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Adsorption of organic compounds from aqueous solution onto the synthesized zeolite

Wen-Tien Tsai [a,*], Kuo-Jong Hsien [b], Hsin-Chieh Hsu [b]

[a] Graduate Institute of Bioresources, National Pingtung University of Science and Technology, Pingtung 912, Taiwan
[b] Department of Environmental Engineering and Science, Chia Nan University of Pharmacy and Science, Tainan 717, Taiwan

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ABSTRACT

A novel zeolite was synthesized, characterized and employed for the adsorption of methylene blue (cationic dye) and bisphenol-A in aqueous solution. The pore properties of the synthesized zeolite have been determined using N_2 adsorption–desorption isotherms, indicating that it is a supermicroporous adsorbent with BET surface area of over 400 $m^2\,g^{-1}$. Based on the XRD image, it was indicative of the probable formation of zeolite-P2 in the hydrothermal synthesis. The metal content and zeta-potential of the zeolite were also measured to examine the hydrophilicity and the effect of pH on the surface charge, respectively. It was found that the synthesized zeolite exhibited significantly higher adsorption capacity for methylene blue than that for bisphenol-A due to the difference in molecular properties. Kinetic studies at 25 °C indicated that the adsorption of methylene blue well followed the pseudo-second-order model and could be elucidated by considering the pore property and surface charge of the synthesized zeolite. The kinetic parameters thus obtained from the fittings of the model were dependent on initial dye concentration, pH, and adsorbent mass.

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1. Introduction

Colored dye effluents, discharged from the dyestuff manufacturing and textile industries, may exhibit toxic effects toward microbial populations and can be toxic and/or carcinogenic to mammalian animal [1]. Therefore, environmental legislation has imposed stringent effluent limits on the concentrations of dye pollutants as chemical oxygen demand (COD) and biochemical oxygen demand (BOD). For example, the limits of BOD and COD in the industrial effluents from dyeing/textile industries have been set at 30 $mg\,dm^{-3}$ and 100–160 $mg\,dm^{-3}$, respectively, according to the Effluent Standard in Taiwan [2]. Physical adsorption has been proven to be the most efficient method for quickly lowering the concentration of dissolved dyes in an effluent [3]. In this regard, activated carbon is the most widely used adsorbent for removal of dyes from the aqueous solution, but it presents some disadvantages. It is flammable and difficult to regenerate as it needs to be reclaimed [4]. Also, mineral impurities and oxygen-containing functional groups naturally occurring in activated carbon could show it to be weakly hydrophilic [5], resulting in the weak affinity for the adsorption of cationic or anionic dyes from the aqueous solution. Therefore, inorganic adsorbents (e.g., zeolite) with high surface areas have been used as alternatives to carbon adsorbent [6,7].

Zeolite is an aluminosilicate mineral with unique characteristics of crystalline and microporous structure. Its adsorption properties are strongly dependent on not only the pore properties, but also the chemical properties. Such materials therefore possess a well-defined bimodal pore size distribution with the intracrystalline micropores (~0.3–1.0 nm) linked together through a network of macropores having a diameter of the same order as the crystal size (~1–5 μm) [5]. With respect to the chemical properties, the ratio of silicon (or silica) to aluminum (or alumina) of zeolite determines its surface chemistry. The dealuminated zeolite provides a hydrophobic adsorbent that the Si/Al ratio is relatively higher than that (1–5) of fresh zeolite [8]. In recent years, commercial zeolites with the unique surface and pore properties have been increasingly studied for the liquid adsorption of dissolved pollutants in water and/or wastewater [9]. However, few studies have focused on the adsorption of cationic dyes by synthesized zeolites [9–11]. Metes et al. [9] studied the adsorption of residual organic pollutants from flocculated printing ink wastewater onto commercially synthesized zeolites including ZSM-5 and NH_4-Beta, and found that the adsorption is effective, fast, and independent of pore structure. Wang et al. [10] investigated the adsorption of basic dyes including methylene blue, crystal violet, and rhodamine B from aqueous solution onto synthesized zeolite (MCM-22). The results showed that the adsorption kinetics and isotherms could be well described by the pseudo-second-order model and the

* Corresponding author. Tel.: +886 8 7703202x7399; fax: +886 8 7740134.
E-mail address: wttsai@mail.npust.edu.tw (W.-T. Tsai).

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two-parameter model (i.e., the Langmuir and Freundlich), respectively. Juang et al. reported an investigation using synthesized zeolite (MCM-41) for the removal of basic dye (i.e., Basic Violet 10) from aqueous solution, and found that MCM-41 was an efficient adsorbent because of its large pore-space and the strong interactions between the basic dye and surface hydroxyl groups of MCM-41. The pseudo-second-order kinetic model also exhibited a good correlation for the removal of basic dye from aqueous solution.

For the purpose of serving it as an effective decolorizing adsorbent, the synthesized zeolite with unique pore structure was prepared using hydrothermal synthesis in the present study and was also used as adsorbent for the adsorption of cationic dye in aqueous solution. A basic dye, methylene blue (i.e., Basic Blue 9, or C.I. 52015), was selected as a model compound in this work mainly due to its adsorption as a means of determining the adsorption characterization of porous adsorbent with a potential applications in the removal of pollutants from aqueous solution [12], and in the use of determining surface areas of porous solids [13]. Also, the water-soluble dye has some industrial applications, which may include the dyeing of silk, leather, paper, wool and cotton, and the production of ink and copying paper [14], the quality control test of concrete and mortar [15], as well as the development of humidity-sensitive material (i.e. methylene blue-loaded zeolite) [16]. Although methylene blue is not highly toxic to human being, it can cause eye/skin irritation, and human systemic effects including cyanosis and blood changes [17]. For comparison, bisphenol-A (i.e., 4,4′-isopropylidenediphenol), one of endocrine disrupting chemicals, was selected as another adsorbate in the work because its molecular size is similar to methylene blue, but its chemical properties are very different from the cationic dye. In the previous study [18], the adsorption behaviors of bisphenol-A from aqueous solution onto hydrophobic zeolite (Si/Al ratio of about 100) at 25 °C have been investigated into the effects of particle size, initial bisphenol-A concentration, initial solution pH, and adsorbent dosage, showing that the Y-type zeolite could be employed as an effective adsorbent for removal of bisphenol-A and the adsorption followed the pseudo-second-order kinetic model. The present study aimed at providing one option for utilizing the synthesized zeolite in the water treatment applications. Thus, the dual objectives of this work were to characterize the chemical/physical properties of the synthesized zeolite under the specified conditions, and also to examine the fitness to pseudo-second-order model of the data for analyzing the adsorption kinetics at different initial adsorbate concentrations, adsorbent masses and initial pH in aqueous solutions.

2. Methods

2.1. Materials

Sodium silicate solution (composition: SiO_2 26.7% and Na_2O 8.2%; Merck Co., Germany), sodium aluminate (composition: Al_2O_3 53.8% and Na_2O 44.3%; Aldrich Chemical Co., USA) and sodium hydroxide (99% purity; Mallinckrodt Chemical Co., USA) were used to make the synthesized zeolite with high surface area. The cationic dye used as the main target adsorbate in the present study is methylene blue (99+% purity), which was purchased from Katayama Chemical Co. (Japan). Bisphenol-A (99+% purity), which was purchased from Aldrich Chemical Co. (USA), was selected as a comparative adsorbate due to its similar size to methylene blue. The molecular structures of these adsorbates were shown in Fig. 1. Table 1 compared selected molecular characteristics of methylene blue and bisphenol-A [19,20]. H_2SO_4 (96 wt%; Merck Co., Germany) and NaOH (99% purity; Mallinckrodt Chemical Co., USA) were used

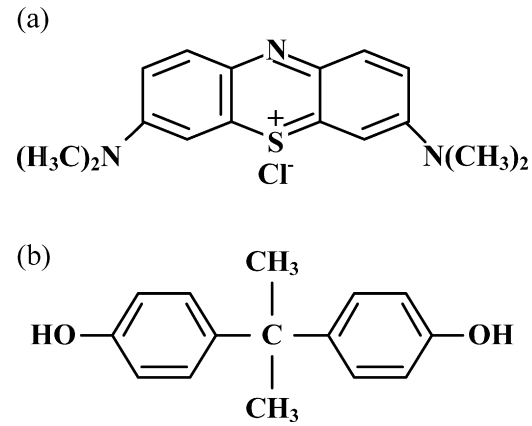

Fig. 1. Molecular structures of (a) methylene blue, and (b) bisphenol-A, used as adsorbates in the study.

for adjusting initial pH value of aqueous solution to obtain the extent of the adsorption. In the work, the reverse osmosis (RO)-purified water was used in the zeolite syntheses and the adsorption tests.

2.2. Zeolite syntheses

As referred to the studies in the literature [21], the zeolite adsorbent was synthesized from seed gel and feed stock gel with molar compositions $10.67Na_2O{:}1Al_2O_3{:}10SiO_2{:}180H_2O$ and $4.3Na_2O{:}1Al_2O_3{:}10SiO_2{:}180H_2O$, respectively. The gel slurries were prepared in the polyethylene bottle by using sodium aluminate, RO water, sodium hydroxide, and sodium silicate solution with specified amounts. Before crystallization, the gels were aged using proper agitation with a magnetic stirrer/hot plate (Model No.: PC-420; Corning Co., USA) while the sodium silicate solution was added drop by drop. The gel slurries prepared were then mixed at a specific ratio to obtain the mixing gel with a molar composition $4.62Na_2O{:}1Al_2O_3{:}10SiO_2{:}180H_2O$. Based on the preliminary results on the surface areas of the resulting synthesized zeolites, the hydrothermal crystallization experiments were carried out in a stirred pressure reactor (Model No.: 4563; Parr Instrument Co., USA) kept at 100 °C, 200 rpm and 1 atm for a synthesis time of 24 h. Afterward, the sample solution was first cooled to room temperature. After the upper layer of the product solution was removed by decanting, the lower product slurry was washed sequentially with RO water and ultrasonic cleaning (about 10 min) three–four times to remove the ions and other residues. The resulting zeolite product was finally dried at 100 °C for 24 h, and stored in the desiccator prior to the physical and chemical characterizations. In order to determine the reproducibility of the hydrothermal synthesis on the basis of pore properties, the zeolite synthesis was replicated three times.

Table 1
Selected molecular characteristics of methylene blue and bisphenol-A used as adsorbates.

Property	Methylene blue[a]	Bisphenol-A[b]
Molecular weight (g mol^{-1})	284.29[c]	228.31
Molar volume (cm^3 mol^{-1})	241.9	191.1
Width (nm)	1.43	0.94
Depth (nm)	0.61	0.53
Thickness (nm)	~0.4	0.43

[a] [19].
[b] [20].
[c] Does not include associated chloride ion.

2.3. Characterization of the synthesized zeolite

The pore structures of the synthesized zeolite relating to surface areas, total pore volume and average pore size were obtained by measuring the nitrogen adsorption–desorption isotherms at −196 °C in a surface area & porosity analyzer (Model ASAP 2020; Micromeritics Co., USA). In order to evaluate its precision, the pore properties of standard alumina used as a reference sample were repeatedly measured at least two times before being measured in the experiments, showing that it seemed to be negligible because relative errors were within 2% according to the data on the BET surface areas. Suppose all the pores in the synthesized zeolite are straight, cylindrical, not interconnected, and have the same diameter and length, the average pore diameters may be thus found by equating the data on V_t and S_{BET} [22]. Further, the true density (ρ_s) of the samples was measured by a helium displacement method with a pycnometer (Model AccuPyc 1330; Micromeritics Co., USA). From the data of V_t and ρ_s, the particle density (ρ_p) and porosity (ε_p) can be thus obtained [22]. The X-ray diffraction (XRD) was employed to observe the crystal components in the synthesized zeolite using a Rigaku MiniFlex instrument (Cu-Kα) between 2θ of 5° and 50° with a scanning velocity of 3°/min. In order to elucidate the particle size of the resulting zeolite, the surface morphologies of the powder sample were examined using the scanning electron microscopy (SEM) by an S-3000N (Hitachi Co., Japan) apparatus. Prior to the observation, the surface of the sample was coated with a thin, electric conductive gold film. The surface charge at the surface of the particle is very important because of the microscopic size of the colloids suspended in the aqueous liquid. The zeta-potentials of the synthesized zeolite at various values of pH were determined by a Zeta Meter System 3.0 (ZETA-METER Inc., USA). The detailed procedure was described in the previous study [18]. Also, main metal elements (i.e., Si, Al and Na) were analyzed by an inductively coupled plasma-atomic emission spectrometer (Model ICAP9000, Jarrell-Ash Co., USA) for examining the chemical compositions in the synthesized zeolite.

2.4. Adsorption studies

All the experiments of adsorption kinetics were carried out in a *ca.* 3-dm^3 stirred batch adsorption apparatus with four baffles as similarly described in the previous study [18]. The effect of agitation speed at 200, 400 and 600 rpm on the adsorption uptake was first tested under the initial adsorbate concentration of 20 mg dm^{-3}, temperature of 25 °C, pH of 7.0 and dosage of 0.5 g per 2.0 dm^3, showing that it seemed to be negligible. This result could be explained from the fact that the strong turbulence and the very small thickness around the adsorbent particles in the boundary layer occurred and induced a significant reduction in the boundary layer resistance [23], which was also in agreement with those of Hsu et al. [24] for the adsorption behaviors of basic dyes on activated clay, those of Al-Qodah [25] for the removal of dyes with shale oil ash, and those of Tsai et al. [26,27] for the adsorption of paraquat onto activated bleaching earth and the adsorption of methylene blue onto acid-activated andesite. Thus, the adsorption behaviors of the synthesized zeolite were studied at a fixed agitation speed (i.e., 400 rpm) under the variations of initial adsorbate concentrations (i.e., 10–50 mg dm^{-3}), pH (i.e., 3–11), and adsorbent dosage (i.e., 0.25–0.75 g dm^{-3}). The solution sample (about 10 cm^3) was taken at specified time up to 2 h and then filtrated with fiber membrane (Cat. No.: A045A025A; ADVANTEC MFS, Inc., Japan). The adsorbate concentration analysis of filtrate solution was immediately measured with UV/Visible spectrophotometer (Model: U-2001; Hitachi Co., Japan) at a 221 nm and 661 nm wavelengths for bisphenol-A and methylene blue, respectively. The amount of adsorbate adsorbed (q_t, mg g^{-1}) was determined as follows:

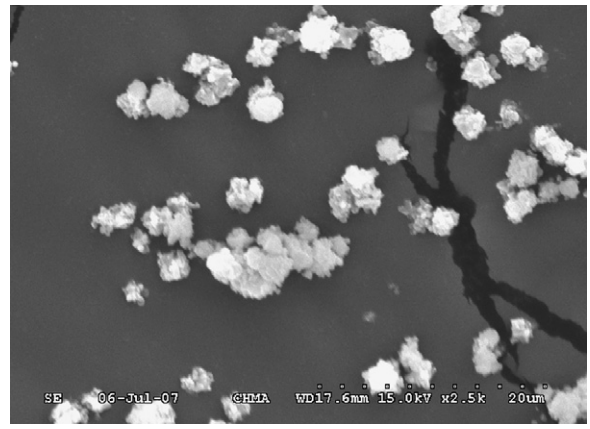

Fig. 2. SEM photograph of the synthesized zeolite used as adsorbent in the study.

$$q_t = (C_o - C_t) \cdot \frac{V}{m} \quad (1)$$

where C_o and C_t are the initial and liquid-phase concentrations of the adsorbate solution at t time (mg dm^{-3}), respectively, V is the volume (*ca.* 2.0 dm^3) of aqueous solution containing adsorbate, and m is the mass of dry adsorbent used (g). In order to evaluate the statistical significance of data in the kinetic experiments, a preliminary experiment was also repeated under identical conditions, showing that the reproducibility of the measurements is within 5% in the adsorption experiments.

3. Results and discussion

3.1. Characterization of the synthesized zeolite

3.1.1. Physical characterization

As shown in the SEM image (Fig. 2), it revealed that the synthesized adsorbent was an aggregation of zeolite crystals with diameters up to ~1 μm. The zeolite powder sample with about 10 μm of the maximum size possesses an appreciable proportion of fine forms with the particle sizes centered near 2 μm. The data in Table 2 indicated the surface areas, total pore volume, particle density, true density, and porosity of the synthesized zeolite. The value of the BET surface area was 400 ± 10 m^2/g, which was lower than the data (about 500 m^2 g^{-1}) of the hydrophobic zeolite [18]. Fig. 3 showed the N_2 adsorption/desorption isotherms of the synthesized zeolite. It is clear that the isotherms are characterized by a very sleep "knee" pattern succeeded by a more gradual approach to the plateau at most of relative pressures (P/P_0), and shows a "tail" as relative pressure is approached to 1, indicating that the zeolite adsorbent is mainly microporous and has a relatively small external surface from the nonporous crystal, and is thus characterized by the combination of the combination of Type I and Type II isotherms

Table 2
Main physical properties of the synthesized zeolite used as adsorbent in the present study.

S_{BET}[a] (m^2/g)	S_L[b] (m^2/g)	V_t[c] (cm^3/g)	D_{avg}[d] (Å)	ρ_s[e] (g/cm^3)	ρ_p[f] (g/cm^3)	ε_p[g] (−)
402.96	608.82	0.27	26.95	1.94	1.27	0.35

[a] BET surface area.
[b] Langmuir surface area.
[c] Total pore volume.
[d] Pore diameter, estimated by $4V_t/S_{BET}$.
[e] True density.
[f] Particle density, calculated by: $\rho_p = 1/[V_t + (1/\rho_s)]$.
[g] Particle porosity, computed by: $\varepsilon_p = 1 - (\rho_p/\rho_s)$.

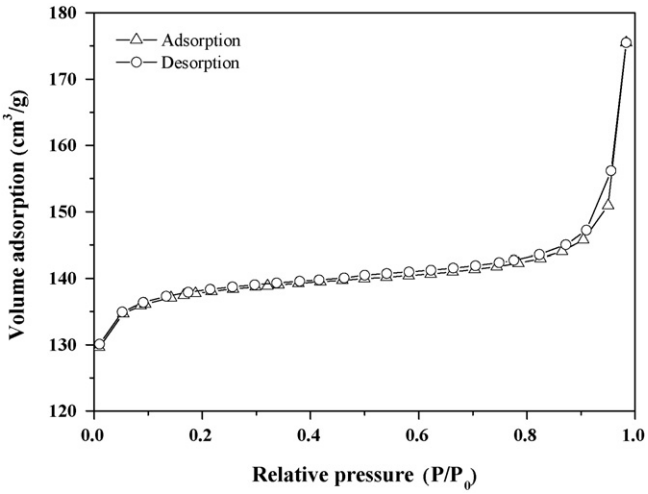

Fig. 3. Nitrogen adsorption/desorption isotherms of the synthesized zeolite.

according to the Brunauer, Deming, Deming and Teller (BDDT) classification [28]. To provide an approximate quantitative framework of the micropores in the synthesized zeolite, the Horvath-Kawazoe method was used for determining its physical geometry, indicating that the size of micropore centered on about 0.5 nm. As compared to the molecular sizes of the adsorbates (Table 1), the rate of diffusion in the synthesized zeolite might become relatively slow because the so-called restricted diffusion or configurational diffusion occurred when the molecular size of adsorbate was close to the pore size of adsorbent [29].

3.1.2. Chemical characterization

It is well known that the zeolites with increased Si/Al or SiO_2/Al_2O_3 ratio make them more hydrophobic [8]. Based on the data obtained by using the inductively coupled plasma-atomic emission spectrometer, the main metal contents of the synthesized zeolite were given below: Al (4.30 wt%), Na (7.79 wt%), and Si (19.4 wt%). The zeolite, as synthesized, has a ratio of about 5, which made it hydrophilic. The surface charges (denoted as zeta-potential) of the synthesized zeolite may arise from the functional groups at the surface such as hydroxyl group (–OH). Fig. 4 showed its zeta-potential values as a function of initial solution pH. As shown in Fig. 4, the surface charge decreased as the pH increased from 3 to 9. Generally, as the pH increased the surface hydroxides lose their protons in response to the increasing number of negatively charged

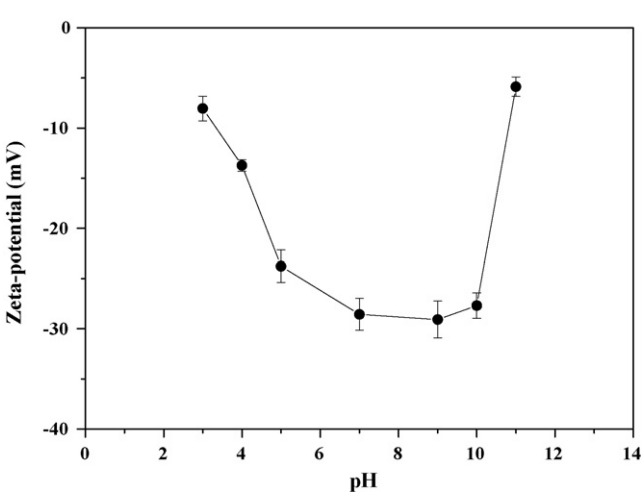

Fig. 4. Variation of zeta-potential of the synthesized zeolite vs. initial solution pH.

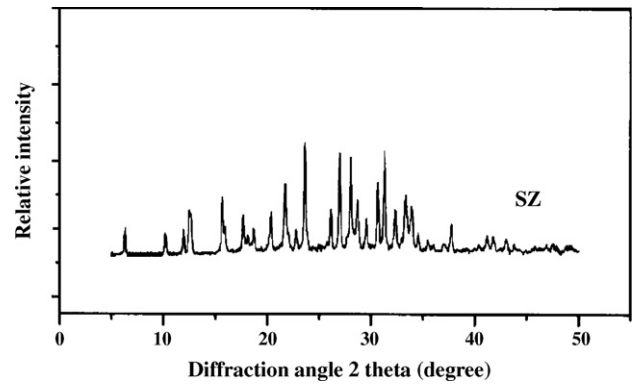

Fig. 5. XRD pattern of the synthesized zeolite.

sites. The surface of the synthesized zeolite at the experimental conditions (i.e., pH > 3.0) will thus exhibit negative charges mainly due to the variable charge from pH dependent surface hydroxyl sites. However, the variation of zeta-potential had a significant increasing trend with pH increased from 9 to 11. The result may be due to the strong reaction between strong base (e.g., NaOH) and zeolite constituent (i.e., SiO_2), making the synthesized zeolite dissolved at the examined pH range. The XRD pattern of the synthesized zeolite was shown in Fig. 5. It was observed from Fig. 5 that the XRD of the samples exhibited some significant peaks of reflections at 2θ of about 13, 16, 22, 23.5, 27, 28, and 32 degrees, which were indicative of the probable formation of zeolite-P2 in the hydrothermal synthesis [21]. For example, the XRD peaks at about 27° and 28° 2θ suggest the presence of zeolite-P, which is topologically related to the natural zeolite called gobbinsite [30].

3.2. Adsorption kinetics

Adsorption studies of bisphenol-A onto the synthesized zeolite were carried out at initial concentration of 20 mg dm^{-3}, adsorbent dosage of 0.5 g 2.0 dm^{-3}, agitation rate of 400 rpm, pH of 7.0, adsorption time of 2 h, and temperature of 25 °C. It was found that the adsorption capacities of bisphenol-A below 0.5 mg g^{-1} were obtained in triplicate, not in proportion to its pore properties listed in Table 2. The result could be attributed to the pK_a value of bisphenol-A ranging 9.6–10.2 [31], implying that the ionization of bisphenol-A occurred at around pH 9–10 to form the bisphenolate anion. As a result, the pore volume and/or particle surface area in the case of the microporous zeolite adsorbent was not determining factors for the removal of bisphenol-A from the aqueous solution probably due to the repulsive interaction between the hydrophilic surface of the synthesized zeolite (Si/Al ≒ 5 and S_{BET} ≒ 400 m^2 g^{-1}) and the target adsorbate; on the contrast, the significant decrease in residual bisphenol-A concentration occurred using the hydrophobic zeolite (Si/Al ≒ 100 and S_{BET} ≒ 500 m^2 g^{-1}) at a short time scale [18], suggesting the adsorption interaction between the zeolite surface and the hydrophobic compound.

In the adsorption of methylene blue onto the synthesized zeolites, it was observed that the significant decrease in residual dye concentration occurred within 2 h. A simple kinetic analysis of adsorption, pseudo-second-order equation [32], was thus used to fit adsorption kinetic data in the present work as reported previously [18]. Its linear form can be denoted as follows:

$$\frac{t}{q_t} = \frac{1}{k \cdot q_e^2} + \left(\frac{1}{q_e}\right) \cdot t \qquad (2)$$

where k is the rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}), q_e and q_t are the amount (mg g^{-1}) of the dye adsorbed at equilibrium and time t, respectively. Rate parameters,

Table 3
Kinetic parameters for the adsorption of methylene blue onto the synthesized zeolite at various initial concentrations.[a].

Initial concentration ($mg\,dm^{-3}$)	Pseudo-second-order model			Intra-particle diffusion model		
	k ($g\,mg^{-1}\,min^{-1}$)	q_e $mg\,g^{-1}$)	R^2	k_{dif} ($mg\,min^{-1/2}\,g^{-1}$)	C	R^2
10	0.012	10.63	0.973	0.841	1.854	0.926
20	0.020	11.20	0.990	0.831	3.127	0.832
30	0.015	11.47	0.968	0.749	3.702	0.737
40	0.015	16.21	0.992	1.178	4.948	0.786
50	0.015	16.86	0.992	1.196	5.379	0.791

[a] Adsorption conditions: adsorbent dosage = 0.5 g 2.0 dm^{-3}, agitation rate = 400 rpm, pH = 7.0, and temperature = 25 °C.

k and q_e, can be directly obtained from the intercept and slope of the plot of (t/q_t) against t.

An adsorption reaction is said to be intra-particle diffusion controlled if the reaction sites are internally located in the porous adsorbents and the external resistance to diffusive transport process is much less than the internal resistance. The intra-particle diffusion model is expressed as follows:

$$q_t = k_{dif} t^{0.5} + C \quad (3)$$

where q_t is as defined in Eq. (2), k_{dif} is the intra-particle diffusion rate constant ($mg\,min^{-1/2}\,g^{-1}$) and C is the intercept. According to Eq. (3), a plot of q_t vs. $t^{0.5}$ should be a straight line with a slope k_{dif} and intercept C. The term k_{dif} is indicative of an enhancement in the rate of adsorption. The value of C gives an idea about the boundary layer thickness.

3.2.1. Effect of initial concentration

The kinetic data obtained from a series of batch adsorption studies have been analyzed using the pseudo-second-order model under different initial dye concentrations at the synthesized zeolite dosage of 0.5 g 2.0 dm^{-3}, mixing speed of 400 rpm, pH of 7.0, and temperature of 25.0 °C. Table 3 listed the model parameters thus obtained. It was seen that the kinetic modeling of the dye adsorption onto the synthesized zeolite followed this model with the correlation coefficients of higher than 0.97 for all the system in the present work. From the results in Table 3, it was further found that the variations of adsorption capacity (i.e., q_e) had an increasing trend with initial dye concentration increased, which is consistent with the previous results for the adsorption of methylene blue onto acid-activated andesite [27]. The result could be attributed to the amount of adsorption areas have been determined by a given adsorbent dosage, indicating that the adsorption capacities will increase with an increased dye initial concentration because the initial concentration provided a powerful driving force to overcome the mass transfer resistance between the aqueous and solid phases. As compared to those obtained by the previous study [27], the adsorption capacities of the acid-activated andesite ($S_{BET} \rightleftharpoons 60\,m^2\,g^{-1}$) for methylene blue were higher than those of the synthesized zeolite ($S_{BET} \rightleftharpoons 400\,m^2\,g^{-1}$). This result may be attributable to the fact that the former was a mesoporous clay adsorbent, which favored to the adsorption of the cationic dye (i.e., methylene blue) having relatively large molecular structure (seen in Table 1 and Fig. 1). By contrast, the latter was a microporous zeolite, suggesting that the diffusion of the dye molecule may be restricted by the so small pore size in the adsorption process. Consequently, the adsorption capacity of the synthesized zeolite for the removal of methylene blue was not proportional to its physical properties. The adsorption kinetic data was further processed to find rate parameters of intra-particle diffusion model. The parameter values of k_{dif} and C were also listed in Table 3. The regression coefficient in Table 3 pointed out that the uptake of methylene blue slightly varies with the half-power of time ($t^{0.5}$) and the straight line did not pass through the origin. The fact implies that the adsorption system is rather complex process that involves both boundary layer diffusion and intra-particle diffusion mechanisms.

3.2.2. Effect of pH

The effect of the initial pH (i.e., 3, 5, 7, 9, and 11) on the intake rate of mathylene blue onto the synthesized zeolite was investigated at the initial concentration of 20 $mg\,dm^{-3}$, adsorbent dosage of 0.5 g 2.0 dm^{-3}, agitation speed of 400 rpm, and temperature of 25 °C. Again, the kinetics of the adsorption well followed this model with the regression coefficients of higher than 0.98, as listed in Table 4. Obviously, the adsorption capacity (i.e., q_e) exhibited a slightly decreasing trend as the pH was increased from 3 to 9, while the zeolite showed an unstable and dissolved phenomenon at the solution pH of 11.0 probably due to the strong reaction between strong base (e.g., NaOH) and silica (i.e., SiO_2) in the synthesized zeolite [33]. Therefore, there are no data on the adsorption capacities of the synthesized zeolite at the examined pH range. It should be further noted that the variation of adsorption capacity (i.e., q_e) had a significant decreasing trend with pH increased from 3 to 5. From the data on the zeta-potential (Fig. 4), the charge sign on the surface of the synthesized zeolite should be slightly negative in a wide pH range (i.e., 3–9), suggesting that the adsorption rate of methylene blue adsorbed on the zeolite could tend to increase with the increase of pH values due to the electrostatic interaction between the charged surface and the positively charged dye molecule. However, the effect of pH on the dye adsorption could be elucidated by considering another determining factor: the increase in the surface area of the synthesized zeolite at lower pH because of the leaching interaction between the hydrogen ion (H^+) and the synthesized zeolite, which favored the adsorption of methylene blue. As listed in Table 5, it was observed that the acid leaching and penetration seemed to inwardly proceed into the interior of the existing pore structure in the synthesized zeolite, leaving a framework possessing more surface areas and pore volume [34].

Table 4
Kinetic parameters for the adsorption of methylene blue onto the synthesized zeolite at various initial pH.[a].

Initial pH	Pseudo-second-order model			Intra-particle diffusion model		
	k ($g\,mg^{-1}\,min^{-1}$)	q_e ($mg\,g^{-1}$)	R^2	k_{dif} ($mg\,min^{-1/2}\,g^{-1}$)	C	R^2
3	0.007	25.84	0.995	2.208	4.428	0.906
5	0.016	11.66	0.986	0.864	3.034	0.864
7	0.020	11.20	0.990	0.831	3.127	0.832
9	0.027	10.71	0.983	0.659	4.436	0.573

[a] Adsorption conditions: initial concentration = 20 mg dm^{-3}, adsorbent dosage = 0.5 g 2.0 dm^{-3}, agitation rate = 400 rpm, and temperature = 25 °C.

Table 5
The main physical properties of comparing the synthesized zeolite with its acid-treatment.

Zeolite adsorbent	S_{BET}[a] (m^2/g)	S_{ads}[b] (m^2/g)	S_{des}[c] (m^2/g)	V_t[d] (cm^3/g)	D_{avg}[e] (Å)
Synthesized zeolite[f]	402.96	30.27	31.69	0.27	26.95
Synthesized zeolite with acid treatment[g]	440.40	209.99	215.86	0.35	32.21

[a] BET surface area.
[b] Adsorption cumulative surface area.
[c] Desorption cumulative surface area.
[d] Total pore volume.
[e] Pore diameter, estimated by $4V_t/S_{BET}$.
[f] S_{BET}, V_t and D_{avg}, seen in Table 2.
[g] The detailed procedure was reported in the reference [34].

Table 6
Kinetic parameters for the adsorption of methylene blue onto the synthesized zeolite at various adsorbent dosages.[a].

Adsorbent dosage ($g\,dm^{-3}$)	Pseudo-second-order model			Intra-particle diffusion model		
	k ($g\,mg^{-1}\,min^{-1}$)	q_e ($mg\,g^{-1}$)	R^2	k_{dif} ($mg\,min^{-1/2}\,g^{-1}$)	C	R^2
0.5	0.020	11.20	0.990	0.831	3.127	0.832
1.0	0.015	9.88	0.945	0.610	3.242	0.693
1.5	0.033	7.88	0.995	0.544	2.650	0.717

[a] Adsorption conditions: initial concentration = 20 $mg\,dm^{-3}$, agitation rate = 400 rpm, pH 7.0, and temperature = 25 °C.

3.2.3. *Effect of adsorbent dosage*

The effect of varying the synthesized zeolite dosage on the adsorption of methylene blue at the initial concentration of 20 $mg\,dm^{-3}$, pH of 7.0, agitation rate of 400 rpm, and temperature of 25 °C has been carried out. The values of parameters for the adsorption system were listed in Table 6. Evidently, the adsorption process still confirmed to fit the pseudo-second-order model with high correlation coefficient. From the results in Table 6, it was suggested that the adsorbability diminished as the adsorbent dosage was increased, resulting in that the amount of dye adsorbed per unit mass of zeolite (i.e., adsorption capacity) decreased with an increasing amount of zeolite added. Such a phenomenon is similar to those for the adsorption of basic dyes onto activated clay and acid-activated andesite in the previous studies [27,35]. This was to be reasonably expected because the monolayer coverage of methylene blue on the outer interface of zeolite dominated the adsorption system at a fixed dye amount even if increasing the adsorbent mass provided a more surface area and therefore the total number of adsorption sites increased. This would further lead to a suggestion that higher initial dye concentrations should be tested in conjunction with appropriate adsorbent mass in order to obtain the optimal adsorbent mass.

4. Conclusions

A novel zeolite adsorbent has been synthesized by using a hydrothermal method, and has been further examined for the adsorption behaviors of two organic molecules (i.e., methylene blue and bisphenol-A), which have similar molecular sizes, but different chemical properties. The physical and chemical properties of the resulting zeolite thus obtained in the study were characterized mainly based on the analyses of the nitrogen isotherms, scanning electron microscope (SEM) image, X-ray diffraction (XRD) pattern and zeta-potential. It was found that the synthesized zeolite exhibited significantly higher adsorption capacity for methylene blue than that for bisphenol-A due to the difference in molecular hydrophilicity. With respect to the suitability of using the synthesized zeolite as a microporous adsorbent for the adsorption of methylene blue from aqueous solution, the time-adsorption uptake has been examined under various process parameters. Furthermore, the adsorption kinetics of the cationic dye onto the zeolite adsorbent can be well described by pseudo-second-order reaction model as compared to the intra-particle diffusion model. The kinetic parameters thus obtained from the fittings of the model were dependent on initial dye concentration, pH, and adsorbent mass.

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