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Implementation of natural zeolite for filtration of secondary municipal effluents

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ABSTRACT

A three column filtration system was designed and operated for the investigation of ammonium and suspended solids removal from wastewater by using natural zeolite. The zeolite is a clinoptilolite from the Bigadic district of Turkey. The process consisted of three parallel columns that operated on a down flow mode; the influent to the system was collected from the effluent of a municipal wastewater treatment plant. Laboratory studies consisted of batch tests for determining the capacity of clinoptilolite and column tests for the assessment of kinetics during contaminants removal from wastewater. During batch tests, samples containing 20 mg/L of ammonium were treated by zeolitic particles with a diameter of 0.5–1 mm at pH 7.3 and resulted to an effluent with about 10.4 mg/g of ammonium. The effect of zeolitic particle diameters on the removal capacity was investigated during column tests by the utilization of particles with the following diameters: (i) 0.5–1 mm, (ii) 1–2 mm, and (iii) 2–4 mm under the same filtration rate and column diameter. Ammonium and suspended solids removal rates were measured and compared for all columns. The optimum results were obtained for the filter in which 0.5–1 mm diameter clinoptilolite particles were used, with 100% ammonium removal and 38% suspended solids removal rates, respectively, for an operation period of 78 h. As a result, the addition of clinoptilolite to sand filters in existing plants may be an efficient alternative for upgrading the performance of a municipal wastewater treatment plant, used as a tertiary treatment step for polishing ammonium content.

Keywords: Ammonium; Clinoptilolite; Filtration; Ion exchange

1. Introduction

The selection of the most beneficial wastewater treatment plant scheme is becoming an important issue for meeting more stringent effluent quality standards. Two of the most important parameters, identified by the corresponding guidelines, are ammonium and suspended solids, especially when effluents are discharged into sensitive areas. These parameters are cited by the European Council directive "Urban Wastewater Treatment Directive" (91/

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Table 1
Requirements for discharges from urban waste water treatment plants (as foreseen by directive 91/271/EEC)

Parameters	Concentration	Minimum percentage of reduction
Biochemical oxygen demand (BOD_5 at 20 ℃) without nitrification	25 mg/l	70–90
Chemical oxygen demand (COD)	125 mg/l	75
Total suspended solids	35 mg/l (>10,000 p.e.)	90 (more than 10,000 p.e)
	60 mg/l (2000–10,000 p.e)	70 (2000–10,000 p.e)
Total phosphorus	2 mg/l P(10,000–100,000 p.e)	80
	1 mg/l P (>100,000 p.e)	
Total nitrogen	15 mg/l N (10,000–100,000 p.e)	70–80
	10 mg/l N (>100,000 p.e)	

271/EEC); according to it, the limits for total nitrogen and total suspended solids may go down to values as low as 10 and 35 mg/L respectively, as shown in Table 1.

Maintaining those standards may not always be possible in wastewater treatment plants with conventional treatment schemes. Such a problem has been reported for the municipal wastewater plant named "Bahcesehir Domestic Wastewater Treatment Plant" from which the wastewater for this study was collected. Characteristic properties of the domestic wastewater of Bahcesehir Domestic Wastewater Treatment Plant are given in Table 2. The results in Table 2 were deduced from the analysis of 10 grab samples taken within a period of 3 months at the beginning of the experimental work.

As shown in the table, the effluent ammonium concentration is high according to 91/271/EEC. An effluent stream of this plant with 20 mg/L ammonium concentration was used in experimental column analysis of this study for determining the behavior of columns as a real polishing stage.

Ammonium is conventionally removed in biological treatment units through nitrification. This is an effective removal technique when influent ammonium concentration is more or less constant, but in the case of variable and peak loads, the same pattern of fluctuations in the influent may be observed in the effluent stream. This can be a significant problem for plants in areas in which standards are altered to more stringent ones by the time. The effectiveness of natural zeolites in removing ammonium from domestic wastewater had been demonstrated in a number of papers [1–6]. The capacity of clinoptilolite towards ammonium has been reported to be between 1–2.27 meq/gr clinoptilolite or 14–32 mg NH_4–N/gr clinoptilolite [4]. Nguyen reported that only the 50% of this capacity can be used in practice.

If high suspended solids removal rate is needed, filters are used for advanced treatment of suspended solids. This study aims to investigate ammonium and suspended solids removal from wastewater by using natural zeolite as filtration material. In experimental analysis, Bigadic clinoptilolite from the western region of Turkey is used as a filter material which with a high ion exchange capacity.

In batch tests, the capacity of Bigadiç clinoptilolite was investigated at pH 7.3 and 0.5–1 mm diameter zeolite is used. In column analysis, three column filtration systems were examined, while ammonium and suspended solids removal rates were observed and compared for all columns. Different diameter zeolite particles were used in column analyses as:

(i) 0.5–1 mm
(ii) 1–2 mm
(iii) 2–4 mm were used as filtration material,

at the same filtration rate, and column diameter. The grain size distribution of the clinoptilolite has a significant impact on the operating ammonium ion exchange capacity. Hlavay et al. [7] investigated grain

Table 2
Wastewater characterization of Bahcesehir domestic wastewater plant

Parameters	Influent	Effluent
NH_4–N (mg/l)	50–85	19–24
Total Kjehldal nitrogen (mg/l)	80–114	30–43
COD	400–800	40–58
BOD_5	180–455	25–35
Total suspended solids	230–300	40–97
pH	7–8	7–7.5

sizes between 0.5–1.0, 0.3–1.6, and 1.6–4 mm. The smallest fraction resulted in the highest ammonium exchange capacity as expected. When using smaller grain sizes, the higher ammonium exchange capacity is probably caused by a more favorable mass transfer into the zeolite [8].

The use of sand in filters for domestic wastewater filtration is reported in a number of papers especially in the recent years [9–12]. Filtration performance was investigated in these papers under different initial concentrations and filtration rates. Promising results were obtained in terms of ammonium removal in systems incorporating clinoptilolite in filters [13–17]. However, no paper was encountered on the use of clinoptilolite in filters as a filtration material. In this study, the effects of using clinoptilolite in wastewater filtration could be observed by the implementation of clinoptilolite to filtration.

2. Materials and methods

The domestic wastewater used for laboratory studies was obtained from the effluent of the secondary clarifiers of Bahcesehir Domestic Wastewater Treatment Plant. The treatment plant is an activated sludge system for 21,000 population equivalent. This treatment plant is next to a town and there is no heavy industry close to the plant.

Clinoptilolite is used as the ion exchanger and as the filter material in the experiments. The grain sizes of clinoptilolite were between 0.5–1 mm. The clinoptilolite was provided from Bigadic district of Turkey which has rich clinoptilolite reserves. Bigadic district is at the northwest part of Turkey and next to Sea of Marmara. The typical chemical analysis of the clinoptilolite is given in Table 3. Chemical pretreatment of clinoptilolite was carried out to transform it to the sodium form which increases its ammonium exchange capacity. In the pretreatment process, the clinoptilolite was washed with distilled water, dried, and conditioned with 1 M NaCl solution for 48 h. After that, it was washed and dried again before using in the experiments [17].

The experimental work consisted of batch and continuous experiments. The batch mode was used for isotherm studies for determining the ion exchange capacity of the clinoptilolite. Different weights of clinoptilolite samples were contacted with known ammonium concentrations at a constant temperature (25 ℃). After 24 h shaking period, the solution and clinoptilolite phases were separated and the ammonium concentrations in solutions were measured. By using the difference between the first and last ammonium concentrations of solutions, ammonium concentrations in the solid phase were calculated and isotherm curves are plotted.

The experimental setup was made up of three plexiglas columns, one peristaltic pump with three head, mono metric tubes, and feed tanks. An automatic sampler was used for sampling at 2 h intervals.

The experimental setup is shown in Fig. 1.

Three columns consisting of clinoptilolite with different diameters were used in continuous runs operating at 10 min hydraulic retention time each. Total bed height of the system was 50 cm.

The suspended solids analysis took place by a straining system while ammonium analysis was made by using an ion meter with ± 0.1 mV accuracy and a Jenway 924 328 model ammonia electrode [19].

Conditions of the column study are given in Table 4.

Table 3
Chemical analysis of Bigadic clinoptilolite [18]

Bigadic clinoptilolite (%)	
SiO_2	67.96
Al_2O_3	10.74
K_2O	3.01
CaO	0.74
Na_2O	0.81
Fe_2O_3	–
MgO	1.49
TiO	–
Si	15.36

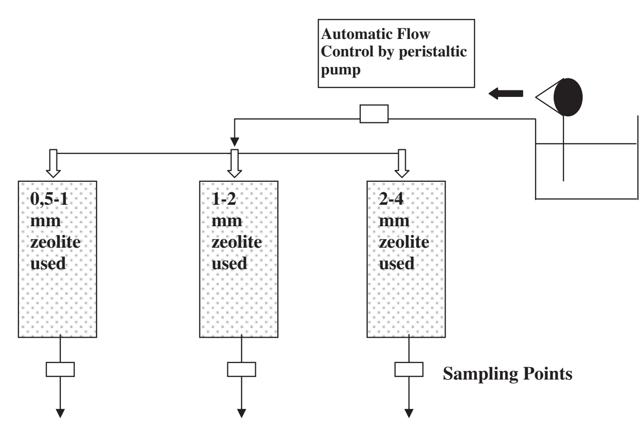

Fig. 1. The experimental setup.

Table 4
Conditions of the column study

T_h hydraulic retention time for the system	10 min
T_c contact time for zeolite	10 min
Column diameter	5 cm
Total bed height	50 cm
Porosity (for 0.5–1 mm clinoptilolite)	0.45
Porosity (for 1–2 mm clinoptilolite)	0.51
Porosity (for 2–4 mm clinoptilolite)	0.64
Influent ammonium concentration	20 mg/l
Influent suspended solids concentration	97 mg/l
Filtration rate	0.3 m^3/m^2 h
Empty bed volume	981 ml

3. Experimental results and discussion

The isotherm curves were drawn for ammonium removal from domestic wastewater. The results of the isotherm study for 0.5–1 mm particle sized clinoptilolite are given in Fig. 2.

As shown in Fig. 2, the adsorption capacity of Bigadic clinoptilolite was determined as 10.4 mg/g for 20 mg/L liquid phase ammonium concentration at pH 7.3 with 0.5–1 mm diameter clinoptilolite. The search for the compatibility of the data with various isotherm models has revealed that the best fit was obtained by the Langmuir model. This result is compatible with the results of similar studies for determining the capacity of Bigadic clinoptilolite [13,14,17].

In continuous column analyses, three columns were operated in parallel under the same initial concentrations and flow rates. In this manner, ammonium and suspended solids removal performances of the three columns were determined for different clinoptilolite grain sizes. Breakthrough curves for each experiment were deduced by monitoring C/C_0 vs. time, where C is the effluent ammonium or suspended solids concentration and C_0 is the concentration corresponding to the influent. As such "$1-C/C_0$" will give the removal efficiencies for each system. The comparison of ammonium removal performances are given in Fig. 3.

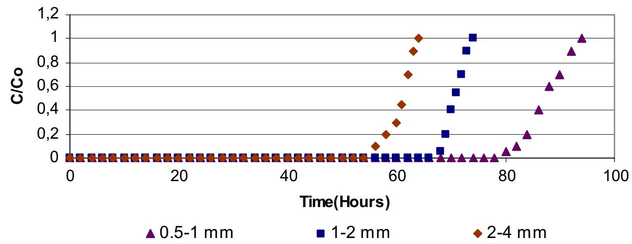

Fig. 3. The comparison of ammonium removal performances.

As can be seen from Fig. 3, almost complete ammonium removal could be obtained for all columns corresponding to a high ammonium removal capacity of clinoptilolite. It has to be underlined that long operation periods were achieved for all columns, with negligible ammonium effluent content. Breakthrough occurred after 54, 66, and 78 h of operation for the columns in which 2–4, 1–2, and 0.5–1 mm diameter clinoptilolite was used, respectively. The best result was obtained for 0.5–1 mm particles corresponding to complete ammonium removal at 78 h operation time. In column studies, the end of operation period was considered as the time when considerable column clogging was observed due to suspended solids or when effluent ammonium concentration started to increase. The suspended solids removal performances of each column containing various particle sizes are shown in Fig. 4.

As can be seen, only 8% suspended solids removal took place when clinoptilolite particles with 2–4 mm diameter were used as filtration material, as porosity was 0.64 at that column. The porosities were 0.51 when 1–2 mm clinoptilolite particles were used and 0.45 for 0.5–1 mm particles as given in Table 3. The best result was achieved for the column containing 0.5–1 mm diameter clinoptilolite particles. This was attributed to the high porosity of clinoptilolite parti-

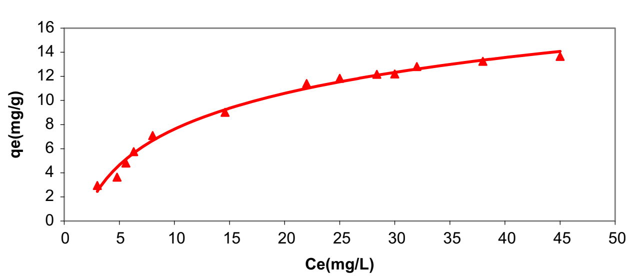

Fig. 2. The results of isotherm study.

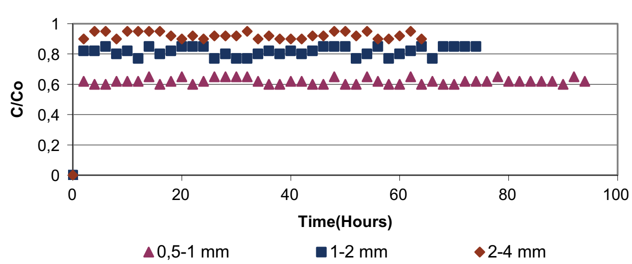

Fig. 4. The comparison of suspended solids removal performances.

cles with a nonspherical shape compared to sand which is a common filtration material.

Performance of sand filters treating domestic wastewater for different initial conditions and filtration rates were investigated in a number of papers [9–12]. The filter performances in these studies were changed according to the filtration material used while the combined use of zeolite in filters has not been reported. In general, sand was used and filtration performance of sand was changed between 60~80% depending on the experimental conditions. Zeolite was used as a filtration material in this paper, in order to determine its behavior against sand in filters and as shown in Figs. 3 and 4, a removal rate of 38% was achieved for suspended solids associated to 100% ammonium removal by using zeolite (0.5–1 mm diameter) in the filter column. This issue is becoming very important for treatment plants subjecting to high fluctuations in effluent ammonium concentration like Bahcesehir Treatment Plant. By using zeolite combined with sand in filters of similar treatment plants, it could be possible to obtain a higher suspended solids removal rate and a complete ammonium removal than using single layer filters containing only sand.

4. Conclusions

The use of a clinoptilolite in filters as filtration material for reduction of ammonium and suspended solids simultaneously is investigated in this paper. In the batch tests, the capacity of Bigadic clinoptilolite was determined by the isotherm analysis and corresponded to 10.4 mg/g for 20 mg/L initial wastewater ammonium concentration at pH 7.3 using 0.5–1 mm particle diameter clinoptilolite.

In column analysis, it was observed that complete ammonium removal obtained for all columns indicated a high ammonium removal capacity of clinoptilolite. Long operation periods were obtained for all columns up to 54, 66, and 78 h. In addition, suspended solids removal rate reaching up to 38% was measured in the column containing 0.5–1 mm clinoptilolite particles. Although, such suspended solids removal rate is low when compared to sand filters, it is an important indication that clinoptilolite might be added in existing sand filters for the simultaneous removal of ammonium and suspended solids, aiming to the reduction of ammonium and suspended solids contents in the effluent, and the prolonged operation times of the system.

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