

Phosphate Adsorption on Aluminum-Impregnated Mesoporous Silicates: Surface Structure and Behavior of Adsorbents

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Phosphorus from excess fertilizers and detergents ends up washing into lakes, creeks, and rivers. This overabundance of phosphorus causes excessive aquatic plant and algae growth and depletes the dissolved oxygen supply in the water. In this study, aluminum-impregnated mesoporous adsorbents were tested for their ability to remove phosphate from water. The surface structure of the materials was investigated with X-ray diffraction (XRD), a N₂ adsorption-desorption technique, Fourier transform-infrared (FT-IR), and X-ray photoelectron spectroscopy (XPS) to understand the effect of surface properties on the adsorption behavior of phosphate. The mesoporous materials were loaded with Al components by reaction with surface silanol groups. In the adsorption test, the Al-impregnated mesoporous materials showed fast adsorption kinetics as well as high adsorption capacities, compared with activated alumina. The uniform mesopores of the Al-impregnated mesoporous materials caused the diffusion rate in the adsorption process to increase, which in turn caused the fast adsorption kinetics. High phosphate adsorption capacities of the Al-impregnated mesoporous materials were attributed to not only the increase of surface hydroxyl density on Al oxide due to well-dispersed impregnation of Al components but also the decrease in stoichiometry of surface hydroxyl ions to phosphate by the formation of monodentate surface complexes. Typical removal methods for high concentration of phosphorus consist of biological treatments such as the conventional activated-sludge process, chemical treatments such as precipitation with Al, Fe, and Ca components, or a combination of both treatments (1-3). However, in the case of a low concentration of phosphorus such as in stormwater runoff, biotreatment and precipitation are not effective. Instead, fixed-bed processes using adsorption methods are recommended as the most effective removal processes for low concentrations (4,5).

In the fixed-bed filtration system, selection of an adsorbent

is important. Diverse solid materials including red mud, activated alumina, polymeric ligand exchanger, and sand coated with iron and aluminum oxide have been applied as adsorbents (3-7). Recently, mesoporous materials have been used for the removal of toxic chemicals from water because of the merits of high surface area and nanosized regular pores. Thiol-impregnated mesoporous materials showed considerably high sorption capacity for cations such as mercury ions in water (8, 9). Zhao et al. (10) reported that mesoporous silicate materials containing surfactants could eliminate organic pollutants from water. Mesoporous alumina aluminum phosphates have been applied to eliminate herbicides or chlorinated phenols from aqueous solution (11, 12).

In our recent research, metal- (Fe, Al, and Zn) impregnated mesoporous materials were used for the removal of anions from water (13). The adsorption behaviors of phosphate on the metal-impregnated mesoporous materials were found to be different than adsorption on activated alumina. Of several metal-impregnated mesoporous materials, Al-impregnated mesoporous material showed the highest sorption capacity for arsenate removal. The different adsorption behaviors were caused by the different surface properties of the materials. In this study, the adsorption isotherms and kinetics of phosphate adsorption on Al-impregnated mesoporous materials and activated alumina were examined. The surface properties of those materials were investigated through characterization with X-ray diffraction (XRD), Fourier transform-infrared (FT-IR), BET microporosity measurement, and X-ray photoelectron spectroscopy (XPS) to understand the different phosphate adsorption behaviors based on the distinctive surface structure of the adsorbents.

Materials and Methods

Materials. A mesoporous silicate, SBA-15, was prepared according to the procedure described elsewhere (14). An aliquot of 4.0 g of Pluronic P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, Aldrich Chemical Co., Milwaukee, WI) was dissolved in 120 g of 2M HCl solution and 30 g of deionized water. Then, 8.5 g of tetraethyl orthosilicate (TEOS) was added into the homogeneous solution at 308 K. The solution was stirred for 20 h at 308 K and then aged for 24 h at 353 K. The solid product was filtered, washed, and air-dried at room temperature. Calcination was conducted by slowly increasing the temperature from room temperature to 773 K in 14 h and heating at 773 K for 6 h to completely eliminate the surfactants.

Aluminum was impregnated into SBA-15 by the incipient wetness impregnation method. The aqueous solution containing an aluminum precursor, aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Aldrich Chemical Co.), was dropped into SBA-15. After impregnation, the samples were dried at room temperature in a hood for 1 day and then oxidized at 673 K for 4 h in air. The amount of aluminum loaded into SBA-15 was controlled by dissolving different amounts of aluminum precursor into the same amount of deionized water. The activated alumina used in this study was also acquired from Aldrich Chemical Co. The surface area and the average pore diameter of activated alumina were 155 m^2/g and 5.9 nm, respectively. Physical properties of the samples used in this study are summarized in Table 1.

Surface Analysis. X-ray diffraction (XRD) patterns of the prepared samples were acquired with a Stoe high-resolution

X-ray diffractometer (Microphotonics, Allentown, PA) using Cu KR radiation (40 kV, 25 mA) of wavelength 0.154 nm to confirm the structure of the mesoporous materials. All XRD patterns were obtained from 0.8° to 3.0° with a scan speed of 0.2°/min. The XPS experiments were conducted with a Perkin-Elmer (Norwalk, CT) 5400 ESCA spectrometer under 10⁻⁸ Torr of vacuum condition to compare the chemical state of the elements loaded into all samples. MgKR radiation was used as an X-ray source.

The IR spectra of each sample were recorded on a Mattson Galaxy 5020 (Mattson Instruments, Madison, WI) to check the change in the functional group of the oxide surface after Al impregnation. All the samples were mixed with KBr, compacted in a uniaxial press under a nominal pressure of 1 GPa, and measured at room temperature. The BET surface area and the pore size distributions of each sample were measured by the N₂ adsorption-desorption technique using a Micromeritics (Norcross, GA) ASAP 2000 analyzer. Degassing of the samples was conducted at 523 K for 1 day.

Phosphate Adsorption Test. Phosphate isotherms for the samples were acquired through batch experiments. Before adsorption experiments, the samples were washed with deionized water and dried at room temperature overnight. Solid samples weighing between 0.01 and 0.4 g were placed in 125-mL bottles with 100 mL of solution that had 10 ppm phosphorus concentration. Sodium dihydrogenphosphate (NaH₂PO₄, Aldrich Chemical Co.) was used as the phosphorus source. The ionic strength of the solutions was maintained at 0.01 M using NaNO₃. The sealed sample bottles were placed in a shaker and shaken at 200 rpm at room temperature. After shaking the sample bottles for 3 h, the pH of the solutions was adjusted to 6.4 through the addition of either acid (HNO₃, 0.1 M) or base (NaOH, 0.1 M) stock solution. Then, all the sample bottles were placed again in a shaker for 48 h at room temperature. The final pH of the solutions ranged from 6.7 to 7.2, depending on the amount and the sort of solid samples. After shaking, the suspension was filtered immediately with a 0.45- μ m microfilter. The phosphorus concentration of the filtered solutions was analyzed by an inductively coupled plasma atomic emission spectrometer (Ultima ICP-AES, Jobin Yvon, Inc., Edison, NJ).

The Langmuir isotherm model was applied to the isotherm data. The Langmuir isotherm is

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where q_e is amount adsorbed at equilibrium (mg/g), b is the Langmuir constant (L/g), Q_{\max} is maximum adsorbate adsorption amount (grams adsorbate/grams adsorbent), and C_e is phosphorus concentration at equilibrium.

Adsorption kinetic experiments were performed in 1-L solutions with 0.4 g of sample powders. The initial phosphorus concentration of the solution was 10 mg/L, and the pH of the solution was maintained at 6.4. The suspension was stirred by a magnetic bar, and the supernatant samples were taken at various times during a 3-h experiment. Also, the phosphorus concentrations of these samples were measured with an inductively coupled plasma atomic emission spectrometer.

All kinetic data were fitted to the pseudo-second-order

kinetic model suggested by Ho and McKay (15). The kinetic rate equations can be written as follows

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where q_t is the amount adsorbed at time t (mg/g) and k is the equilibrium rate constant of the second-order sorption (g/mg \cdot min). Nonlinear regressions using a least-squares fitting program (Origin 7.0, OriginLab Corp., Northampton, MA) were conducted to acquire the best estimate of all constants for all the models.

Full text is available at :

<http://pubs.acs.org/doi/abs/10.1021/es030488e>