



Removal of nitrate by modified pine sawdust: Effects of temperature and co-existing anions



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ABSTRACT

The effect of temperature, sulphate and phosphate, and the initial nitrate concentration on nitrate removal was studied with synthetic solutions. Chemically modified pine sawdust (*Pinus sylvestris*) anion exchange resin (MPSD) was used in the sorption studies. The resin was synthesized by reacting pine sawdust with epichlorohydrin, ethylenediamine and triethylamine in the presence of N,N-dimethylformamide. Nitrate removal was successful at 5–70 °C. Higher temperatures caused nitrate removal to decrease moderately, but sorption capacities of 22.2–32.8 mg/g for NO₃-N were achieved. The removal of nitrate in the presence of sulphate or phosphate was studied at concentrations of 30 mg N/l, 10–500 mg S/l and 1–50 mg P/l. A significant decrease in nitrate reduction was observed at sulphate and phosphate concentrations of 100 mg S/l and 50 mg P/l, respectively. The effect of initial nitrate concentration was studied in column. Nitrate sorption was clearly dependent on the initial concentration. Desorption of nitrate in column was completed using about 80 bed volumes of 0.1 M NaCl solution. The sorption data were fitted to the Langmuir, Freundlich and Redlich–Peterson adsorption models. The Redlich–Peterson and Langmuir models gave the best fit, which suggests monolayer sorption. Thermodynamic studies revealed that the sorption of nitrate was spontaneous and exothermic in nature. The results imply that modified pine sawdust could be a feasible alternative in the treatment of real industrial wastewaters.

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1. Introduction

A vast variety of contaminants is found in mining wastewaters, depending on the type of mining activity. Nitrate emissions originate typically from the use of explosives in mining. High concentrations of nitrate in drinking water cause significant problems for human health (methaemoglobinaemia, formation of carcinogens) (Fewtrell, 2004) and the environment through eutrophication (Wiesmann et al., 2006). Besides heavy metals, sulphate is a major contaminant in mining effluents causing salination of soil and waterways. The sulphate in mining effluents is due to the use of sulphuric acid in mineral processing and the minerals in the bedrock. Phosphate is present in wastewaters, originating from a phosphate mine or other field of industry as well as in municipal wastewaters. As a nutrient, phosphate is a major contributing factor in eutrophication.

Numerous methods for the removal of nitrate are available, such as biological treatment (Wiesmann et al., 2006), electrodialysis (El Midaoui et al., 2001), reverse osmosis (Häyrynen et al., 2008), adsorption (Çengelöglu et al., 2006; Mishra and Patel, 2009), ion exchange (Ebrahimi and Roberts, 2013), and reduction by zero-valent iron (Su and Puls, 2004). In the past decade, growing interest in the utilization of biomass has induced extensive research on cheap lignocellulosic sorbents for the removal of nitrate. Lignocellulosic materials, such as sawdust, tree bark, fruit peels, pomace and straw, can be used as such in the adsorption of cations (Sousa et al., 2010; Su et al., 2012), but to enable binding of anions chemical modification (cationization) is required. For this purpose, several modification methods involving the incorporation of quaternary ammonium groups have been introduced. Orlando et al. (2002) produced anion exchange resins from agricultural residues through reactions with epichlorohydrin and dimethylamine in the presence of pyridine. A maximum sorption capacity of 16.9 mg/g for NO₃-N was achieved with rice hull (Orlando et al., 2002). Abbott et al. (2006) reported the successful cationization of cotton wool with a chlorcholine chloride-based eutectic solvent. Wang et al. (2010) and Xu et al. (2010) prepared anion exchangers from giant reed and wheat straw using epichlorohydrin, ethylenediamine,

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triethylamine and N,N-dimethylformamide (ETM method). Xu et al. (2010) achieved a sorption capacity of 11.9 mg/g for NO₃-N. N-(3-chloro-2-hydroxypropyl) trimethylammonium chloride (CHMAC) has been used to produce anion exchange resins from Chinese reed together with epichlorohydrin (Namasivayam and Höll, 2005) and from coconut shell fibres in the presence of NaOH (de Lima et al., 2012). A calculated sorption capacity of 7.6 mg/g for NO₃-N was obtained by de Lima et al. (2012). Karachalios and Wazne (2013) produced a quaternized biosorbent by treating pine bark with a mixture of choline chloride derivative and urea, and imidazole, achieving a sorption capacity of 40.7 mg/g for NO₃-N.

In our previous studies, the sorption of nitrate onto modified pine sawdust (MPSD) was found to be very rapid, efficient (30.1 mg N/g) and reversible, and the sorption efficiency was maintained well over a wide pH range (3–10) (Keränen et al., 2013). The sorbent was synthesized by reacting pine sawdust with epichlorohydrin, ethylenediamine and triethylamine in the presence of N,N-dimethylformamide (ETM method). The effects of temperature and co-existing anions for this sorbent have not yet been investigated. The temperature of the wastewater to be treated plays a key role in the treatment process. The efficiency of sorption phenomena is temperature-dependent. The temperature of mining effluents, especially in the Northern hemisphere, is usually in a range 5–15 °C. On the other hand, wastewaters originating from other industrial processes can be much warmer, e.g. 40–60 °C. In addition, the ion concentration of the wastewater and co-existing ions affect the lifetime of the biosorbent material and sorption efficiency. It is important to know the effects of these factors when the sorbent is applied on industrial scale. This study aims at elucidating the effects of temperature and initial nitrate concentration as well as the effect of phosphate and sulphate on the removal of nitrate from synthetic solutions.

2. Materials and methods

Pine sawdust (*Pinus sylvestris*) was acquired from the Stora Enso pulp mill in Kemi, Finland. The sawdust was dried, ground, sieved and chemically modified as reported in our previous work (Keränen et al., 2013). Two grams of sawdust were reacted with a combination of 16 ml of N,N-dimethylformamide and 12 ml of epichlorohydrin for 45 min at 60–70 °C under constant stirring. Then, 13 ml of triethylamine was added and the mixture was stirred for 45 min at 60–70 °C. Finally, 2.5 ml of ethylenediamine was added and the mixture was stirred for 2 h at 60–70 °C (ETM method). The final product (8–10 g, oven-dry weight) was washed carefully with water and dried at 105 °C. A nitrogen content of 9–10% was achieved for the modified pine sawdust prepared by the ETM method (Keränen et al., 2013).

All chemicals used in the experiments were of analytical grade. Stock solutions of nitrate (1000 mg N/l), sulphate (1000 mg S/l) and phosphate (1000 mg P/l) were prepared by dissolving sodium nitrate (NaNO₃, Merck), sodium sulphate (Na₂SO₄, Merck) and sodium phosphate (Na₃PO₄, Sigma–Aldrich) in ultrapure Milli-Q water (Merck Millipore). Solutions used in the sorption tests were diluted from the stock solutions. Sodium chloride solution (Merck) was used in the column desorption studies.

2.1. FESEM and EDS analyses

Field emission scanning electron microscopy (FESEM, Zeiss Ultra Plus) was used to investigate the structure of five samples: untreated pine sawdust, fresh MPSD, and MPSD loaded with nitrate, with nitrate and sulphate, and with nitrate and phosphate. The samples were mounted on an aluminium disc and coated with carbon (15 nm, Jeol Vacuum Evaporator JEE-420) for the EDS

analyses and with platinum (5 nm, Agar High Resolution Sputter Coater) for the FESEM imaging. An energy dispersive X-ray spectroscope (EDS, Inca x-act, Oxford Instruments) was attached to the FESEM instrument and used simultaneously with FESEM to detect elements present in the MPSD structure. The EDS areal analyses were run in triplicate on each sample, and the elemental distribution data were normalized.

2.2. Batch sorption experiments

A constant dosage of 3 g/l of MPSD resin was used in all batch sorption experiments. The sample preparation and shaking conditions are described in detail in Sections 2.2.1 and 2.2.2. The resin was separated from the liquid sample by centrifugation (Jouan C4.12, 10 min at 800 × g). The residual nitrogen content was determined using Hach Lange test cuvettes for total nitrogen (LCK 138 for 1–16 mg N/l, LCK 238 for 5–40 mg N/l and LCK 338 for 20–100 mg N/l) and using a Hach Lange HT 200S thermostat and a Hach Lange spectrophotometer DR 2800. Sulphate was determined using a Dionex ICS 1000 ion chromatograph equipped with Dionex IonPac AG22 4 mm and AS22 4 mm columns, a Dionex ASRS 300 suppressor and a Dionex DS6 conductivity cell. Phosphate (as PO₄-P) was determined by a Lachat QuikChem FIA+ 8000 auto-analyzer. The pH of the liquid samples was measured with a Metrohm 744 pH meter. All batch shakings were performed in triplicate. The reduction *R* as a percentage was calculated as follows:

$$R = \frac{C_0 - C_r}{C_0} \cdot 100 \quad (1)$$

where *C*₀ is the initial nitrogen concentration (mg/l) and *C*_r is the residual nitrogen concentration (mg/l).

2.2.1. Effect of temperature

The temperature dependence of nitrate sorption was studied by conducting batch shaking tests at 5, 23 and 40 °C. For each test, the nitrate solution was pipetted in to the test flasks at the corresponding temperature. This led to a minor error in the volume of the sample: +0.2% at 5 °C and –0.6% at 40 °C and has been taken into account in the calculations.

In the tests at 5 °C and 23 °C, 0.15 g of MPSD resin was weighed in 250-ml polyethylene bottles and 50 ml of nitrate solution (10–500 mg N/l) was added. The initial pH of the nitrate solutions was 5.8–7. Preliminary studies had revealed that equilibrium was reached in 2 h at 5 °C (only 2 h and 4 h were tested, data not shown) and in 10 min at room temperature (Keränen et al., 2013). Thus, the bottles were then shaken in a horizontally rotating shaker in a cold room or at room temperature for 2 h. The separation of the resin from the liquid sample was done quickly after shaking at 5 °C had finished, to prevent the sample from warming up.

In the tests conducted at 40 °C, 0.15 g of MPSD resin was weighed in 100-ml round bottom flasks and 50 ml of nitrate solution (10–500 mg N/l) was added. The flasks were immersed in a hot water bath, the temperature of which was controlled with a JP Selecta Tectron Bio immersion thermostat. The temperature of the bath was measured with an analogue thermometer (±0.5 °C). Stirring was induced with a multi-position magnetic stirrer (JP Selecta Multimatic 5-S) for 2 h. The separation of the resin from the liquid sample was done quickly after shaking had finished.

In order to extend the tests on temperature dependence, temperatures of 50, 60 and 70 °C were chosen to be studied at a single NO₃-N concentration. Batch shakings with three repetitions were conducted at each temperature using a constant nitrogen

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