Synthesis of Nd-doped ZSM-5 and its application to treating slightly polluted water
Mang Lu, Lin He and Yue Cheng

ABSTRACT
In this study, ZSM-5 zeolite was synthesized using diatomaceous mud as the raw material, and then doped with different amounts of Nd2O3. The orthogonal experiments were performed to investigate the influence of Nd:Si molar ratio, zeolite dosage, contact time, solution pH and temperature on the removal of humic acid (HA). The removal of HA was comprehensively evaluated by chemical oxygen demand (COD), UV254 and UV410 of the solution. The results demonstrate that solution pH and zeolite dosage are the two most important factors influencing HA adsorption. The optimum experimental conditions were determined to be: 35°C, Nd:Si molar ratio of 1:100, 2.0 g/L zeolite, pH 4 and 50 min contact time. Under these conditions, the removal efficiencies of UV254, UV410 and COD are 82.70%, 76.00% and 82.10%, respectively, corresponding to a comprehensive removal of 81.02%.

Key words | adsorption, diatomaceous mud, Nd2O3, ZSM-5

INTRODUCTION
Humic acid (HA) is an important component of natural organic matter produced by biological decomposition of organic matter from plants and other organisms. As primary natural organic matter, HA is noteworthy because it dissolves in water to produce a dark-colored solution, causing color, taste and odor problems in water use (Lin & Zhan 2012). Moreover, HA molecules can bind various pollutants including toxic heavy metals and synthetic organic chemicals tightly, thus increasing the difficulty of removing these pollutants during drinking water treatment (Li et al. 2011). More seriously, HA can react with chlorine during drinking water treatment to form strongly carcinogenic disinfection by-products (Dong et al. 2014). Thus, it is important to remove HA from water to provide clean drinking water and to prevent the formation of HA-derived compounds.

The main methods of removing HA included membrane filtration, coagulation/flocculation, oxidation, ion-exchange and adsorption (Lin & Zhan 2012). Among them, adsorption is an important method with high removal efficiency, simplicity of design, ease of operation and no harmful by-products (Rashed 2013). Recently, adsorption using low-cost adsorbents, which are abundant in nature or are waste materials from other industries, has become a hot research topic. Zeolite is a crystalline aluminosilicate of alkali and alkaline earth metals composed of SiO4 and AlO4 in a framework structure (Breck 1984). In recent years, various types of zeolites have been proven to exhibit good affinity for HA (Li et al. 2011; Lin & Zhan 2012; Elsheikh et al. 2016).

ZSM-5 zeolite is one of the most industrially important zeolites, which exhibits very similar properties to natural zeolites (Traa & Gehring 2004). ZSM-5 has been studied and used extensively for adsorption of air pollutants (Bhatia et al. 2009), in biomass pyrolysis (Foster et al. 2012), in the petrochemical industry (Schmidt et al. 2013) and for adsorption/reduction of heavy metals (Shao et al. 2009; Wang et al. 2015). The silanol (SiOH) groups, AlOH
groups and OH (SiOHAl) groups on the ZSM-5 surface can bond with contaminants (Bhatia et al. 2009; Wang et al. 2015). However, to the best of the authors’ knowledge, no reports about ZSM-5 as an adsorbent in the adsorption of HA from aqueous solutions are available.

In this study, ZSM-5 zeolite was synthesized using diatomaceous mud and doped with Nd\textsubscript{2}O\textsubscript{3}, and the adsorption of HA on the zeolite as a function of solution pH, adsorbent dosage, contact time, initial adsorbate concentration and temperature was investigated by using batch experiments. Adsorption kinetics and adsorption isotherms at different temperatures were determined.

**MATERIALS AND METHODS**

**Materials**

Silica sol (25\% SiO\textsubscript{2}, \(\rho = 1.184 \text{ g cm}^{-3}\)) was purchased from Shanghai Second Reagent Factory, China. Sodium humate (C\textsubscript{9}H\textsubscript{8}Na\textsubscript{2}O\textsubscript{4}) was obtained from Leping Chemical Factory, Jiangxi, China. Diatomaceous mud was supplied by Beijing Dajin Diatom New Materials Co., Ltd., China. The chemical composition of diatomaceous mud is (wt. \%) SiO\textsubscript{2} 89.53\%, Al\textsubscript{2}O\textsubscript{3} 3.16\%, Na\textsubscript{2}O 3.20\%, MgO 0.24\%, K\textsubscript{2}O 0.48\%, CaO 0.27\%, TiO\textsubscript{2} 0.17\%, Fe\textsubscript{2}O\textsubscript{3} 1.59\%, P\textsubscript{2}O\textsubscript{5} 0.03\%, Cl 0.41\% and loss on ignition 0.91\%. All the other chemicals used were of analytical grade. Distilled water was used throughout the study. A stock solution of 500 mg L\textsuperscript{-1} was prepared by dissolving appropriate amounts of HA in distilled water, and a working solution (30 mg L\textsuperscript{-1}) was prepared by diluting the stock solution. The pH was adjusted using 0.1 M HCl and 0.1 M NaOH.

**Nd/ZSM-5 preparation**

Nd/ZSM-5 was prepared by a conventional hydrothermal method technique. In a typical preparation procedure, 4.1245 g of tetrapropylammonium bromide (TPABr) and 4.4582 g of NaOH were added to a beaker containing 106 mL of deionized water. The mixture was stirred for 10 min before 5.00 g of diatomaceous mud and appropriate amounts (0, 0.078, 0.1954 or 0.78 g) of Nd\textsubscript{2}O\textsubscript{3} (dissolved in 0.1 M HNO\textsubscript{3}) were added with stirring. Then 35.11 mL of silica sol was added dropwise with stirring. After stirring for 2 h at room temperature, the obtained sol was sealed and aged for another 24 h. The sample was crystallized at 180 °C for 24 h, and the product was rinsed with deionized water several times until the pH of the supernatant was neutral. The precipitate was dried and calcined at 550 °C for 2 h. After cooling to room temperature, the product was stored in a desiccator until used. The preparation of the material resulted in a molar ratio of: 25Na\textsubscript{2}O:150SiO\textsubscript{2}:1Al\textsubscript{2}O\textsubscript{3}:10TPABr:2500H\textsubscript{2}O. To evaluate the influence of Nd content on the Nd/ZSM-5 property, the Nd:Si molar ratios are 0:100, 1:100, 2.5:100 and 10:100.

**Characterization**

Chemical composition analysis was performed using an Axios X-ray fluorescence spectrometer (AXIOS, PANalytical, The Netherlands). X-ray diffraction (XRD) patterns were collected using a Bruker D8 advance diffractometer (Bruker, Germany) with Cu K\textalpha\textsubscript{\textgamma} radiation from 5° to 70° at a rate of 0.02°/s. All samples were scanned under the same conditions (2\(\theta = 1–25^\circ\)). Crystal size and morphology were investigated on a JSM-6380 high-resolution field emission scanning electron microscope (JEOL, Japan) and SU8010 new high-resolution field emission scanning electron microscope (Hitachi, Japan). The energy dispersive spectroscopy (SDD detector, IXRF, USA) was used to analyze the dispersion of Nd in the zeolite sample. The nitrogen adsorption–desorption isotherm was obtained by using a Micromeritics ASAP2020M analyzer at 77 K under continuous adsorption conditions. Based on the N\textsubscript{2} adsorption–isotherm data, the specific surface area was calculated according to the Brunauer–Emmett–Teller (BET) method. The pH of zero point of charge (pH\textsubscript{ZPC}) was determined by an automated electrophoresis instrument (S3000, PenKem, Bedford Hills, NY, USA).

**Adsorption studies**

Adsorption experiments were conducted at various solution pH values, zeolite dosages, contact time, zeolite types and temperatures in batch mode. In order to investigate factors influencing HA adsorption, a statistical experimental design method was employed in the application of the
orthogonal experimental design L16 (45) (5 factors, 4 levels, 16 experiments) (Table 1). Adsorption experiments were carried out in conical flasks containing 100 mL of HA solution (30 mg L−1) and the required dosage of zeolite at a specified temperature. The flasks were shaken at 150 rpm on a shaker equipped with a thermostat. After a pre-defined contact time, the aqueous sample was passed through a 0.45 μm syringe filter. The filtrate was analyzed in terms of chemical oxygen demand (COD) content and UV absorbance (UV254, UV410). A 722 UV–Vis spectrophotometer (Shanghai Precision and Scientific Instrument Co., Ltd., China) equipped with a 1-cm quartz cell was used in UV adsorption measurements. Measurement of COD was conducted using the conventional method, namely K2Cr2O7 digestion/(NH4)2Fe(SO4)2 titration. Removal efficiencies obtained after the required contact time were calculated using the following equation:

\[
R = \frac{C_0 - C_t}{C_0} \times 100\%
\] (1)

where \(R\) is removal efficiency (%), \(C_0\) and \(C_t\) are the initial and equilibrium UV254, UV410 and COD content, respectively.

The comprehensive evaluation index in the orthogonal table is calculated by the following equation:

\[
K = 20\%R_1 + 20\%R_2 + 60\%R_3
\] (2)

where \(K\) is combined removal efficiency, \(R_1\) UV254 removal, \(R_2\) UV410 removal and \(R_3\) COD removal.

All the adsorption experiments were performed in batch mode taking three replicates and mean values are reported. Standard deviations were found to be within ±3%.

**RESULTS AND DISCUSSION**

**Characterization**

The Nd/ZSM-5 zeolite exhibits main XRD peaks (Figure 1) at 2θ degrees of 7.8°, 8.7°, 23.9°, 24.9°, 26.8° and 29.3°. These peaks correspond to the pattern of the standard ZSM-5 zeolite. No diffraction peaks derived from metal or metal oxide clusters are observed, suggesting that the species are well dispersed as amorphous metal species, or aggregated into mini-crystals that are too small to be detected by XRD (Dou et al. 2015).

The scanning electron microscopy image of the sample is shown in Figure 2. The sample exhibits typical crystalline

**Table 1** Factors and levels for orthogonal test to the adsorption of HA using Nd/ZSM-5

| Level | Factor A (T (°C)) | Factor B (Nd:Si ratio) | Factor C (pH) | Factor D (Contact time (min)) | Factor E (Zeolite dosage (g L−1)) |
|-------|------------------|------------------------|---------------|-------------------------------|----------------------------------|
| 1     | 25               | 0:100                  | 4             | 30                           | 0.5                              |
| 2     | 30               | 1:100                  | 6             | 40                           | 1.0                              |
| 3     | 35               | 2.5:100                | 8             | 50                           | 1.5                              |
| 4     | 40               | 10:100                 | 10            | 60                           | 2.0                              |

**Figure 1** XRD patterns of Nd/ZSM-5 particles prepared with a Nd:Si molar ratio of 1:100.

**Figure 2** SEM image of Nd/ZSM-5 particles prepared with a Nd:Si molar ratio of 1:100.
particles with a size of 3–4 μm. It can be clearly seen that the Nd/ZSM-5 zeolite sample is a rounded crystal with a quite rough surface, which is typical for high aluminum contents.

The energy dispersive spectroscopy analysis spectrum of the Nd/ZSM-5 zeolite is presented in Figure 3. The zeolite membrane layer consisting of O, Na, Al, Si and Nd atoms is revealed. The Si and Al atoms can be attributed to the ZSM-5 membrane. The content of Nd is very low (Table 2), thus Nd was not detected by XRD. These results confirm that Nd is well dispersed on the surface of ZSM-5 zeolite membrane. Additionally, the Nd/ZSM-5 zeolite has a BET surface area of 328.6266 m²/g and a pHzpc of 6.6.

The orthogonal experiments

We performed orthogonal experiments to explore the influence of various factors on HA adsorption by the Nd/ZSM-5 zeolite. The initial values of UV254, UV410 and COD were 1.06, 0.342 and 52.5 mg L⁻¹, respectively. The experimental design and the final removal efficiencies of UV254, UV410 and COD from the HA solution are listed in Table 3. K₁, K₂, K₃ and K₄ are the sum scores of level 1, level 2, level 3 and level 4 for each factor; k₁, k₂, k₃ and k₄ are the average sum scores of level 1, level 2, level 3 and level 4 for each factor; R is the difference between the maximum and the minimum of the average values of the experimental results, under different levels of the same factor or the range. The higher the value of R is, the larger the influence of the factor is on the HA adsorption. The level which achieves the largest score is chosen as the optimal level of each factor. It can seen in Table 3 that the influences of various factors decrease in the following order: C > E > D > A > B. Therefore, the optimal formulation was found to be A₃B₂C₁D₃E₄, corresponding to: 35 °C, Nd:Si molar ratio of 1:100, 2.0 g/L zeolite, pH 4 and 50 min contact time.

Effect of operational factors on HA adsorption

The influences of five factors in the orthogonal experiments on HA adsorption were further explored by visual analysis. Figure 4(a) displays the comprehensive removal of HA at different temperatures. It can be seen that the adsorption capacity is enhanced when the temperature is increased to 35 °C. This feature indicates that higher temperatures could improve the adsorption capacity of Nd/ZSM-5 for HA, suggesting that the adsorption of HA to Nd/ZSM-5 is an endothermic reaction. The maximum removal (53.80%) occurs at 35 °C, compared to 45.43% removal at 25 °C. However, a higher temperature (40 °C) is not conducive to HA adsorption.

The effect of Nd:Si molar ratio on HA removal is shown in Figure 4(b). It can be seen that Nd:Si ratio strongly influences the HA adsorption. When the Nd:Si ratio changes from 0:100 to 1:100, the comprehensive removal increases from 44.79% to 52.45%. At the lower Nd:Si ratio, adsorption sites of ZSM-5 could be fully exposed to HA. Thus, the adsorption of HA to ZSM-5 could be faster and reached a higher adsorption capacity (Liao & Shi 2005). However, when the Nd:Si ratio is relatively high, the adsorption sites of ZSM-5 are restricted from being exposed to HA. As a
result, a lower adsorption capacity is observed at the higher Nd:Si ratios (2.5:100 and 10:100).

ZSM-5 has shown promising capacity to remove HA from water. Since HA-containing water can also include other molecules, the pH of the aqueous solution can vary, thereby influencing adsorption capacity. Therefore, in this study, four pH levels of 4, 6, 8 and 10 were used to investigate the effect of pH on HA removal. Figure 4(c) shows that an increase in solution pH from 4 to 10 causes an obvious decrease in removal from 57.27% to 45.37%. This indicates that the adsorption of HA on Nd/ZSM-5 is favored at lower pH values. The HA solution is considered as a mixture of compounds with weakly acidic functional groups, such as carboxylic and phenolic groups. The pKa values of carboxylic and phenolic groups are around 3.0 and 9.0, HA is expected to be negatively charged by deprotonation of carboxylic groups at pH above 3 (Lin & Zhan 2012). At lower pH, the adsorption might be controlled by carboxylate groups of HA molecules and Nd/ZSM-5 as well as hydrogen bonding

### Table 2 | EDS elemental analysis of the samples

| Element | O | Na | Al | Si | Nd | Sum |
|---------|---|----|----|----|----|-----|
| mole%  | 64.132 | 1.026 | 1.273 | 33.476 | 0.093 | 100.000 |
| wt.%   | 50.358 | 1.158 | 1.686 | 46.143 | 0.655 | 100.000 |

Table 3 | Orthogonal experimental design and the results obtained from the full 4^5 factorial experimental matrix

| Set no. | Design variable | Removal (%) |
|---------|-----------------|-------------|
|         | A (C) B (Nd:Si ratio) C (pH) D (min) E (g L^{-1}) | UV254 | UV410 | COD | Comprehensive |
| 1       | 25 0:100 4 30 0.5 | 36.13 | 34.21 | 40.95 | 38.64 |
| 2       | 25 1:100 6 40 1.0 | 56.32 | 49.71 | 35.24 | 42.35 |
| 3       | 25 2.5:100 8 50 1.5 | 46.42 | 34.50 | 57.52 | 50.70 |
| 4       | 25 10:100 10 60 2.0 | 51.23 | 45.61 | 50.67 | 49.77 |
| 5       | 30 0:100 6 50 2.0 | 38.02 | 41.23 | 66.10 | 55.51 |
| 6       | 30 1:100 4 60 1.5 | 48.30 | 64.04 | 69.90 | 64.41 |
| 7       | 30 2.5:100 10 30 1.0 | 40.28 | 37.43 | 40.19 | 39.66 |
| 8       | 30 10:100 8 40 0.5 | 44.25 | 57.31 | 45.52 | 47.63 |
| 9       | 35 0:100 8 60 1.0 | 42.26 | 27.49 | 52.95 | 45.72 |
| 10      | 35 1:100 10 50 0.5 | 51.70 | 90.94 | 40.38 | 52.76 |
| 11      | 35 2.5:100 4 40 2.0 | 65.85 | 48.25 | 78.29 | 69.79 |
| 12      | 35 10:100 6 30 1.5 | 48.68 | 20.76 | 55.05 | 46.92 |
| 13      | 40 0:100 10 40 1.5 | 58.11 | 17.25 | 40.38 | 39.30 |
| 14      | 40 1:100 8 30 2.0 | 59.15 | 14.04 | 59.43 | 50.29 |
| 15      | 40 2.5:100 6 60 0.5 | 60.19 | 9.06 | 46.29 | 41.62 |
| 16      | 40 10:100 4 50 1.0 | 53.11 | 52.63 | 58.48 | 56.23 |

K1 181.454 179.169 229.075 175.507 180.643
K2 207.198 209.808 186.394 199.066 183.961
K3 215.183 201.767 194.339 215.194 201.522
K4 187.453 200.545 181.481 201.522 225.359
k1 45.364 44.792 57.269 43.877 45.161
k2 51.800 52.452 46.598 49.766 45.990
k3 53.796 50.442 48.585 53.799 50.332
k4 46.863 50.136 45.370 50.380 56.340
R 8.452 7.660 11.899 9.922 11.179
between hydroxyl surface groups and carboxylates of HA. Moreover, at lower pH, the charge of Nd/ZSM-5 is positive and this may facilitate the adsorption of negatively charged HA. As pH increases, the dissociation of functional groups on both HA and Nd/ZSM-5 increases while Nd/ZSM-5 becomes negatively charged. The electrostatic repulsion interaction between the negative charges on Nd/ZSM-5 and HA results in a decrease in HA adsorption on Nd/ZSM-5. Furthermore, HA may exist in a spherical structure at lower pH but can exist

Figure 4 | Effect of (a) temperature, (b) Nd:Si molar ratio, (c) solution pH, (d) contact time and (e) zeolite dosage on HA adsorption by Nd/ZSM-5.

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in a linear or stretched structure at higher pH (Wan Ngah et al. 2008). This would cause less adsorption of HA in the adsorbent pores at higher pH. Therefore, an increment in the size of HA macromolecules with the increase of solution pH may be another factor contributing to the lower adsorption capacity at higher pH.

The variation in adsorption efficiency with contact time is presented in Figure 4(d). It is observed that rapid adsorption of HA occurred within the initial 30 min and, thereafter, the adsorption efficiency gradually approaches equilibrium in about 50 min. At this point, the adsorbed amount of HA onto the zeolite is in a state of dynamic equilibrium with the amount of the HA desorbing from the zeolite. After 50 min, the adsorption efficiency decreases slightly, which may be due to desorption of HA molecules under prolonged agitation conditions.

The effect of zeolite dosage on the adsorption of HA is shown in Figure 4(e). As shown, an increase in zeolite dosage from 0.5 to 2.0 g L⁻¹ results in the increase of the comprehensive removal efficiency from 45.16% to 56.34%. The increase in HA removal efficiency with increasing zeolite dosage is due to the increase of adsorption active sites on the zeolite surface with the increase of zeolite dosage (Dawood & Sen 2012).

Based on the above-mentioned results and discussion, a verification experiment was conducted under the optimum conditions, namely 55°C, Nd:Si molar ratio of 1:100, 2.0 g L⁻¹ zeolite, pH 4 and 50 min contact time. The results demonstrate that the removal efficiencies of UV₂₅₄, UV₄₁₀ and COD are 82.70%, 76.00% and 82.10%, respectively, corresponding to a comprehensive removal of 81.02%.

**CONCLUSIONS**

In summary, when Nd species was doped in ZSM-5 zeolite, the Nd/ZSM-5 zeolite shows higher adsorption capacity towards HA. Adsorption of HA by Nd/ZSM-5 was enhanced at acidic pH levels and higher temperatures. The results demonstrate that Nd/ZSM-5 is a potential wide-spectrum adsorbent for water treatment to remove different pollutants with fundamentally different chemical properties.

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