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Characterization zeolite modified with cation active polyelectrolyte and its effect on biological wastewater treatment

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The bound organic carbon (BOC) content, chemical stability, and homogeneity of clinoptilolite-rich zeolitic tuff (C_z) modified with cation active polyelectrolyte (CAP), as well as the effect of CAP-modified C_z (CAPMZ)on carbonaceous biochemical oxygen demand (CBOD), nitrogenous biochemical oxygen demand (NBOD), reaction rate, and order in laboratory batch experiments were determined. Full-scale biological degradability experiments using CAPMZ at a wastewater treatment plant (WWTP) were carried out. We found that the BOC content of CAPMZ was 2.3 mg_{BOC}/g_{Cz}. CAPMZ was stable to pH 9 and its homogeneity was 3.5%. CAPMZ increased the reaction rate and decreased the reaction order of the biochemical oxidation of organic constituents in wastewaters.

Introduction

The most common wastewater (WW) treatment method is aerobic biological, in which the organic and inorganic pollutants are decomposed and converted to gases and cell tissue by bacteria in the presence of oxygen. The culture of bacteria forms a living, activated sludge. The capacity and the loadability of WWTPs depend on the activity and settling characteristics of the activated sludge. These sludge parameters, however, can be improved with the addition of C_z into the raw WW.

Since both the C_z and bacteria have negative surface charges, the adsorption of bacteria on the C_z surface is hindered. The C_z-bacterium bond is formed and attributed to the extracellular polymers (ECP) produced by the bacteria, since the ECP molecules can bridge the bacteria and the C_z surface.

If positively charged CAP molecules are bonded to the C_z particles, the CAP molecules are able to bind the bacterium flocs to themselves, i.e., to the C_z in a prompt reaction by their free, positively charged groups. The CAP molecules attached to the C_z particles change the sorption characteristics of zeolite crystals, because its external cation exchange capacity is converted to an anion exchange, i.e., CAPMZ can adsorb not only cations, but anions, as well.

This paper demonstrates the properties of a CAPMZ and its effects on biological degradability of WWs.

Experimental Methods

Materials: C_z samples, with a particle size range of 50–110 μm, were obtained from the Bodrogkeresztúr Zeolite Mine in Hungary. CAP of polyacrylamine type [poly-2-hydroxypropyl-N, N-dimethyl ammonium chloride, $(C_5H_{12}NOCl)_n$ n = 360, molecule weight: 50,000] was used for surface modification of C_z.

The dry modification method was applied for manufacturing CAPMZ. The bound CAP content of CAPMZ was determined in the form of BOC by total organic carbon (TOC) measurements. CAPMZ were washed through with TOC-free water to remove the mechanically adhered CAP molecules. Thereafter, the TOC of the unwashable, bound CAP content of CAPMZ was determined.

Examination of the stability of C_z-CAP bond was as follows: CAPMZ was suspended in TOC-free water. The suspension was intensively stirred and the TOC concentration in the aqueous phase was measured as a function of pH and time.

The thermogravimetric (TG) method combined with a mass selective (MS) detector was used to determine the homogeneity of CAPMZ. The MS detector measured the quantity of the methyl (CH_3^-) ions liberated from a 3 mg CAPMZ sample at a high temperature.

The effect of CAPMZ on CBOD and NBOD was tested by the determination of the oxygen requirement of a communal WW sample with and without CAPMZ. During the CBOD measurements, nitrification was suppressed with a nitrification inhibitor. Measurements were accomplished according to Standard Methods. Dissolved oxygen (DO) concentrations in the samples were measured with an oxygen membrane electrode. Fujimoto's method was used for calculating the ultimate CBOD (UCBOD) values.

Biological degradability tests were carried out to determine the effect of CAPMZ on the reaction rate and reaction order of biochemical oxidation. The mixture of a WW sample and activated sludge was aerated in a 50 L batch reactor. In parallel experiments CAPMZ was added to the WW-activated sludge mixture. The chemical oxygen demand (COD), biochemical oxygen demand (BOD_5) and NH_4-N concentration in the control and CAPMZ samples were determined as a function of time.

The WW treatment technology (WWTT) employing CAPMZ was installed at the WWTP located at Veresegyháza in Hungary. One of the cleaning lines of the WWTP was fed with CAPMZ, while the other one served as a control.

Results and Discussion

The data of TOC measurements and stability tests showed the BOC content of CAPMZ was 2.3 mg/g and 92% of the CAP-C_z bonds remained stable in an aqueous suspension of pH 9. Since the pH of communal WW is always less than 9, the CAP-C_z connection can be considered stable in the process of biological WW treatment.

Homogeneity, characterized by the standard deviation (SD) of the TG-MS measurements of seven CAPMZ samples, was 3.5%.

The batch scale tests showed that CAPMZ accelerated the aerobic decomposition of organic matters, but did not increase the amount of the biodegradable constituents of WW.

CAPMZ suspended in WW decreased the reaction order and increased the reaction rate of the biological oxidation of organic matters by 20–30%.

The pilot scale experiments, in conjunction with the laboratory ones, showed that applying CAPMZ, resulted in significantly better effluent water quality and verified that CAPMZ additive was capable to increase the loadability of WWTP expressed in COD (5–40%), BOD (5–40%), NH_4-N removal (20–80%), phosphorous removal (15–20%) and suspended solids removal (30–40%).

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