



Hydrothermal synthesis of needle-like nanocrystalline zeolites from metakaolin and their applications for efficient removal of organic pollutants and heavy metals

Hongwei Luo^{a,b}, Wei Wee Law^c, Yichao Wu^{c,d}, Weiping Zhu^c, En-Hua Yang^{c,*}

^a College of Environment, Zhejiang University of Technology, Hangzhou, 310014, China

^b Energy Research Institute, Nanyang Technological University, Singapore 637553

^c School of Civil and Environmental Engineering, Nanyang Technological University, Singapore 639798

^d State Key Laboratory of Agricultural Microbiology, College of Resources and Environment, Huazhong Agricultural University, Wuhan, 430070, China

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ABSTRACT

In this study, an environment-friendly and sustainable route to convert clay minerals into highly efficient sorbents for organic pollutants and heavy metals removal was reported. Needle-like nanocrystalline zeolites were hydrothermally synthesized from metakaolin (MK) and their properties and efficiency for organic pollutants and heavy metals removal were investigated. After hydrothermal treatment, the morphology of metakaolin markedly transformed from layered structures to aggregations of needle-like zeolites, thereby resulting in substantial increases of total and meso porosities, N₂ sorption capacity and specific surface area. The hydrothermally synthesized MK-based zeolites exhibited much stronger sorption capacity toward aniline (AN), 3-chloroaniline (3-CA), and humic acid (HA). The electrostatic attraction and surface complexation dominated by chemisorption likely accounted for the enhanced sorptive interactions between zeolites and organic compounds. Similarly, the adsorption capacity of the newly formed zeolites toward Cu(II) and Pb(II) increased almost 20-fold, which was 431.0 mg g⁻¹ for Cu(II) and 337.8 mg g⁻¹ for Pb(II). Ionic exchange reactions between heavy metal ions and the enriched sodium ion resulted in heavy metal removal by the MK-based zeolites. Thus, the hydrothermally synthesized MK-based zeolites may be employed as sorbents for wastewater treatment to remove organic pollutants and heavy metals with no significant toxicity risk.

1. Introduction

Zeolites are a large group of natural and synthetic hydrated aluminosilicate minerals commonly used as commercial adsorbents and catalysts [1]. The special crystal structures of zeolites consist of three-dimensional frameworks of (SiO₄)⁴⁻ and (AlO₄)⁵⁻ tetrahedra with variable pore size and morphology [2]. The net negative charge of lattice is compensated by the exchangeable cations such as Na⁺, K⁺ and Ca²⁺. These exchangeable cations in zeolites are usually innocuous, making them particularly suitable for removing toxic heavy metal ions (Cu²⁺, Pb²⁺, Cd²⁺, Mn²⁺, Hg²⁺, etc.) from industrial effluent [3]. In addition, the removal of organic pollutants (dyes, humic substances, phenolic compounds, pesticides, pharmaceuticals, etc.) by natural zeolites and their modified forms has been extensively investigated [4–8], although zeolites exhibit relatively weak affinity toward organic pollutants. The electrostatic attraction and surface complexation dominate the chemisorption. To keep up with the global rapidly growing water demand, it

is of great interest to develop low-cost and sustainable adsorbents for the removal of toxic heavy metals and organic pollutants from wastewater [9]. The applications of zeolites for water and wastewater treatment have been focused mainly due to their properties and significant worldwide occurrence. Currently, the use of zeolites is still a promising technique in environmental remediation processes [1]. Zeolites are preferably prepared from pure chemicals of sodium silicate and sodium aluminate. Nevertheless, their production from cheap natural clay minerals is of economic importance and therefore it is necessary to optimize the synthesis route [10].

Metakaolin (Al₂O₃·2SiO₂), a calcined product of kaolin (Al₂O₃·2SiO₂·2H₂O) with Si/Al ratio of 1, is a very convenient raw material for the synthesis of zeolites due to its low cost and natural abundance. Several synthetic methods have been reported to use the natural raw materials (kaolin and metakaolin) for the production of zeolites. For example, zeolite A was previously synthesized from metakaolin using a microwave-assisted heating procedure [11,12].

* Corresponding author.

E-mail address: ehyang@ntu.edu.sg (E.-H. Yang).

However, hydrothermal method was a more popular way to produce zeolites and only few research work has been carried out using metakaolin as a starting material [3]. The removal of organic pollutants and heavy metals by the hydrothermally synthesized zeolites from raw metakaolin has not been well established and sufficiently documented. As a promising method, hydrothermal synthesis of zeolites is a multi-phase reaction containing dissolution and crystallization process, which commonly involves at least one liquid phase and both amorphous and crystalline solid phases [13]. Thus, hydrothermal transformation of metakaolin into zeolites provides an alternative solution to sustainability of both clay mineral utilization and water contamination.

The main objective of this study is to explore the hydrothermal transformation of metakaolin into zeolites and their applications in efficient removal of organic pollutants and heavy metals. A layer-structured metakaolin was converted into needle-like nanocrystalline zeolites through hydrothermal treatment, thereby showing strongly enhanced sorption performance toward organic pollutants and heavy metals. The chemical, morphological and mineralogical properties of raw metakaolin and the converted zeolites were characterized. The specific surface area and pore size distribution were determined. The removal efficiencies of aniline (AN), 3-chloroaniline (3-CA), and humic acid (HA) were investigated using raw metakaolin and the hydrothermally synthesized MK-based zeolites. Their adsorption capacities toward Cu(II) and Pb(II) were further examined via sorption isotherms. Together, these experimental results are of environmental significance because they are useful to understand zeolites formation from metakaolin and subsequent removal of pollutants at contaminated sites.

2. Materials and methods

2.1. Hydrothermal treatment of metakaolin

Raw metakaolin (MK) samples were provided by BASF (Germany), and directly used without further treatment. The chemical compositions of the raw and the hydrothermally treated MK were determined using a sequential X-ray fluorescence (XRF) spectrometer (S8 Tiger, Bruker).

In previous publications, the synthesis of zeolite was carried out through two different routes: (1) conventional hydrothermal alkaline activation [14,15]; and (2) alkaline fusion prior to hydrothermal reaction [16]. In the first method, a calculated amount of NaOH pellets was added to distilled water in reaction plastic beakers (150–250 mL) to prepare NaOH solutions, in which metakaolin was added. In the second method, an alkaline fusion step was introduced prior to hydrothermal treatment. Metakaolin was dry mixed with NaOH powder and the resultant mixture was fused at 600 °C for 1 h. The fused product was ground in a mortar and then a calculated amount of the ground powder was added to distilled water under stirring conditions. In both routes, chemical reagents, such as CaCO₃, Al(OH)₃, and precipitated SiO₂, were used as activators to control the Si/Al ratio.

In the current study, only raw metakaolin and NaOH were used as the starting materials, no additional Ca, Si and Al elements were introduced. Hydrothermal treatment of metakaolin was performed in slurry using a 45 mL Teflon-lined acid digestion bomb (Parr Instrument Company, USA). Initially, 5.0 g metakaolin powder was mixed with 30 mL of 2.0 M NaOH solution (liquid-to-solid ratio = 6) in a 50 mL plastic centrifuge tube and stirred for 30 min. The slurry was then transferred into the stainless steel autoclave, carefully sealed and incubated under 180 °C in the oven for 20 h. After hydrothermal reactions, the products were cooled to room temperature and subsequently washed three times by repeated centrifugation (5 min at 8000 g, 25 °C) using deionized water, and finally dried in oven at 105 °C for 6 h to recover the robust materials [15].

2.2. Characterization of raw and treated metakaolin

The morphology of the raw and the hydrothermally treated

metakaolin was observed on a field emission scanning electron microscope (FESEM, JSM-7600F, JEOL). Before the test, the samples were treated by gold coating. Powder X-ray diffraction (XRD) patterns were taken on a Bruker AXS D8 advance diffractometer using Cu K α radiation ($\lambda = 0.15406$ nm). The tube voltage was 40 kV and the current was 40 mA. The XRD diffraction patterns were obtained in the 2θ range of 5–80° at a scan speed of 4° min⁻¹. Phase identification was carried out by searching the ICDD powder diffraction file database and comparing with those included in the Joint Committee on Powder Diffraction Standards (JCPDS) files [3,16]. Infrared (IR) spectra of metakaolin samples before and after hydrothermal treatment were recorded in the range of 480–4000 cm⁻¹ on a Nicolet iS50 FT-IR spectrometer (Thermo Scientific, USA).

An automated surface area and pore size analyzer (Quadrasorb evo, Quantachrome Instruments) was employed to determine the specific surface area upon the Brunauer-Emmett-Teller (BET) nitrogen adsorption/desorption isotherms. Accordingly, the pore size distributions were calculated using the desorption Barrett-Joyner-Halenda (BJH) method. The outgas temperature and time were set at 180 °C and 18 h, respectively. Data analysis was performed using the QuadraWin software.

Thermogravimetric analysis (TGA) of the raw and converted materials was conducted with a TGA 8000 thermal analyzer (PerkinElmer, USA). Experiments were performed under a nitrogen atmosphere with a flow rate of 20 mL min⁻¹ and at a heating rate of 10 °C min⁻¹ from 30 °C to 900 °C.

2.3. Batch sorption experiments

Two heavy metals (Cu²⁺ and Pb²⁺) and three organic pollutants (aniline (AN), 3-chloroaniline (3-CA), and humic acid (HA)) were chosen as models for sorption investigation. Pb(II) and Cu(II) ions were used in the form of Pb(NO₃)₂ and Cu(NO₃)₂, respectively. Aniline and 3-chloroaniline were provided by Sigma-Aldrich, USA. Humic acid was purchased from International Humic Substances Society (IHSS).

The sorption kinetics were obtained by adding 0.1 g of metakaolin samples into 50 mL working solutions with either 400 mg L⁻¹ organic pollutants or 1000 mg L⁻¹ heavy metals. All assays were prepared in triplicate. The solution pH was adjusted to 3.0–5.0 for heavy metals and 7.2 for organic pollutants using 2 wt% HNO₃ or NaOH. The mixture was stirred at 200 rpm and 25 °C. At specified time intervals, 1 mL of the mixture was taken and sacrificed to quantify the residual concentrations of each species e.g. Cu(II), Pb(II), AN, 3-CA, and HA. Samples were ten-times diluted and then filtered through 0.2- μ m Acrodisc polyethersulfone membrane syringe filters (Pall Corp., Singapore) prior to analysis. The concentration of humic acid was characterized with total organic carbon and determined using TOC measurements (TOC-LCPH, Shimadzu Corp., Japan). The concentrations of AN and 3-CA in the aqueous solution were quantified using a reverse-phase high-performance liquid chromatography (HPLC, LC-20A, Shimadzu) equipped with a SIL-20A autosampler, LC-20AD solvent delivery system, and SPD-M20A photo-diode array (PDA) detector [17]. Operating conditions included an Acsentis C18 column (100 mm \times 2.1 mm, 5 μ m particle size), mobile phase of methanol-water (50/50 v/v), flow rate of 0.6 mL min⁻¹ and detector set at 254 or 280 nm. The concentrations of Cu(II) and Pb(II) in the solution were measured by an inductively coupled plasma-mass spectrometer (ICP-MS, ELAN DRC-e, PerkinElmer).

To obtain the adsorption isotherm of MK toward Cu(II) and Pb(II), batch sorption experiments were conducted using 100 mL shaking flasks, in which 50 mL of Cu(II) or Pb(II) working solution and 0.1 g of metakaolin samples were added. Initial concentrations of heavy metals were 50–2500 mg L⁻¹ in the raw MK and 100–5000 mg L⁻¹ in the treated MK, respectively. To prevent the precipitation, the solution pH was adjusted to 5.0 using 2 wt% HNO₃. The reactants were mixed together and allowed to react at 25 °C for 18 h and equilibrate on an

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