Surfactant-Modified Hierarchical Nanozeolites: Super-adsorbents for nitrate removal from contaminated water

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Abstract

Hierarchical *BEA-type nanosponges zeolite with a high external surface area (116 $m^2.g^{-1}$) and small crystal size, synthesized in the presence of a dual-porogenic organic compound, were modified with a cationic surfactant ($HDTMA^+Br^-$: hexadecyltrimethyl ammonium bromide) in order to create a new anion exchanger system: the surfactant-modified zeolite nanosponges (SMZ_{NS}). A maximum nitrate removal capacity of 1338 $mmol.Kg^{-1}$ / 83 $mg.g^{-1}$ was obtained for these materials. This value is the highest ever observed for nitrate removal using surfactant-modified zeolite.

Introduction

Nowadays, among the major biogeochemical cycles, problems are mostly encountered with the nitrogen cycle. Fertilizers in their different categories and especially those rich in nitrogen are widely applied in agriculture to enhance the growth of plants and increase the yield (Liu, 2014). Nitrates diffused from fertilized soils into ground water and wells (which are the main source of drinking water all over the world) due to their low adsorption affinity with different kinds of soil and their high-water solubility. Their biodegradability can cause one of the most severe water perturbation: the eutrophication phenomenon (Thompson, 2001). In addition, once accumulated into the human body (in high concentration: > 50 $mg.L^{-1}$, according to the World Health Organization), it can be reduced (by enzymes and micro-organisms) into nitrite NO_2^-, which can participate in the development of digestive cancers in an acidic medium (stomach). Different processes have been applied to remove nitrates from contaminated water. Biological treatments based on denitrification of nitrates using microbial biomass, micobioalgal biomass, or bacteria are widely applied due to their low-cost requirements. However, these processes have common disadvantages concerning the used of toxic compound such as methanol or other additional organic substrates (such as electron donor) (Thalasso, 1997). In addition, since bacteria are very sensitive to pH and temperature, very specific working conditions are needed. Chemical treatments based on nitrate chemical reduction (using for example zero-valent iron or magnesium), are highly pH and temperature dependent. These methods are also known to be high-energy consumers. Physico-chemical treatments that consist on the removal of nitrate using processes such as electrodialysis, adsorption and ion exchange can be also used.

Bowman et al. showed in 1994 that the surface of zeolites can be modified by a physico-chemical treatment of the surface using a cationic surfactant such as hexadecyltrimethyl ammonium ($HDTMA^+$) or 1-hexadecylpyridinium (HDP^+) bromide in order to create an anion exchanger system: SMZ (Surfactant Modified Zeolite) for the removal of inorganic oxyanions in waste water (Haggerty, 1994). Another anion exchanger system for the nitrate removal has been suggested by our group*:* the SMZN (Surfactant Modified MFI-Zeolite Nanosheets) using $HDTMA^+Br^-$ (Schick, 2011). These materials show a nitrate removal capacity 2 times higher than the natural treated zeolite (clinoptilolite): 37.2 $mg.g^{-1}$ and 19.2 $mg.g^{-1}$, respectively. This value was the highest nitrate removal capacity reported for SMZ materials.

In the present work, the effect of *BEA-type particle's morphology on their nitrate adsorption capacities has been studied. For this aim, *BEA-type zeolites nanosponges were synthesized and its external surface was modified using $HDTMA^+Br^-$ as cationic surfactant to obtain SMZ_{NS}. The samples were fully characterized at each step of the synthesis by N_2 adsorption/desorption, XRD techniques, scanning and transmission electron microscopies (SEM and TEM). These SMZ materials were then used for nitrate removal from water.

Experimental part

*BEA-type zeolites nanosponges were obtained by hydrothermal synthesis following the protocol published by El Hanache *et al.* (2019) The surfactant modified zeolites (SMZ_{NS}) were prepared as shown in figure 1 by treating 1 g of the as-synthesized zeolites with 20 mL of a 50 $mmol.L^{-1}$ hexadecyltrimethyl ammonium bromide surfactant solution ($HDTMA^+Br^-$ in demineralized water) at 60 °C for 24 h. $HDTMA^+Br^-$ is a cationic surfactant-quaternary ammonium salt with a critical micelle concentration (CMC) equals to 0.94 $mmol.L^{-1}$ at 30 °C. After achieving equilibrium, samples were recovered by filtration and washed with 50 mL of distilled water in order to remove the excess of $HDTMA^+$. Nitrate sorption tests were carried out at room temperature by adding a specific amount of SMZ materials in a 2 mL capacity vials containing a volume of aqueous solution of KNO_3 (in demineralized water) (Fluka). A horizontal mechanical shaking was used to reduce the sedimentation of the powder (SMZ) at room temperature. The solid fractions were removed by filtration using 0.2 µm syringe filters, then the supernatants were diluted and analyzed using a UV-Visible spectrometer.

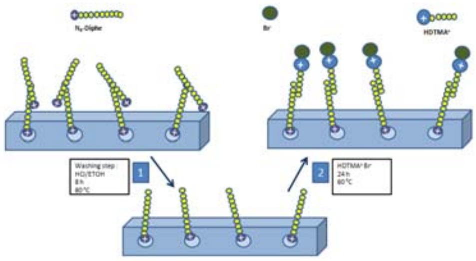

Figure 1. Schematic representation of the surface modification of *BEA-type nanosponges in order to obtain the SMZ_{NS} materials.

Results and discussion

Adsorption isotherms were carried out by increasing the concentration of the pollutant [NO_3^-] from 0.8 to 24.2 mmol.L^{-1}, with a S/L ratio equal to 2 mg.mL^{-1} for the SMZ_{NS} and 25 mg.mL^{-1} for the SMZ_{NC}, and at pH of 5.5.

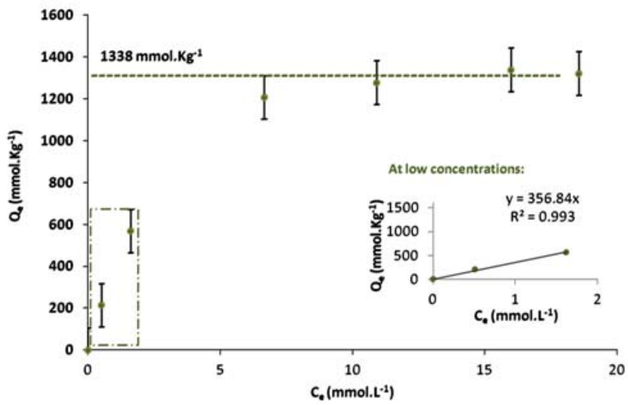

Figure 2. Nitrate adsorption isotherm (at pH = 5.5) on SMZ_{NS} with S/L ratio equal to 2 mg.mL^{-1}.

At low concentrations, as shown in figure 2, the shape and the slope of the adsorption isotherm indicate a good selectivity of SMZ_{NS} for the nitrate removal. The slope of the isotherm at these concentrations is 357 L.Kg^{-1}. As expected, Q_e values increase with the increase of nitrate concentration until a plateau is reached indicating the maximum removal capacities equal to 1338 mmol.Kg^{-1} (83 mg.g^{-1}) for the SMZ_{NS} (El Hanache, 2019). In order to get better insight of the adsorption mechanism, the Langmuir and Freundlich adsorption models were applied to the nitrate adsorption isotherms of SMZ_{NS}. The best correlation was found with the Langmuir adsorption model with linear regression coefficient equal to 0.957.

Conclusion

Adsorption isotherm of SMZ_{NS} was plotted in a large concentration range [0.8-24.2] mmol.L^{-1} and fitted with Langmuir isotherm model, with a maximum nitrate removal capacity found to be 1338 mmol.Kg^{-1} (83 mg.g^{-1}) at high nitrate concentrations and a pH of 5.5. The removal kinetic is very fast and fit the pseudo second-order model.

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