PHOSPHATE REMOVAL FROM WASTEWATER BY SURFACTANT-MODIFIED CLINOPTILOLITE

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ABSTRACT

The hexadecyltrimethylammonium (HDTMA) bromide was used to modify the surface of natural zeolitized tuff (NZ) from partial monolayer to the bilayer coverage. The modification of NZ resulted in the change of zeta potential of the surface from negative to positive which enhanced the phosphate (P) adsorption capacity. Only in reactors containing the partial monolayer coverage of the surfactant-modified zeolites (SMZs), the P was efficiently removed from wastewater by combined adsorption onto the SMZs and bacterial uptake in the biomass. The SMZs with monolayer, partial bilayer or bilayer coverage showed the bactericidal effect.

Keywords: bacteria, phosphate, surfactant, zeolite, wastewater

INTRODUCTION

The low cost of natural zeolitized tuffs (NZ), their superior hydraulic characteristics and high cation exchange capacities (CEC) makes their use attractive in wastewater treatment. However, the NZ have negligible affinity for adsorption of anions [1,2] such as phosphate (P). Treatment of the NZ with cationic surfactants changes their surface chemistry, and the electrical charge reversal induced by the surfactant bilayer allows the retention of anions by ion exchange [3]. Such modified zeolites are commonly known as the surfactant-modified zeolites (SMZs). By the adsorption of P onto SMZs great amount of P can be removed from wastewater. But, the maximum capacity of SMZs will be reached and there will be no further retention.

There appears to be much opportunity for combining the P adsorption by SMZs with bacterial accumulation of P in order to improve the P removal from wastewater. The aim of this study was to determine the P removal from wastewaters by use of SMZs and P-accumulating bacteria from the standpoint of basic science and possible application.

EXPERIMENTAL

The NZ tuff from Bigadic, Turkey of particle size <0.122 mm was used. The NZ sample consists of approximately 70% of clinoptilolite and was free of clay minerals. The NZ sample had the CEC of 1350 meq/kg and an external cation exchange capacity (ECEC) of 120 meq/kg [4,5]. The cationic surfactant, quartery ammonium salt, hexadecyltrimethylammonium (HDTMA) bromide, $C_{16}H_{33}N(CH_3)_3Br$ (Merck) was used to modify the surface of NZ. The amounts of HDTMA used for modification of NZ surface normalized with regard to ECEC of NZ were 19.9, 64.0, 107.8, 152.7 and 215%. A 100.0 mL of each HDTMA solution in deionised water (0.477, 1.535, 2.586, 3.665 and 5.187 mmol/L) and 2.000 g of the NZ were shaken during 48 h at 30ºC. Thereafter mixtures were filtered through filter units of pore diameter 0.2 μm and concentrations of residual surfactant in the supernatants were determined as a content of total organic carbon on Shimadzu TOC-5050A analyzer. The concentrations of sorbed HDTMA cations were calculated from the mass

balance equation. The obtained SMZs were filtered through the filter paper, washed with distilled water until negative reaction to Br^- ions was reached and air dried. The SMZs were named as 1SMZ, 2SMZ, 3SMZ, 4SMZ and 5SMZ, respectively.

The P-adsorption capacity of the NZ and SMZs was determined by equilibrating 1.0 g of material in a range of 100 mL of P solutions made from KH_2PO_4, at 25ºC during 72 h. The P ($P\text{-}PO_4^{3-}$) concentration in filtered water samples was measured spectrophotometrically in a DR/2500 Hach spectrophotometer by the molybdovanadate (Hach method 8114) method. The P that disappeared from the solution was considered to have been sorbed by the NZ/SMZs. The zeta potential of the NZ and SMZs was measured by using a Zetasizer 3000- Malvern Instruments, equipped with microprocessor unit [4].

In experiments the sterile synthetic wastewater was used. Its composition in mg/L of distilled water was: Na-propionate 300; peptone 100; $MgSO_4$ 10; $CaCl_2$ 6; KCl 30; yeast extract 20; KH_2PO_4 88. All experiments were done at pH 7.00. A P-accumulating bacterium *Acinetobacter junii* (DSM, 1532) was employed. Bacteria were pre-grown on the nutrient agar (Biolife, Italy) for 20 h at 30°C. Thereafter the biomass was suspended in sterile 0.3% NaCl and inoculated into 100 mL of synthetic wastewater. In each flask 1.0 g of the NZ or SMZs was added. The flasks were sealed with a sterile gum cap and thereafter aerobically agitated in a water bath at 30°C. The aeration rate of 1 L min^{-1} with filtered air was provided during 24 h of experiment. Experiments without bacteria were carried according to the same procedure. All experiments were carried out as triplicate tests with mean values presented.

RESULTS AND DISCUSSION

The results of the sorption of HDTMA cations onto NZ are presented in Table 1. The amount of sorbed HDTMA cations on the NZ was depended on the HDTMA cations available in aqueous solution and occupied 18.8 to 170.0% of the ECEC (120 mmol/kg). The obtained SMZs were used for future experiment and named as 1SMZ, 2SMZ, 3SMZ, 4SMZ and 5SMZ, respectively.

Table 1. The sorption of HDTMA cations after equilibrating the natural zeolite (NZ) in different HDTMA solutions during 48 h at 30ºC.

HDTMA solution (%ECEC)	HDTMA sorbed (mmol/kg)	Occupied ECEC (%)	Name of material
0.0	0.0	0.0	NZ
19.9	22.6	18.8	1SMZ
64.0	73.6	61.3	2SMZ
107.8	123	102.5	3SMZ
152.7	164	136.7	4SMZ
215.0	204	170.0	5SMZ

The results of measurements of zeta potential of NZ and SMZs are presented in Table 2. The zeta potential of 1SMZ stayed negative as that of NZ, probable because of low concentration of formed hemimicelles in relation to the number of active exchangeable positions on the outer surface of NZ [6]. The surface modification of the NZ with higher HDTMA loadings resulted in the change of zeta potential of particles from negative to positive. Isoelectric point is characterised by the value zero for electrokinetic potential. Sorption above this level is expected to be in the form of a bilayer or patchy bilayers, while sorption below this point is likely in the form of monomers or hemimicelles [7]. As can be estimated on zeta potential, 1SMZ and 2SMZ have a partial monolayer, 3SMZ a monolayer, 4SMZ a partial bilayer, and 5SMZ a bilayer HDTMA coverage (Table 2). The P adsorption

capacity of the NZ was greatly enhanced by surface modification with HDTMA cations (Table 2). The estimated P adsorption capacity of SMZs showed significantly positive linear correlation with the zeta potential of SMZs.

Table 2. Zeta potential and phosphate (P) adsorption capacity of natural zeolite (NZ) and surfactant-modified zeolites (SMZs).

Name of material	Zeta potential (mV)	Type of HDTMA coverage	P adsorption capacity (mg P/kg)
NZ	-18.2	none	80.00
1SMZ	-18.7	partial monolayer	165.29
2SMZ	-15.2	partial monolayer	206.19
3SMZ	3.9	monolayer	395.26
4SMZ	22.4	partial bilayer	689.66
5SMZ	26.1	bilayer	789.47

The results of P removal from wastewater by NZ/SMZs without and with bacteria are shown in Table 3. Without presence of bacteria, P from wastewater was removed by sorption onto NZ or SMZs and P removal increased with increasing the HDTMA loading levels (Table 3, column 6). After 24 h of bacterial cultivation in reactors containing the NZ, 1SMZ, 2SMZ and 3SMZ one part of the total bacterial population was immobilised (Table 3, column 2) onto particles by adsorptive growth while the other part of the bacteria remained as planktonic cells (Table 3, column 3). With the 4SMZ and 5SMZ no bacterial growth was detected. The total number of bacteria (Table 3, column 4) was higher in reactors containing 1SMZ and 2SMZ than in the reactor containing NZ. In contrast, decay of bacteria was observed in reactors containing 3SMZ, 4SMZ and 5SMZ. It is obvious that more active bacteria can take up more P. Therefore, the significantly higher percent of P removal was achieved in reactors containing 1SMZ and 2SMZ than in the reactors containing NZ (Table 3, column 5). In reactors containing higher HDTMA loading levels of the SMZs (3SMZ, 4SMZ and 5SMZ) no enhancement of P removal was achieved when compared to the reactors containing no bacteria (Table 3, column 6).

Table 3. Performance of reactors containing natural zeolite (NZ) or surfactant-modified zeolites (SMZs) with bacteria; [c_0 CFU (10^6 CFU/mL)] = 17.33±6.65; [c_0 P-PO_4 (mg/L)] = 22.24±0.37) and without bacteria; [c_0 P-PO_4 (mg/L)] = 20.03±2.31.

Name of material	Immobilised bacteria (CFU/g)	Planktonic bacteria (CFU/mL)	Total bacteria (CFU/mL)	P removal with bacteria (%)	P removal without bacteria (%)
NZ	3.36×10^9	8.00×10^7	1.13×10^8	45.50	3.50
1 SMZ	5.28×10^9	1.17×10^8	1.66×10^8	63.41	7.61
2 SMZ	3.18×10^9	1.68×10^8	1.96×10^8	72.45	10.07
3 SMZ	7.40×10^2	1.40×10^2	1.47×10^2	14.76	13.02
4 SMZ	0.00	0.00	0.00	24.14	21.19
5 SMZ	0.00	0.00	0.00	32.76	32.33

The EC_{50} values of the aqueous HDTMA for the inhibition of CFUs in the pure culture of *A. junii* was $3.27 \pm 1.12 \times 10^{-7}$ mol/L and complete inhibition was observed by the HDTMA concentration of 10^{-5} mol/L and higher [8], proving a high acute toxicity of free HDTMA. The potential desorption of HDTMA cations from SMZs can result in the formation of toxic unbound HDTMA cations. The experimental data on the release of HDTMA cations from

SMZs in the synthetic wastewater (Table 4) demonstrate that no release occurred in reactors containing NZ and 1SMZ. The HDTMA release increased by increasing the HDTMA loading on SMZs and was significantly lower in reactors with bacteria when comparing to the reactors without bacteria. Desorption of HDTMA from SMZs can explain the toxicity of 3SMZ, 4SMZ and 5SMZ against *A. junii.* Although the HDTMA in aqueous solution is bactericidal, if adsorbed onto the SMZs, *A. junii* can remain viable. In this case P removal from wastewater can be achieved by the combined adsorption of P onto SMZs particles and bacterial uptake of P in the biomass.

Table 4. The HDTMA release from surfactant-modified zeolites (SMZs) in experiments with and without bacteria during 24 h.

Name of material	HDTMA release (mmol/L)	
	with bacteria	without bacteria
NZ	0.000	0.000
1SMZ	0.000	0.000
2SMZ	0.123	0.262
3SMZ	0.283	0.440
4SMZ	0.383	0.535
5SMZ	0.454	0.557

CONCLUSION

The SMZs can be used to enhance the P removal from wastewater in the aerated biological system, but the special attention should be given to the configuration of sorbed HDTMA cations and its potential desorption. The SMZs with monolayer, partial bilayer or bilayer HDTMA coverage showed the bactericidal effect. The efficient P removal from wastewater can be achieved by the addition of SMZs with partial monolayer HDTMA coverage by the combined mechanisms of P adsorption onto SMZs and bacterial uptake of P in the biomass.

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