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Combined removal of pesticides and nitrates in drinking waters using biodenitrification and sand filter system

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Abstract

A submerged biological denitrification system was employed to remove selected pesticides and nitrate from drinking waters. Ninety-five percent nitrate removal and over 76, 50, and 72% of mineralization of trifluralin, fenitrothion, and endosulfan ($\alpha+\beta$) were obtained, respectively after three days. Approximately 13 mg SS/l of microbial growth was obtained in the batch unit. After determining the optimum C/N ratio as 1.5 in a biodenitrification batch test, experiments were carried out in a continuous mode. Between 93 and 98% of nitrate removal efficiency was observed and nitrite concentrations were quite low for θ_h values higher than 2 h. Although no significant improvement in nitrate and organic carbon eliminations was observed at $\theta_h = 12$ h, the highest trifluralin, fenitrothion, and endosulfan ($\alpha + \beta$) removal efficiencies (about 100%) were observed. A sand filter system provided good turbidity and suspended solids removal efficiencies.

Keywords: Trifluralin; Fenitrothion; Endosulfan ($\alpha + \beta$); Biological denitrification; Drinking waters; Pesticides

1. Introduction

Water pollution by pesticides and nitrate from routine agricultural practices is a common and growing problem in the major agricultural areas of the world. Over the last decades, concern about the contamination of water sources has been raised due to increasing nitrate and pesticides concentrations. In regions where pesticide contamination is a problem, nitrate concentrations are often high [1].

Regulations for drinking water are required in order to limit human risks and environmental pollution. Pesticides and nitrates in drinking water are limited to 0.1 μg/l for a single pesticide, 0.5 μg/l for the sum of all pesticides and 45 and 50 mg/l for nitrates, respectively by Turkish Drinking Water Standards [2] and the World Health Organisation [3].

Activated carbon/ion exchange processes and reverse osmosis [4], combined membrane bioreactor/powdered activated carbon adsorption [5], biofilm-electrode reactor (BER) [6] and BER/adsorption process [7], fluidised biodenitrification reactor [8], and bioelectrochemical/adsorption process [9] were developed in order to remove both pesticides and nitrate from drinking water. Removal of pesticides and nitrates using wheat straw as solid particles and carbon source was studied by Aslan [10].

Biodenitrification is a promising technique for the simultaneous removal of nitrate and pesticides from drinking waters. The majority of biodenitrification relies on heterotrophic bacteria that require an organic carbon source. Since drinking water has a low carbon content and pesticides cannot be used as sole carbon source, an additional carbon source is required.

The pesticide usage is not equally distributed in all the agricultural areas in Turkey. For example, a dense pesticide application can be seen in some areas, while in some other areas almost no application is observed.

Uncontrolled use of agricultural chemicals in intensive agricultural areas of Turkey causes serious soil, surface, and groundwater pollution. If the pesticides are classified according to their volatilization, mobility, persistence characteristics and groundwater pollution potential, this classification indicates that nearly 65% of the pesticides commonly used in Turkey have a high pollution potential [11].

Evaluation of pesticides used in Turkey has led to a preliminary selection of compounds, trifluralin, fenitrothion, and endosulfan ($\alpha + \beta$ or I + II), which are used widely in Turkey, as relevant substances for this study. This

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Table 1
The characteristics of the selected pesticides

Pesticides	Molecular formula	Molecular weight (g/mol)	Solubility in water (mg/l)	Partition coefficient ($\log K_{ow}$)	Toxicity[a]	Half-life (days)
Endosulfan	$C_9H_6Cl_6O_3S$	406.95	0.32–0.33 (22 °C)	4.74–4.79	1	30–70
Fenitrothion	$C_9H_{12}NO_5PS$	277.2	21 (20 °C)	3.43	2	4–20
Trifluralin	$C_{13}H_{16}F_3N_3O_4$	335.3	0.184 (pH 5)	5.27	3.5	57–126

[a] 1 indicates high toxicity (EPA).

selection was based on their use in Turkey and persistency. The characteristics of the selected pesticides are summarized in Table 1.

The main objective of this study was to research the simultaneous microbial removal of nitrate and endosulfan ($\alpha + \beta$ or I + II) ($C_9H_6Cl_6O_3S$), fenitrothion ($C_9H_{12}NO_5PS$), and trifluralin ($C_{13}H_{16}F_3N_3O_4$) in a biodenitrification reactor using ethanol as carbon source. Removal of selected pesticides and nitrate was first investigated by batch biodenitrification experiments and experiments were than carried out in continuous reactor and a sand filter unit.

2. Materials and methods

Each medium was spiked with 7 μg/l trifluralin, 7.6 μg/l fenitrothion and 10.9 μg/l endosulfan ($\alpha + \beta$) solutions during the experiments.

2.1. Pesticide adsorption on the plastic coils materials and PAC

In order to determine adsorption capacities of the plastic materials and powdered activated carbon (PAC) for the removal of pesticides, batch experiments were performed. Plastic materials, which were used in the continuous reactors as a support particles and PAC were placed in separate shake flasks at pH 6.0, 125 rpm rotation speed at room temperature (19 °C).

In this experiment, 500 mg PAC and plastic materials having about 8 cm^2 surface areas each were placed in various shake flasks containing 125 ml distilled water spiked with the selected pesticides. Solutions were stirred with the shaker and samples were taken at the beginning, 5th, 15th, and 30th minute, 1st, 2nd, 4th, and 24th hour.

2.2. Batch experiments

Batch experiments were performed to determine the optimal C/N ratio for microbial activity. The C/N ratios varied from 0.3 to 3.2 for ethanol while the nitrate concentration was kept constant at 100 mg/l (22.58 NO_3–N mg/l). The initial pH was adjusted to 7.5 with NaOH solution. After determining the optimal C/N ratio, batch experiments were performed at a ratio of 1.5 of C/N for 100 and 200 mg/l of nitrate concentrations in the medium solution, which was spiked with selected pesticides. The initial SS concentration was 1.7 mg/l. Batch experiments were carried out for two and three days for 100 mg NO_3–N/l and 200 mg NO_3–N/l, respectively.

2.3. Experimental set-up of the biological denitrification reactor and sand filter

The experimental set-up consisted of a cylindrical stainless steel biological reactor, 15 cm inner diameter and 60 cm height, completely submerged and operating with an upward flow mode. The sand filter column, which had 8 cm diameter and 30 cm height, was filled with filter sand of an effective diameter of 0.5 mm and uniformity coefficient of 1.23 (Fig. 1). The packed column was filled with 10 mm pieces of plastic coils, which supported bacterial growth. Denitrification column had a liquid volume 5.3 l and the support particle surface area was 1 m^2 resulting in 190 m^2 surface area/m^3.

Denitrification microorganisms were taken from the denitrification reactor used in the laboratory. The column packed with plastic materials was fed with medium solution prepared in distilled water and pH adjusted to 7.5 using NaOH solution. A medium solution spiked with selected pesticides was prepared daily.

2.4. Synthetic medium composition

The liquid medium used consisted of a mineral base supplemented with nitrate as sole electron acceptor and ethanol as donor. Other constituents were KNO_3 (100 mg NO_3/l), KH_2PO_4 (150 mg/l), and $NaHCO_3$ (325 mg/l). This basal medium was supplemented with 1% v/v of a solution containing $FeSO_4{\cdot}7H_2O$, titriplex (0.565 mg/l), and with 0.1% (v/v) of a trace nutrient solution containing $ZnSO_4{\cdot}7H_2O$ (0.1 g/l), $MnCl_2{\cdot}4H_2O$ (0.03 g/l), H_3BO_3 (0.3 g/l), $CoCl_2{\cdot}6H_2O$ (0.2 g/l), $CuCl_2{\cdot}2H_2O$ (0.01 g/l), $NiCl_2{\cdot}6H_2O$ (0.02 g/l), and $NaMoO_4{\cdot}2H_2O$ (0.03 g/l). The final pH of the medium was adjusted to 7.5 using NaOH solution and the batch units were placed in an incubator at 29 °C. The C/N ratio was varied from 0.33 to 3.02 while the nitrate concentration was kept constant at 100 mg/l.

The synthetic medium solution spiked with the selected pesticides for reactor study included mineral base media; 100 mg NO_3/l and CH_3CH_2OH, which were prepared daily. Nitrate and ethanol were added so that the C/N ratio was 1.5.