

# Equilibrium and kinetics of nitrate removal by protonated cross-linked chitosan

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## Abstract

Nitrate, contained in surface or groundwater, can be removed by sorption on protonated cross-linked chitosan gel beads. The sorption capacity is pH-dependent and large enough to meet the standard of drinkable water. The isothermal equilibrium curves are straight lines, which implies that the removal is independent of the initial concentration. The main reactive process, which probably depends on the secondary ammonium groups, involves the total bead volume and not only its surface. If required, the sorption capacity is easily recovered by increasing the pH to 12. The main competitor is fluoride but, even in its presence, the sorption capacity of nitrate remains significant. The sorption kinetics, which can be represented by a mass transfer equation, is not limited by pore or by film diffusion.

## Introduction

Water resources are, in many countries, heavily polluted by nitrate (Laigla et al., 1990). Nitrate concentration in groundwater or surface freshwater reaches, in some places, more than 100 mg/l. The actual European standard, of less than 50 mg/l in drinkable water, could become more stringent (25 mg/l). The major concern is the blue-baby syndrome resulting from the conversion of haemoglobin into methaemoglobin, which cannot carry oxygen (Golden and Weinstein, 1998). If more than half the haemoglobin is converted, death is likely. Moreover, the adverse effects on adults are not well documented.

Nitrate removal is hampered by its low reactivity. Two treatment techniques are currently used: biological denitrification and ion exchange. Biological denitrification (Richard and Leprince, 1980) requires a carbonaceous substrate and a subsequent polishing treatment like filtration and disinfection. This technique, which is not efficient at a temperature of lower than 7°C, is carried out for groundwater which is constantly at a temperature of around 12°C. Treatment by an ion-exchange resin replaces nitrate by chloride (Deguin, 1988). The resin retains also some sulphate and hydrogen-carbonate, inducing significant changes in the water composition and an increase of the chloride concentration. Moreover, the disposal of the concentrated effluent, obtained after regeneration, should be cautiously considered. Of course electrodialysis or reverse osmosis could also remove nitrate, but their applications are actually hampered by their high cost.

Chitosan is a natural product derived by desacetylation from the polysaccharide chitin. Chitin is found in the exo-skeletons of shrimp, crab and other shellfish. Thanks to its exceptional properties, chitin protects these animals in their natural environment and its applications are growing in a large variety of other fields, e. g. carrier for immobilised cells, artificial skin, membrane synthesis, etc. (Milot, 1998). Chitosan gel beads proved to be a particularly

interesting adsorbent in the field of industrial wastewater treatment for the removal of heavy metals (Milot, 1998). However, no reference was found about its capacity to remove nitrate but the presence of amino groups (Muzzarelli, 1977), particularly in cross-linked chitosan, could favour anion adsorption. Considering that chitosan is a soil conditioner that is able to prevent crop diseases (El Ghaout et al., 1992), saturated chitosan could be used as a fertiliser that slowly liberates nitrate. This work is focused on the feasibility of nitrate removal by cross-linked chitosan gel beads.

## Experimental

Chitosan gel beads were made by means of the following procedure: chitosan powder, provided by France Chitine, was dissolved in an acetic acid solution of same concentration as the solid (3.5% mass). The solution was then pumped through a hypodermic needle allowing drops to fall down into a tank containing a 2 M NaOH solution. Heterogeneous precipitation induced the formation of highly porous spherical gel beads, which settled at the bottom of the tank. Injecting air, at different flow-rates, around the falling drop allowed varying the bead size. After 12 h, the beads were washed with distilled water in order to reach neutrality. Cross-linked gel beads were obtained after 24 h residence time in a glutaraldehyde solution (5 g/g dry chitosan) (Yoshida et al., 1993). The beads were then cautiously washed with distilled water. The material (100 g/l beads) was protonated by 30-min gentle stirring in a HCl solution the concentration of which conditioned the equilibrium pH of the sorption runs.

Potentiometric studies of the different gels were carried out with 100 g/l beads in a 0.3 N HCl solution. The pH was measured as a function of the added volume (micro-drops) of 0.5 N NaOH.

All the equilibrium and kinetics runs were carried out in 0.5 l batch reactors, mechanically stirred, at 80 RPM in current operation. Equilibrium was reached after 20 to 30 min. Saline solutions were prepared with NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, NaCl and NaF dissolved in distilled or tap water free of nitrate. Contaminated surface or groundwater from the Montpellier region, in France, was also tested. All the runs were carried out at room temperature which was maintained at 20°C. Nitrate concentration was determined by the spectro-

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