure SD1), we deduce that the value of the adsorption capacity of these compounds, except salicylic acid, varies linearly with the solubility.

Figure 4. Adsorption isotherms of phenol in HBEA zeolite at 20°C (■), 30°C (▲) and 40°C (◆). Lines represent fitting curves by Fowler-Guggenheim model.

However, salicylic acid has lower adsorption capacity than chlorophenol and phenol although it is much less soluble. also, at $\text{pH} = 10$ (Table SD1 and SD2), we observe a modification in the order of adsorption capacity of molecules, This indicates that other parameters as the effect of pK_a have affected highly the adsorption.

This result may be related to the pK_a of nitrophenol which is 7.17. At pH 10, ortho-nitrophenol molecules are in the dissociated form, so adsorption is difficult and is less than that of ortho-chlorophenol whose pK_a is 8.49. Similar results were obtained by adsorption over activated powder carbon [24, 25].

3.3. Effect of particle size

The influence of contact time on 3 particle size ranges of BEA zeolite was investigated using particles having size of 0.05–0.07, 0.2–0.4 and 0.6–0.7 mm. The effect of uptake was studied at using the following conditions ($\text{pH} = 4$, $[\text{phenol}] = 1 \text{ g/L}$, $[\text{zeolite}] = 1 \text{ g/L}$).

As can be noticed in Figure 3, the equilibrium capacity was not affected by changing particle size. Although adsorption kinetics became faster with the decrease of particle size. This fact indicates that the smaller the adsorbent particle diameter, for a given zeolite, the adsorption sites are more easily accessible and the adsorption kinetics increase.

3.4. Effect of temperature on phenol adsorption

The influence of temperature on the adsorption of phenol was studied between 20 and 40°C.

The results (Figure 4) indicated that adsorption capacity was decreased as temperature was increased as shown in Figure 4. This comes from the fact that phenol adsorption by HBEA is an exothermic process. Similar results were obtained over HFAU and HMOR (not presented here).

Table 3. Parameters of Fowler-Guggenheim model and Thermodynamic parameters of phenol over HBEA zeolite at different temperature.

T (°C)	20	30	40
K (L/g)	1.25	1.17	1.12
W (J/mol)	−1990	−2050	−2060
Q_{ads} (mg/g)	40	32	27
ΔG° (J/mol)	−536	−402	−312
ΔH° (J/mol)	−3790	−3790	−3790
ΔS° (J/mol · K)	−11.2	−11.2	−11.2

That is also observed with the parameters of the Fowler-Guggenheim model (Table 3). K is the equilibrium constant for adsorption of the adsorbate on an active site. It represents the interaction between the adsorbate and the adsorbent. Therefore, the highest K value at $T = 20^\circ\text{C}$ ($K = 1.24$) indicates the important interaction between phenol molecules and HBEA zeolite.

While the interaction energy (W) between the adsorbed molecules (Table 3) is negative and of similar value for the three adsorbates studied (-2.0 kJ/mol) indicating a possible interaction between the adsorbed molecules. The equilibrium constant K and the interaction energy W were determined using Excel software.

The Langmuir model, the Freundlich model were also used to fit the isotherms. The parameters obtained from the isotherms are given in Table SD3. As seen from the table, although correlation coefficients (> 0.91) of all equations at all temperatures, the Fowler-Guggenheim model exhibited better fit to the adsorption data than the Langmuir model and the Freundlich model.

Thermodynamic parameters of adsorption

The adsorption process of phenol drifts can be summarized by the following reversible process which represents a heterogeneous equilibrium. The equilibrium constant may be expressed in terms of enthalpy change of adsorption (ΔH°) and entropy change of adsorption (ΔS°) as a function of temperature. The relationship between the K and the temperature is given by the van't Hoff equation. ΔH° and ΔS° can be obtained from the slope and intercept of a van't Hoff plot of $\ln K$ versus $1/T$.

Thermodynamic parameters, *i.e.*, free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) changes, were also calculated based on the adsorption isotherms using Fowler-Guggenheim and are given in Table 3.

The plot $\ln K$ versus ($1/T$) permits to calculate the enthalpy and entropy of adsorption of phenol on zeolite. As noticed ΔG° for all cases is negative which indicates the spontaneous nature of adsorption over HBEA. The negative values of ΔH° confirm the exothermic nature of adsorption. The negative values of the entropy change show the sys-

Figure 5. The adsorption kinetics of phenol with the initial concentration of 1 g/L over HBEA (◆), HFAU (▲) and HMOR (○). Solid line represents the simulation data based on the pseudo second-order adsorption kinetics.

tem exhibits random behaviour that have been decreased randomness at the solid/solution interface with some structural changes in the adsorbate and the adsorbent and an affinity of the adsorbent toward those molecules.

3.5. Influence of zeolite structure

Figure 5 shows the adsorption kinetics of phenol removal at room temperature by plotting the phenol up take capacity, q , versus time at 1 g/L initial phenol concentrations. For the given concentrations, the amount of phenol adsorbed by zeolite has been increased linearly with time in the beginning (first 5 minutes), then non-linearly at a slower rate and finally a plateau has been reached after 30 min which is called the equilibrium time.

To distinguish the effect of structure of these zeolites, experiments were performed with various zeolites (HFAU Si/Al ratio = 19), HBEA (Si/Al = 19) and Mordenite zeolite (Si/Al = 18).

Figure 5 shows that for a similar framework Si/Al ratio, HBEA and HFAU zeolites appear to be more efficient than HMOR. The high adsorption capacity of these adsorbents can be explained by the high micropore volume (0.245) compared to that of HMOR (0.170). On the other hand, HBEA zeolites have smaller pore size in comparison with HFAU zeolite, so the electrostatic interaction between phenol molecules and the pores becomes greater causing better adsorption.

A study of adsorption kinetics is desirable as it provides information about the mechanism of adsorption which is important for the efficiency of the process. Linear regression is used to determine the best fitting kinetic model, and the method of least squares is used for finding the parameters of the kinetic models.

The pseudo first order kinetic constant K and q were calculated from the plot of $\ln(q_e - qt)$ versus t as shown in Figure SD2a. The pseudo second-order kinetic constant, q_e and K were calculated from the plot of t/qt versus t as shown in Figure SD2b. In addition, the intraparticle diffu-

Figure 6. Adsorption isotherms obtained at pH 4 on (■) HFAU zeolite and (◆) HBEA zeolite for (black) nitrophenol and (grey) chlorophenol. Isotherms described by Fowler-Guggenheim model.

sion constant K_w (diffusion coefficient) was obtained from the plot of qt versus $t^{1/2}$ sorption process (Figure SD2c). The calculated kinetic constants and their corresponding coefficient of determination (R^2) are given on the figures. From Figures S2Da, S2Db and S2Dc, it was observed that except pseudo-second-order expression, no other model provided a better fit to the experimental kinetic data. The change in the sorption capacity with time is found to fit the pseudo-second-order equation relationship which is based on the adsorption capacity of solid phase. Because this equation is basically based on the sorption capacity, the description of sorption phenomenon suggests that the chemical reaction is rate controlling. It is indicated that these chemisorption systems involve vacancy forces through sharing or exchanging of electrons between the sorbent and the solutes. This confirms perfectly the hypothesis based on two types of sites [26–29]:

- the highly active sites: which react at the beginning time and are present in low concentrations on zeolite;
- less active sites: which react when the first sites are saturated, and are highly present at the surface of zeolite. Figure SD3 shows the different types of sites on HFAU zeolite.

Then, the influence of structure during ONP and OCP adsorption was studied. The results obtained are presented in Figure 6.

Figure 6 shows that nitrophenol and chlorophenol adsorption are favoured by using HFAU zeolite although it has the same Si/Al ratio than HBEA zeolite. This result can be explained by the difference in size between the adsorbents. Nitrophenols and chlorophenols (kinetic diameter 8.1 Å) are larger than phenols (6.7 Å), so they face difficulties in adsorption over HBEA. HBEA with the smaller pore diameter exhibits a lower adsorption capacity than HFAU.

Figure 7. Infrared spectra of the HBEA zeolite before and after adsorption of nitrophenol.

3.6. Adsorption mechanism

3.6.1. Infra-Red Spectroscopy

The sorption mechanism of nitrophenol on HBEA zeolite has been investigated firstly using IR spectroscopy. FTIR spectra of HBEA is shown in Figure 7, strong absorption bands near 1200–1000 cm^{-1} were observed and attributed to Si–O–Si asymmetric stretching vibrations. The broad band within the 3000–3750 cm^{-1} interval encompassing several not-well-resolved vibrations were ascribed to hydrogen-bonded SiOH groups [30, 31]. The band at 3745 cm^{-1} corresponds to external silanol groups.

The infrared spectra of HBEA zeolite after adsorption of nitrophenol in the 1100–1650 cm^{-1} region has confirmed the presence of adsorbed nitrophenol as shown in Figure 7. The bands between 1369 and 1479 cm^{-1} are attributed to HCH bending modes in nitrophenol. Infrared spectrum shows also a number of bands at 1620 assigned to OH deformation modes; 1590 is ascribed to C=C aromatic stretching vibrations, and 1531 is attributed to antisymmetric NO_2 stretching vibrations. While 1479 is described as C–H in-plane bending vibrations, 1336 and 1307 cm^{-1} are described by symmetric NO_2 stretching vibrations C–O stretching vibrations [32]. After the adsorption, the bands corresponding to (SiOSi) between 1100 and 1225 cm^{-1} were strengthened. This indicates that ONP was adsorbed principally by hydrogen bonding between zeolite oxygen and the hydrogens of the aromatic cycle and the ones of functional group.

3.6.2. Thermal desorption

Derivative weight thermograms of HBEA zeolite before and after nitrophenol adsorption are shown in Figure 8. HBEA zeolite had one degradation peaks at 80°C. These peaks are also visible after the nitrophenol adsorption which

Figure 8. TGA curves of the HBEA zeolite before (---) and after (—) adsorption of nitrophenol and derivative weight curves of the HBEA zeolite before (red line) and after (black line) adsorption of nitrophenol.

always translates the loss of hydration water. It is clear from the thermogram of the HBEA zeolite after nitrophenol adsorption that the two high temperature degradation peaks between 165–600°C are due to the presence of nitrophenol molecules. The first peak around 235°C represents the beginning of desorption of nitrophenol from HBEA micropores. The second peak around 525°C represents the oxidation of nitrophenol linked to the acid sites in the HBEA zeolite.

The presence of two peaks around 235 and 525°C highlights the Possibility for phenol to adsorb on two types sites over BEA zeolite, with two separate levels of adsorption strength.

3.7. Desorption and regeneration studies using Methanol

Desorption tests were conducted using methanol. The desorption was conducted on the spent adsorbent samples stemming from tests performed with initial PhOH concentrations ranging from 0.2 to 1.5 g/L and the adsorbent loading of 5 g/L. The spent adsorbents were agitated methanol solution. After filtration and washing with deionized water, the solid was dried at room temperature and weighed. We noticed that desorption was total.

Figure 9 shows consecutive adsorption–desorption cycle data. As noticed, no significant loss (around 6%) of adsorbent capacity was observed during five cycles of adsorption–desorption, demonstrating that the adsorbent was suitable for the design of a continuous sorption process.

3.8. Comparison of adsorption capacity of different adsorbent

Table 4 shows the parameters for phenol adsorption over different materials collected from the literature, in which the data is sorted by adsorption capacity Qads at equilibrium. Activated carbons have been shown to be the most effective adsorbents for phenol, apparently due to their surface areas,

Figure 9. Effect of regeneration by methanol of HBEA zeolite after adsorption of PhOH: (□) fresh zeolite, (Δ) after one cycle, (○) after five cycles.

Table 4. Adsorption capacity for the adsorption of phenols on various adsorbents collected from literature.

Adsorbent	Qads mmol/g	Reference
HBEA	0.44	This work
Rice husk	0.231	Kennedy <i>et al.</i> [33]
CAC	0.075	Radhika <i>et al.</i> [34]
LAC	0.102	Srivastava <i>et al.</i> [35]
Hexaniobate	0.18	Wei <i>et al.</i> [36]
BPC	0.945	Dursun <i>et al.</i> [37]
AP2.5	1.03	Moreno-Castilla <i>et al.</i> [25]
XAD4	0.5	Ming <i>et al.</i> [38]
Neutralized red mud	0.042	Tor <i>et al.</i> [39]

and other favourable surface properties [25, 37]. However, the carbon was partially regenerated under all the technics were used [7, 8]. There is thus our research is focused on zeolites efficient and recyclable adsorbents.

4. Conclusion

In this study, the adsorption of phenol drifts from aqueous solutions was investigated using zeolites. The results indicated that adsorption capacity of the adsorbent was considerably affected by the initial pH, the temperature and the solubility of molecule. For phenolic compound as SA with lower pKa value, along with the lower adsorption capacity on Zeolite that had been used were observed due to repulsion between dissociated molecules and the negative charge of framework oxygen of zeolite. Results obtained by FTIR proved that adsorption of phenol and its derivatives had occurred by physical interactions as Hydrogen bond interactions.

The equilibrium data were well described by the Fowler-Guggenheim model and the adsorption kinetics had followed the pseudo-second-order model. The equilibrium, kinetic and thermodynamic parameters for the adsorption of phenol onto zeolites were also determined. Thermody-

namic calculations indicated that the adsorption of phenol drifts over zeolite was spontaneous and exothermic reaction.

Regeneration tests showed that no significant loss of adsorbent capacity was observed during five adsorption-desorption cycles.

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