Adsorption of Phenol by N-cetylpridinium-modified Beta Zeolite

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Abstract-In this study, the removal of phenol from aqueous solution by β zeolite and surfactant-modified zeolite has been studied. Zeolite beta prepared by the hydrothermal method was modified by N-cetylpridinium bromide. The adsorbents were characterized by XRD, SEM, FTIR, and thermal method techniques. Under optimized conditions, the adsorption capacity ranges from 10 to 40 mg/g depending on the amount of the immobilized surfactant and the pH of the solution. Kinetic and thermodynamic issues of the reaction were studied and the corresponding parameters were calculated. At the studied temperatures, the ΔG of the reaction was negative. Equilibrium data was fitted to the Langmuir model indicating that the phenol adsorption was monolayer and chemisorption in nature.

Key words-Phenol; Adsorption Isotherms; Adsorption Kinetics; Adsorption Thermodynamics

I. INTRODUCTION

Phenol is one of the most common organic pollutants. It is toxic even at low concentrations and its presence in water can lead further to the formation of substituted compounds during disinfection and oxidation processes.

Many industries such as petroleum and petrochemical, coal conversion, pesticide, paint, pharmaceutical, plastic, paper, and phenol producing industries release phenolic compounds to the environment [1]. Removal methods of phenolic pollutants from aqueous solutions can be divided into three main categories physical, chemical, and biological treatments. Among them, physical adsorption is generally considered to be the most effective, low-cost and most frequently used method [2]. The most popular and widely used adsorbent material is activated carbon [3], [4], carbon nano tubes [5], modified granular charcoal [6] and zeolites [7]. Zeolites are hydrated aluminosilicate materials having cage-like structures with internal and external surface areas of up to several hundred square meters per gram and cation exchange capacities of up to several meq/kg [8]. Due to the net negative charge on the framework, natural zeolites usually have little or no affinity for anions or organics materials. To change the surface properties, one modification method which is widely employed is to use organic surfactants [9]. Thus, surfactant-modified zeolites (SMZ) have complex functional groups with positively charged exchange sites formed by the positive groups –NR+ of the surfactant directed towards the surrounding solution in the bilayer [10].

Beta zeolite is the only high silica zeolite possessing a three-dimensional system of large rings (rings of 12 oxygen atoms as the minimum constricting apertures). This gives β zeolite interesting potential applications in reactions where high thermal and hydrothermal stability and low steric restrictions are of paramount importance. The purpose of this study was to synthesize and to modify β zeolite for removal of phenol from the aqueous solutions. The effects of different experimental parameters on the adsorption capacity were studied and optimized.

II. METHODS

A. Synthesis and Modification of β zeolite

β zeolite was synthesized by hydrothermal method. A mixture containing of 120 g tetraethyl ammonium hydroxide (20 wt% in water), 2.23 g of NaAlO2, 0.90 g of KCl and 0.15 g of NaOH was stirred until it became transparent. Then 32.59 g of aerosil-200 was added to the mixture. The resulting homogeneous sol was transferred into a teflon-lined stainless-steel autoclave and heated to 170°C statically. After 40 h, the autoclave was quenched, the content filtered, and the solid washed with deionized water. After drying at 96°C overnight, the solid was calcined at 540°C for 20 h.

For modification, the concentration of CPDBr solution was kept under its CMC value (0.9mmol). 100 mL of CPDBr solution (50 or 100mmol.L-1) was placed in a flask containing 10 g of β zeolite. The mixture was shaken for 24 h at room temperature. The solid was filtered, washed with distilled water, and dried at 80°C.

The products were designated as SMZ-50 and SMZ-100 respectively. To calculate the amount of adsorbed CPDBr, its concentration in the filtrate was determined using a UV–Vis spectrophotometer (PG Instruments T70) at wavelengths of 255 nm. The values of 0.35mmol/g and 0.41mmol/g were respectively obtained for SMZ-50 and SMZ-100.

B. Characterization of the Adsorbent

The FTIR spectra of the adsorbents were prepared by a PerkinElmer Spectrum 65 spectrophotometer. Crystallinity of the materials was examined by X-ray diffraction method at 2θ range of 5-60° using a XRD: D8 Advance Bruker. The morphology of the synthesized adsorbents was studied by scanning electron microscopy (SEM) (AIS 2100, Japan). Thermal curves (TG and DTG) of the samples were taken by a Labsys TG/DSC analyser from 0 to 700°C at heating rate of 10°C/min under N2 atmosphere.

C. Adsorption Experiments

By dissolving appropriate amount of pure crystals of phenol (Merck) in double-distilled water, the standard stock solution (1000ppm) was prepared. The calibration plot of the absorbance versus concentration was linear up to 50ppm with correlation coefficient of (R² = 0.99).

To study the kinetics and equilibrium of the adsorption, batch technique was used by placing known quantity of the adsorbent in glass bottles containing 50ml of aqueous solution of phenol with predetermined concentration. In order to evaluate the kinetic data, separate flasks were prepared for...
each time interval (1h to 16 h) and only one flask was taken at the desired time. The adsorbent was separated by centrifugation and the concentration of phenol in the filtrate was determined using a UV–Vis spectrophotometer (PG Instruments T70) at wavelengths of 270 nm [11]. The amount of adsorbed phenol was calculated according to the following equation:

\[ q_e = \frac{(C_0 - C_e) V}{m}. \]  (1)

Where \( q_e \) is the amount of adsorbed phenol (mg/g), \( C_0 \) and \( C_e \) are respectively the initial and equilibrium concentrations of phenol in liquid phase (mg/L), \( V \) is the volume of the solution (L), and \( m \) is the mass of the adsorbent (g). To construct the adsorption isotherms, known amount of the adsorbent was added to 25 ml of the phenol solution in concentration range of 50 to 400ppm. Initial pH of 2.5 to 10.5 and temperatures of 25, 35, 45 and 55ºC were examined.

III. EXPERIMENTS AND RESULTS

A. Characterization of Synthesized Adsorbents

The FTIR spectra of β zeolite, SMZ-50 and SMZ-100 are shown in Fig. 1. The characteristic aluminosilicate bands of β zeolite were identified in the regions of (420–500cm\(^{-1}\)) and (950–1200cm\(^{-1}\)) (Fig. 1a). In the first region (420–500cm\(^{-1}\)), the band arising at 457cm\(^{-1}\) refers to the bending mode of Si–O–Al vibration and is assigned as T–O bending mode (where T=Si or Al). In the second region (950–1200cm\(^{-1}\)), the band at 1089cm\(^{-1}\) refers to the asymmetric stretching mode of Si–O–Si vibration and is assigned as T–O stretching mode. The band at 797cm\(^{-1}\) is assigned to the symmetric stretching vibration mode of O–T–O groups. In the spectra of SMZ-50 and SMZ-100 (Fig. 1b, Fig. 1c), three new bands corresponding to the CPDBr immobilized on zeolite were appeared. The C–H stretching vibrations of the hydrocarbon chain at 2917 and 2850 cm\(^{-1}\) were observed. The band at 1400-1500 refers to the symmetric stretching mode of N–C vibration and the band at 3418cm\(^{-1}\) refers to aromatic ring of CPDBr vibration [12].

![Fig. 1 FT-IR spectra of (a) β zeolite, (b) SMZ-50 and (c) SMZ-100](image)

The relative intensity of these bands increases with increasing the amount of CPDBr. In these spectra, the variations in the frequency of the bands assigned to the β zeolite were insignificant. This indicated that the zeolite structure remains unchanged after modification.

The XRD patterns of SMZs are very similar to that of the parent zeolite indicating that the crystalline nature of the zeolite remained intact after the immobilization of CPDBr. The sharp diffraction lines at 7.8° and 22.4° along with the small peaks of β zeolite were observed in the modified samples (Fig. 2).

![Fig. 2 XRD pattern (a) β zeolite, (b) SMZ-50 and (c) SMZ-100](image)

The surface morphology of β zeolite and SMZs samples were examined by SEM technique (Fig. 3). Aggregation of the surfactant molecules on the zeolite surface is clearly observed in SMZ-100 sample (Fig. 3c). The mean particle size of β zeolite determined from the SEM images was 70 nm.

In the TG and DTG curves of β zeolite, the weight loss observed between 40-150ºC is attributed to the loss of water (Fig. 4). Another weight loss peaks between 250 and 400ºC observed in the thermal curves of SMZ-50 and SMZ-100 corresponded to the thermal decomposition of CPDBr. The relative intensity of this peak increases with increasing the amount of CPDBr.

B. Effect of Adsorbent Dosage

![Fig. 3 SEM images of (a) β zeolite, (b) SMZ-50 and (c) SMZ-100](image)

The effect of adsorbent dosage on the removal of phenol is shown in (Fig. 5).
At adsorbent dosage of 0.125 to 4.0 g and at concentration of 300 mg/L, the phenol uptake by SMZ-100 varied from 6.95 to 45 mg/g, from 6.3 to 43 mg/g for SMZ-50 and from 4.1 to 40 mg/g for β zeolite. It was concluded that with increasing adsorbent dosage more active sites were available, making phenol penetration to the adsorption sites easier and increasing the adsorption capacity [13]. The removal of phenol remained almost constant at adsorbent dosage higher than 0.2 g.

This type of interaction is expected to enhance the adsorption as the pH decreases.

At pH greater than the pHZPC of β zeolite, which is 6.7, the surface of the adsorbent is negatively charged, and above the pKa of the solute, phenol exists mainly in the phenolate anions. Therefore, as the pH increases, the concentration of the phenolate and hence, the negative charge of β zeolite increases which results in high electrostatic repulsion between the solute molecules and β zeolite surface. Thus, it could be concluded that β zeolite is a potential adsorbent for phenol only at lower pH because its capacity sharply decreases at pH higher than 8.0.

In the SMZ samples, adsorption capacity increased with increase of pH values. There are three potential mechanisms controlling phenol adsorption on the SMZ: (i) electrostatic interactions between the positively charged head groups of the surfactant and the negatively charged functional groups phenolate anions, (ii) partitioning of phenol molecules into surfactant layers and (iii) hydrophobic interactions between the hydrophobic tails of surfactant monolayer and the hydrophobic functional groups of phenol molecule [15]. This may be explained on the assumption that phenol will be dissociated to C6H5O− at pH > pKa (pKa = 9.7) and such negatively charged species are easily adsorbed on positive zeolite surfaces. This is the pre-dominant parameters for phenol adsorption at higher pHs [16]. It is concluded that at low pH, the removal capacity of β zeolite and the SMZ forms is very close to each other but the capacity of SMZ sharply increased at pH higher than 8.0. In this work the optimized pH for SMZ-100 and SMZ-50 was 10.5 and for β zeolite was 2.5.

C. Effect of pH on Phenol Adsorption

Adsorption of phenol by SMZ-100, SMZ-50 and β zeolite at pH ranges of 2.5 to 10.5 is illustrated in (Fig. 6). Phenol adsorption capacity at unmodified zeolite decreased with increasing pH. To account for this observation, the adsorption mechanisms should be contemplated. The factors that affect phenol–zeolite interaction are solubility of phenol in water, repulsion between phenolate anions and negatively charged zeolite, possible encapsulation of phenols into the pores and hydrogen bonding between hydroxyl groups of phenols and zeolite surface. The aromatic rings of the adsorbate act as the electron acceptors and the basic sites on surface silanol/aluminoil sites of zeolite serve as the donors [14].

D. Effect of Initial Concentration

Increasing the initial phenol concentration would increase the mass transfer driving force and therefore the rate at which phenol molecules pass from the solution bulk to the particle surface.

In this research, the adsorption capacity at equilibrium (qe) increased with an increase in the initial phenol concentrations from 50 to 400 mg/L Fig (7). As the adsorbent offers a limited number of surface binding sites, the adsorbent showed saturation at high phenol concentration.

E. Adsorption Isotherms

Adsorption isotherm reflects the relationship between the amount of an adsorbed solute and its concentration in the...
TABLE I ISOTHERM PARAMETERS OF PHENOL ADSORPTION BY SMZ-100, SMZ-50 AND β ZEOLITE AT 25°C

<table>
<thead>
<tr>
<th>Isotherm parameters</th>
<th>SMZ-100</th>
<th>SMZ-50</th>
<th>β zeolite</th>
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<tbody>
<tr>
<td><strong>Langmuir</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_0$</td>
<td>37.037</td>
<td>38.461</td>
<td>58.823</td>
</tr>
<tr>
<td>$b$</td>
<td>0.125</td>
<td>0.037</td>
<td>0.0083</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.997</td>
<td>0.983</td>
<td>0.981</td>
</tr>
<tr>
<td><strong>Freundlich</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_f$</td>
<td>7.046</td>
<td>3.380</td>
<td>1.106</td>
</tr>
<tr>
<td>$1/n$</td>
<td>0.365</td>
<td>0.482</td>
<td>0.676</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.938</td>
<td>0.969</td>
<td>0.978</td>
</tr>
</tbody>
</table>

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called separation factor (or equilibrium parameter), RL, which is defined by the following equation:

$$RL = 1/(1 + b C_0).$$

The adsorption is considered as irreversible when $RL = 0$, favourable when $0 < RL < 1$, linear when $RL = 1$, and unfavourable when $RL > 1$. The values of $RL < 0.2$ obtained in this research indicated that the sorption of phenol by the adsorbents is favourable. Value of $0 < b < 1$, suggesting the adsorption is favourable.

In this study the values of $b$ were found to be 0.127, 0.037 and 0.0083 and the value of $q_0$, was 37.037, 38.461 and 58.823 for SMZ-100, SMZ-50 and β zeolite, respectively at 25°C, indicating the data are well fitted with the Langmuir model of adsorption. The propedit of equilibrium data in the Langmuir isotherm expression predicted the monolayer coverage of phenol by the studied adsorbents.
The pseudo-first-order rate equation of Lagergren is generally described by the following equation \[19\].

\[
d\frac{q_t}{dt} = k_1(q_e - q_t). \quad (5)
\]

Where, \(k_1\) is the pseudo-first-order rate constant (1/h).

After integration, by applying the conditions, \(q_t=0\) at \(t=0\) and at \(t=t\), \(q_t=q\) becomes:

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

Where \(q_e\) is the amount of phenol adsorbed at equilibrium (mg/g) and at time \(t\) (h). Value of \(k_1\) was calculated from the plots of \(\log (q_e - q_t)\) versus \(t\) for different concentrations of phenol (Fig. 10). The value of \(k_1\) and the correlation coefficients showed that the plots were linear (\(R^2 >0.93\)) (Table 2). The values of \(k_1\) were 0.227, 0.278, and 0.359 (1/h) and the \(q_e\) values were 40.644, 47.424 and 51.05 (mg/g) respectively for SMZ-100, SMZ-50 and \(\beta\) zeolite at 25°C.

The sorption data were also analyzed in terms of a pseudo-second-order mechanism by the following equation \[20\]:

\[
d\frac{q_t}{dt} = k_2(q_e - q_t)^2. \quad (7)
\]

Integrating and applying the boundary condition, \(t = 0\) and \(q_t=0\) to \(t = t\) and \(q_e=q\), equation takes the form:

\[
t/q_t = 1/k_2q_e^2 + (1/q_e) t. \quad (8)
\]

If the second-order kinetics model is applicable, the plot of \(t/q_t\) against \(t\) should give a linear relationship from which the constants \(q_e\) and \(k_2\) can be determined (Fig. 11). Also, the predicted values of \(q_e\) using the pseudo-second order model are very close to the theoretical values (55.55, 52.631 and 58.823 (mg/g) for SMZ-100, SMZ-50 and \(\beta\) zeolite, respectively with phenol initial concentration of 300 mg/g). Moreover, they defined the second order rate index, \(k_2 q_e\), and proposed that this index was suitable to describe the adsorption kinetics. In this study, the values of \(k_2 q_e\) was 0.461, 0.499 and 0.058 respectively or SMZ-100, SMZ-50 and \(\beta\) zeolite. As the \(k_2 q_e\) value is the inverse of the half-life of adsorption process, the adsorption kinetics gets faster in this order, which is consistent with the experimental observations.

The intra-particle diffusion model was also used to analyse and elucidate the diffusion mechanism \[21\].

The overall adsorption process may be controlled either by one or more steps. Film or external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface, or a combination of more than one step. In a rapidly stirred batch
adsorption, the diffusive mass transfer can be related by an apparent diffusion coefficient, which will fit the experimental adsorption-rate data. The intraparticle model equation is given as follows:

$$q_t = kp t^{1/2} + C.$$  \hspace{1cm} (9)

Where, $q_t$ is the amount of phenol adsorbed at equilibrium (mg/g) at time t, C is the intercept and kp is the intra-particle diffusion rate constant (g/g h$^{-1}$). According to Equation 11, if the Weber–Morris plot of $q_t$ versus $t^{1/2}$ gives a straight line, then the adsorption process is controlled by intra-particle diffusion (Fig.12). The adsorption constant kp, at phenol concentration of 300 mg/L for β zeolite was found to be 9.276, 9.732 and 8.019 for β zeolite, SMZ-50 and SMZ-100 respectively (with R$^2$ values of 0.97, 0.96 and 0.96 respectively) therefore, intra-particle diffusion has been reported to be the rate-limiting factor (Table 2).

Good correlation coefficients higher than 0.98 were obtained within the contact time of only 8h, which shows that the uptake process follows the pseudo-second-order rate expression. In addition, a good fit of experimental data to pseudo-second-order equation suggests that the overall rate of adsorption process appears to be controlled by chemisorption process, which involved forces through sharing or exchange of electrons between the adsorbent and adsorbate. This result is consistent with the results obtained in [22].

**H. Effect of Temperature**

The effect of temperature on the adsorption of phenol on SMZs and β zeolite is shown in Fig.13. With the increase in temperature, the adsorptivity of phenol increases from 29.991 to 31.52 (mg/g) for SMZ-100, 26.791 to 28.94 (mg/g) for SMZ-50 and 22.32 to 25.11 mg/g for β zeolite respectively. Since adsorption is an exothermic process, it would be expected that an increase in temperature of the adsorbate–adsorbent system would result in decreased sorption capacity. However, if the adsorption process is controlled by the diffusion process the adsorption capacity will show an increase with an increase in temperatures. This is basically due to the fact that the diffusion process is an endothermic process [23]. With an increase in temperature, the mobility of the phenolate ions increases and the retarding forces acting on the diffusing ions decrease, thereby increasing the adsorptive capacity of adsorbent. Therefore, the increase in adsorption capacity with an increase in temperature may be attributed to chemisorption. This result is consistent with the results obtained in [24].

**I. Thermodynamic Parameters**

The change in Gibbs free energy, enthalpy and entropy of adsorption were calculated using the following equations:

$$K_c = q_e / c_e.$$  \hspace{1cm} (10)

$$\Delta G_o = \Delta H_o - T \Delta S_o.$$  \hspace{1cm} (11)

Where R is gas constant and Kc is the equilibrium constant and T is the temperature (K). According to Van’t Hoff equation

$$\log K_c = \Delta S_o/R – \Delta H_o/RT.$$  \hspace{1cm} (12)

Plot of log Kc versus 1/T was linear (Fig.14). Positive values of $\Delta H_o$ (8.38 KJ/mol for SMZ-100, 8.85 KJ/mol for SMZ-50 and 5.40 KJ/mol for β zeolite) showed the endothermic nature of adsorption.

The change in the standard free energy $\Delta G_o$ with negative values of -7.24 kJ/mol for SMZ-100, -5.15 kJ/mol for SMZ-50 and -3.01 kJ/mol for β zeolite showed that adsorption of phenol by these three adsorbents was feasible and spontaneous at 25, 35, 45 and 55°C. The positive values of $\Delta S_o$ (22.106 J/molK for SMZ-100, 15.75 J/molK for SMZ-50 and 9.21 J/molK for β zeolite) suggested the increased randomness at the solid/solution interface during the adsorption of phenol on adsorbents [25]. The thermodynamic parameters for the removal of phenol by SMZ-100, SMZ-50, and β zeolite were given in Table 3.

**TABLE III THERMODYNAMIC PARAMETERS PHENOL ADSORPTION BY SMZ 100, SMZ 50 AND β ZEOLITE**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Thermodynamic parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta H^o$ (KJ/mol)</td>
</tr>
<tr>
<td>SMZ-100</td>
<td>8.38</td>
</tr>
<tr>
<td>SMZ-50</td>
<td>8.85</td>
</tr>
<tr>
<td>β zeolite</td>
<td>5.40</td>
</tr>
</tbody>
</table>
IV. CONCLUSION

In this study the capability of β zeolite and SMZs for removal of phenol from aqueous solution was evaluated. The results showed that the increase of pH to high alkalinity resulted in the increase in adsorption capacity of SMZs and decrease in adsorption capacity of β zeolite. Increase in the CPDBr concentration, initial phenol concentration, contact time and temperature increased the phenol adsorption capacity. The kinetic data showed that the adsorption of phenol followed the pseudo-second-order kinetic model and the equilibrium adsorption isotherm of phenol followed the Langmuir model. Thermodynamic calculations showed that the phenol adsorption process was feasible and spontaneous and endothermic in nature.

Fig. 14 Plots of log Ke versus (1/T) ((phenol concentration=400ppm, contact time=8h, adsorbents dosage=0.2g, and optimized pH at 25-55°C)

REFERENCES