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Nitrate removal from water by nano-alumina: Characterization and sorption studies

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ABSTRACT

The present study was conducted to evaluate the feasibility of nano-alumina for nitrate removal from aqueous solutions. The nature and morphology of sorbent was characterized by XRD, FTIR, BET and SEM analysis. Batch adsorption studies were performed as a function of contact time, initial nitrate concentration, temperature, pH and influence of other interfering anions. Nitrate sorption kinetics was well fitted by pseudo-second-order kinetic model. The maximum sorption capacity of nano-alumina for nitrate removal was found to be ca. 4.0 $\mathrm{mg\,g^{-1}}$ at $25 \pm 2\,^{\circ}\mathrm{C}$. Maximum nitrate removal occurred at equilibrium pH ca. 4.4. The nitrate sorption has been well explained using Langmuir isotherm model. Results from this study demonstrated the potential utility of nano-alumina for nitrate removal from water.

1. Introduction

The presence of elevated concentrations of nitrate ($NO_3{}^-$) in potable water has become a serious concern worldwide over the past few decades. Nitrate is a water soluble ion that does not readily bind to the soil causing it to be highly susceptible to run-off migration [1]. Point and non-point sources of nitrate contamination can include agricultural and urban runoff, disposal of untreated sanitary and industrial wastes in unsafe manner, leakage in septic systems, landfill leachate, animal manure, NO*x* air stripping waste from air pollution control devices. Nitrate, due to its high water solubility, is possibly the most widespread groundwater contaminant in the world, imposing a serious threat to drinking water supplies and causing ecological disturbances [2,3]. Increasing nitrate concentrations in drinking water causes two adverse health effects: induction of “blue-baby syndrome” (methemoglobinemia), especially in infants, and the potential formation of carcinogenic nitrosamines [4,5].

Keeping the view of serious health problems associated with excess nitrate concentrations in drinking water, various environmental regulatory agencies including the U.S. Environmental Protection Agency (U.S. EPA) have set a maximum contaminant level (MCL) of 10 $\mathrm{mg\,L^{-1}}$ of nitrate-N in drinking water. Nitrate contaminated water must be treated properly to meet applicable regulations.

The commonly used treatment methods for nitrate removal include chemical denitrification using zero-valent iron (Fe^0) [6–8], zero-valent magnesium (Mg^0) [9], ionic exchange [10], reverse osmosis [11], electrodialysis [12], catalytic denitrification [13] and biological denitrification [14]. However, current available technologies for nitrate removal are found to be expensive, inefficient and generate additional by-products. Generally, reverse osmosis, ion exchange and electrodialysis processes are considered the best available technologies (BAT) to treat nitrate-contaminated water [15–17]. Nevertheless, these traditional technologies do not solve the problem related to the excess of nitrate in the environment; in turn, they produce nitrate concentrated waste streams that pose a disposal problem due to the high saline content [14,17,18]. BATs are relatively expensive [16] and moreover, cause process complexity to be used in in situ application for direct decontamination of groundwater [19].

Zero-valent iron (ZVI) has been extensively studied for its ability to reduce different contaminants including nitrate in groundwater [6–8,20–22]. However, this technology has some limitations as discussed by various researchers in different articles. For example, Cheng et al. [6] reported that the main disadvantages of nitrate reduction using ZVI are ammonium production and the pH control requirement (by initial pH reduction or using a buffer). When

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applying ZVI in an in situ remediation technique for nitrate removal, these disadvantages are even more critical [21]. Furthermore, biological denitrification processes are difficult to apply to inorganic wastewater treatment because additional organic substrates of electron donors are required [23].

Comparatively, adsorption seems to be a more attractive method for the removal of nitrate in terms of cost, simplicity of design and operation. Different adsorbents have been tested for the removal of nitrate from water [24–32]. Conventionally, nitrate removal by different adsorbents has been employed using micron-sized particles, however, in recent years, nanotechnology has emerged as one of the attractive technologies for water treatment. The benefits of using nano-materials may derive from their self-assembly, large surface area and enhanced reactivity [33] and can be potentially utilized for water remediation [34].

In the present study, adsorption feasibility of nano-alumina has been assessed for nitrate removal from aqueous solution. The characterization of nano-alumina in the form of scanning electron micrographs (SEM), X-ray diffraction (XRD), Fourier transform infra-red (FTIR) and Brunauer Emmett Teller (BET) has been conducted and its performance was further assessed for nitrate removal from water. Adsorption studies were conducted under various experimental conditions, such as pH, contact time, initial nitrate concentrations, temperature, and the presence of competing anions. The data from the experiments were fitted with different models to identify the adsorption mechanism. The results have been thoroughly discussed which would help in the better understanding of nitrate sorption mechanism by nano-alumina.

2. Material and methods

2.1. Materials

Nano-alumina (Al_2O_3 nanopowder) was purchased from Sigma–Aldrich. Nitrate stock solution was prepared by dissolving sodium nitrate (Sigma–Aldrich) in deionized (DI) water. Standards and nitrate spiked samples at a required concentration range were prepared by appropriate dilution of the stock solution with DI water. All reagents used were of analytical reagent grade.

2.2. Characterization of the adsorbent

The morphology of the sorbent was determined by scanning electron microscopy (SEM) using Quanta 200 (FEI, Netherlands) field-emission gun (FEG) scanning electron microscope. The X-ray diffraction (XRD) pattern of the nano-alumina was obtained using a Bruker AXS D8 Advance X-ray diffractometer. FTIR spectra of the sorbent was collected using Nicolet 8700 FTIR spectrometer (Thermo Instruments, USA). Nitrogen adsorption/desorption isotherms were obtained using a BEL Japan Inc. Belsorp-Max surface area analyzer at 77 K.

2.3. Nitrate analysis

The concentration of nitrate in the solutions was determined by ion chromatography (Dionex, ICS-90, Ion Chromatography system, USA). The mobile phase consisted of a mixture of 7.0 mM sodium carbonate (Na_2CO_3) and 2.0 mM sodium bicarbonate ($NaHCO_3$) delivered at the flow rate of 1.0 mL min^{-1}. AS40 autosampler (Dionex, USA) was assembled with a 10-μL injection loop. A separation column, IonPac® AS9-HC, 4.0 mm × 250 mm (Dionex, USA), a guard column, IonPac® AG9-HC, 4.0 mm × 50 mm (Dionex, USA), and membrane suppressor, AMMS III 4-mm were used. The data acquisition was performed using Chromeleon 6.5 (Dionex, USA).

2.4. Nitrate adsorption studies

Adsorption of nitrate onto nano-alumina was studied by batch experiments. A stock nitrate solution (1000 mg L^{-1}) was used in adsorption experiments. The required concentration of the nitrate solution was prepared by serial dilution of stock solution. A fixed amount of the adsorbent was added to nitrate solution taken in 50 mL capped tubes, which were placed in a thermostat cum shaking assembly. The solutions were stirred continuously at constant temperature to achieve equilibrium. After equilibrium, the solid was separated by centrifugation (5000 rpm) and filtration through IC Millex-LG filter (Millipore). The filtrates were kept in refrigerator at 2 °C for next day analysis. The concentration of the nitrate in the solution was analyzed by ion chromatography. Reproducibility of the measurements was determined in triplicates and the average values are reported. Relative standard deviations were found to be within ±3.0%. The amount of nitrate adsorbed (q_e in mg g^{-1}) was calculated as follows:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations of nitrate in solution (mg L^{-1}), V is the volume of solution (L) and m is mass of the adsorbent (g).

2.4.1. pH studies

In order to investigate the effect of pH on nitrate adsorption, the pH of the nitrate solutions (20 mg L^{-1}) were adjusted from 3 to 12. The initial pH of the solution was adjusted by using 0.1 M HCl or 0.1 M NaOH and nano-alumina (0.025 g) was added to 25 mL solution. The mixture was shaken using a temperature-controlled water bath shaker. After adsorption, the final pH of all solutions was measured and the value providing the maximum nitrate removal was determined.

2.4.2. Kinetic studies

The rate of adsorption of nitrate was studied at different time intervals (1 min–24 h). In kinetic studies, 25 mL nitrate solution (10 and 20 mg L^{-1}) with an initial solution pH of 3.1 were agitated with nano-alumina (0.025 g) using a temperature-controlled water bath shaker. After a fixed time interval, the adsorbent was separated as described in section 2.4 and the filtrate was analyzed to determine the equilibrium concentration of nitrate. Experiments were repeated for different periods until reaching the adsorption equilibrium.

2.4.3. Equilibrium adsorption studies

The adsorption of nitrate on nano-alumina was conducted at two temperatures (25 and 10 ± 2 °C) by batch experiments. Twenty five millilitres of nitrate solution of varying initial concentrations (1–100 mg L^{-1}) with an initial solution pH of 3.1 in 50 mL capped tubes were shaken with 0.025 g of adsorbent after adjusting the pH to the desired value, for a specified period of contact time in a temperature-controlled shaking assembly. After equilibrium, samples were filtered and the filtrate was then analyzed for residual nitrate concentration by ion chromatography.

2.4.4. Competing anions studies

The effects of competing anions (chloride, fluoride, carbonate, sulphate and phosphate) on nitrate adsorption were investigated by performing nitrate adsorption under a fixed nitrate concentration (20 mg L^{-1}), and initial competing anion concentrations of 20–100 mg L^{-1} with sorbent dosage of 1 g L^{-1}.