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Short Communication

Application of barley straw to remove nitrate from drainage water

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ABSTRACT-Nowadays, farmers often use N-fertilizers to increase crop yield. On the other hand, in agricultural lands, nitrogen fertilizers are usually lost quickly by leaching, cause contamination of water resources and soil, which is reported as the most important source of nitrate pollution. Also, treating and reusing drainage water is necessary because of shortage of water resources especially in arid and semi-arid regions. Although biofilters are useful for removing nitrate from drainage water, but many researches show that they need an external carbon source to sustain denitrification. Numerous researchers have studied this issue using different methods, but most of them need equipment or materials that are suitable for conducting laboratory experiments. For example, mixing these biofilters and soil in large-scale underground drainage systems is very difficult and costly. So, this study describes laboratory experiments that investigated nitrate removal with barley straw layered or mixed with soil in different percentages. Results showed the layering method was more effective for removing nitrate. The percentages of optimum volume mixture of barley straw in layering and mixing methods were 20% and 30%, respectively, both removing approximately 80% of the influent nitrate. So, barley straw can be used in a layered form as an effective, prompt, feasible and inexpensive method to remove nitrate.

INTRODUCTION

Farmers often use N-fertilizers to increase crop yield, but they are not aware of the fact that these fertilizers are lost quickly as a result of leaching causing contamination of soil and water resources. Nitrate ion is highly soluble and fluid. Excess nitrate that cannot be absorbed by plants may be directly released to groundwater (Chun et al., 2009).

In recent decades, nitrogen compounds leaching from agricultural lands or leaving irrigated lands through drainage water have been known to be a serious problem (Jalali, 2005). For example, in Illinois in USA, 50% of surplus nitrogen used in agricultural lands enters rivers (David et al., 2001). This high load has been attributed to the excessive corn and soybean cultivation and is intensified by tile drainage. Another study conducted in Illinois indicated that 100% of residual nitrogen leached into streams in tile-drained watersheds (McIsaac and Hu, 2004). Also, a potential for cancer risk from water and food containing nitrate has been reported (Ono et al., 2000).Nitrate concentrations in excess of 45 mg/L in drinking water may pose risk to young animals and human infants (Matson et al., 1997).

The methods for using low-quality drainage water or wastewater in order to apply to irrigation projects or artificial discharge are diverse. There is an important point, these methods must be inexpensive, conceivable and safe and has no side effects to ecosystem. Also these methods must be usable anytime and anywhere and do not need specialized equipment, materials, and etc. One of the best of these methods (for removing nitrate) is reinforcing biological denitrification. In this method, organic carbon sources are used because, denitrification rate has a strong relationship with the carbon available to soil microorganisms and is generally limited (Greenan et al., 2006).

Dentrificationis the transformation of nitrate into nitrous oxide or elemental nitrogen (Shah et al., 1978). Biological denitrification occurs under certain specific conditions: an adequate supply of nitrate, an energy (carbon) source and a marginally anaerobic environment. During this reaction, the nitrate serves as an electron acceptor (Tiedje et al., 1989).

Saliling et al. (2007) used wood particles for denitrification and removing nitrate from water. They found that more than 90% of the nitrate was removed by using these substances.

Namasivayam and Sangeetha (2008) applied coconut coir for removal of anions from water. They reported that the efficiency of this material (especially for nitrate) was very satisfactory.

Fernandez-Nava et al. (2010) used alternate C sources to remove nitrate from wastewater. They demonstrated that this kind of C application may be an economical alternative for denitrification of wastewaters containing high nitrate concentration.

Hashemi et al. (2011) used wood, barley straw, rice husk and date palm leaf to sustain denitrification for removing nitrate from drainage water. They reported that all of the items that were examined stimulated denitrification, with date palm leaf supporting the greatest level of denitrification, followed by barley straw, rice husk, and wood.

According to what was stated above, two goals have to be pursued to save quality of soil and water resources: 1) using appropriate methods and substances for nitrate removal from drainage and leached water (short-term objective), and 2) Instructing farmers to use proper amount (especially N-fertilizer) and type of fertilizers (known as low-release) that do not leach easily (long-term objective). It is important to achieve the first goal with low-cost and prompt schemes, which are practicable and simple. In most recent studies, carbon source has been used either in combination with soil or with complicated mechanisms to remove nitrate from water that need hi-tech equipment, but these methods are inconceivable and uneconomical to be applied in subsurface drainage systems of vast agricultural lands. As a matter of fact, these methods require an expenditure of time, money and applying advanced machinery.

Therefore, the aim of this study was to investigate the capability of barley straw as a carbon source for nitrate removal from drainage water in sandy clay soil. Barley straw was used in a layered form (simple method) and in combination with 10, 20 and 30 percent volume of soil and its relationship with ammonium concentration; pH and water velocity was examined.

MATERIALS AND METHODS

In this study, barley straw (particles of 8-12 mm size) as a carbon source was combined with a sandy clay soil in columns. There were two groups of treatments in this study. In the first group, the columns were filled with 3 layers of soil and 2 layers of barley straw between them (L- layered treatments). In the second group, the columns were filled with a mixture of soil and barley straw (M- mixed treatments). In both treatments, barley straw was used in three levels of 10, 20 and 30 percent of volume. In layered treatments, the thickness of the 2 layers of barley straw was equal and proportionate to the percentages of its usage. For example, "10M" was used for the mixing treatment that had 10 percent of barley straw and "20L" was used for layering treatment that had 20 percent of barley straw. Also, "Control" was used for the treatment that did not have any barley.

All treatments were tested with three replications. The bottom and top of all the columns were covered with polyethylene caps. These caps were sealed with stoppers and taped to ensure that the pressure built-up inside the column would not push the stopper out of the column. The columns were fed via an upward water flow. The upward flow ensured that the entire soil pores were filled with water and preferential flow didn't occur. The inlet of the columns was supplied from a reservoir with a fixed height to create a fixed variance in pressure. The variance in pressure between the reservoir water level and columns' outlet was 100 cm (Fig.1).

The experiment lasted for 77 days. The reservoir was filled with water contaminated with nitrate of 80 mg/L concentration. The source of nitrate was KNO_3. The levels of pH, nitrate and ammonium concentrations in influent and effluent of all treatments were monitored weekly. Furthermore, water outflow velocities of the treatments were measured for each column. The ammonium concentration sweremeasured using a multi Direct photometer (Tintometer GmbH, Lovibond Water Testing, Germany); nitrate concentrations and pH were measured using a pH-electrode and ion-selective electrode (Metrohm, Switzerland), respectively. SAS 9.0 was applied for statistical analysis in the form of factorial experiments with complete randomized design. Means were compared using LSD at 5% probability level. Table 1 shows the results of qualitative analysis of the soil, barley straw and influent water samples.

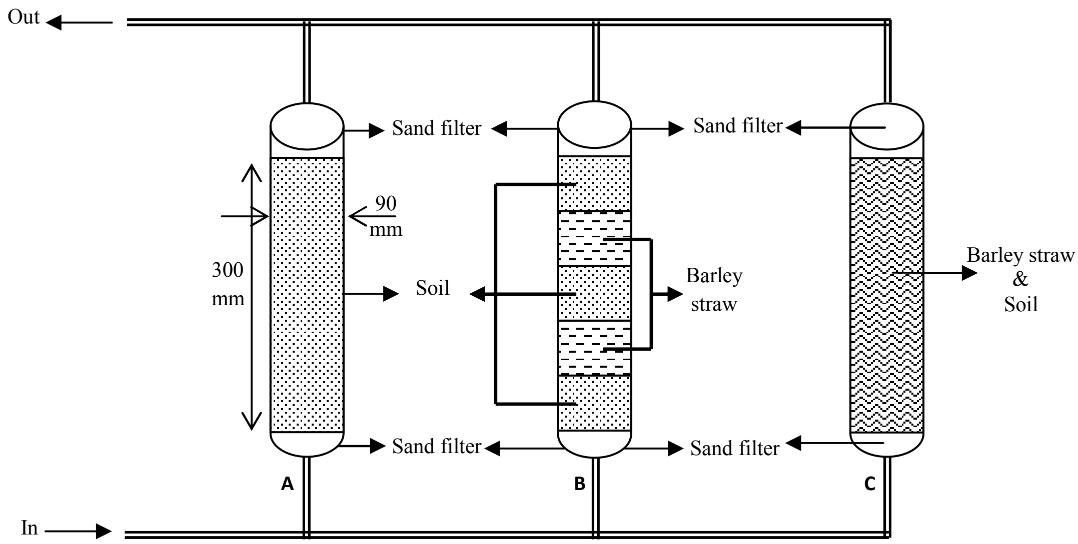

Fig. 1. Schematic representation of experimental setup (A: Layered, B: mixed and C: control treatment)

Table1. Analysis of the soil saturated extract, barley straw and influent water samples

Item	Value		
	Soil	Water	barley straw
Lignin (%)	----	----	23.32
Hemi-cellulose (%)	----	----	19.01
Cellulose (%)	----	----	31.17
EC (dS/m)	1.7	0.3-0.619	----
pH	7.76	7.61-7.96	----
NO_3^- (mg/L)	0	78-81	----
NH_4^+ (mg/L)	0	0.2-0.4	----
Total Nitrogen (%)	0.09	----	1.47
Organic Matter (%)	0.6	----	44.28
Organic Carbon (%)	0.35	----	25.68
$CaCO_3$ (%)	25.5	----	----
$CaSO_4$ (%)	0	----	----
Ca^{2+} (mg/l)	160	----	----
Mg^{2+} (mg/l)	48	----	----
Na^+ (mg/l)	166	----	----
K^+ (mg/l)	16.4	----	----
Sand (%)	46	----	----
Silt (%)	18.5	----	----
Clay (%)	35.5	----	----
Bulk density (gr/cm^3)	1.37	----	----
Porosity	0.39	----	----

RESULTS AN DISCUSSION

Nitrate concentrations and water velocities

The changes in the concentrations of nitrate discharged from treatments are shown in Fig. 2. These concentrations decreased with the passage of time for all treatments. The highest percentage of barley straw was more effective in removing nitrate. The control treatment reduced less than 25% of the nitrate concentration of the influent. Bedessem et al. (2005) similarly reported that the average total nitrogen removed in soil columns was about 31%. Meanwhile, Jensen and Siegrist (1990) reviewed several studies and concluded that denitrification and water infiltration account for an average of 20% of total N lost from soil columns, Where as USEPA (2002) reported about 10-40% of total nitrogen is removed by passing of water through the soil column. Although these values are different, they are paltry compared to the efficiency of biofilters. So, the lump of earth cannot often reduce nitrate significantly due to a shortage of carbon source while water passes through it.

Nitrate removal and water velocity in the effluent of treatments are shown in Fig. 3. This Fig showed that nitrate removal increased and water velocity decreased with time. Reduction of water velocity was fast during the first two weeks and then slowed down. Similarly in the drainage systems, water velocity decreases with the passage of time and ultimately almost comes to a halt; because of blockage in the filters.

When water passes through the columns, very small soil particles move and cause obstruction ofsoil pores at the end of stream path. Mixing barley with soil reduces this obstruction. This obstruction decreases as the percentage of barley increases. But, in layered treatments, obstruction occurs in soil layer that does not have any barley. This phenomenon causes the increase of drainage water velocity in mixed treatment into rival layered treatment (Fig. 3).

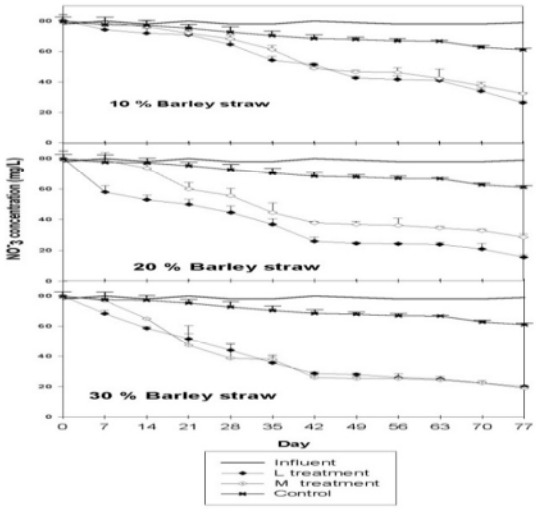

Fig. 2. Effluent nitrate from treatments consisting of three percentages (by volume) of barley straw (L= layered and M= mixed treatments)

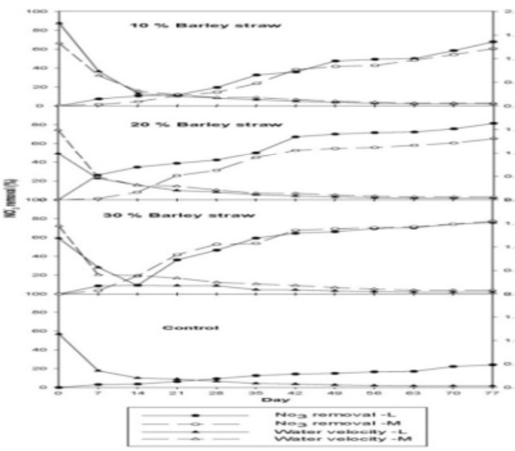

Fig. 3. Nitrate removal percents and water velocities of the effluent for treatments (L= layered and M= mixed treatments).

It must be specified that almost 30-50% (depending on the treatment) of nitrate removal occurred when water velocity was less than 0.09 m/h. Furthermore, the greatest decrease of nitrate concentration in the outlet occurred when the water velocity was less than 0.06 m/h. Soares and Abeliovich (1998) also showed that maximum reduction of nitrate concentration in the columns filled with mixture of wheat straw and soil happened when water velocity was less than 0.054 m/h.

Hashemi et al.(2011) used several substances to reduce nitrate concentration from drainage water and reported the most nitrate removal was achieved at flow rates about 0.1 m/d. Volokita et al. (1996) observed that complete removal of nitrate was achieved at flow rates of up to 0.8 m/d when newspaper was used as a C source. Therefore, it can be inferred that biological denitrification rate is proportionate to water velocity but its effect is circumscribed after some stages. For example, when water velocity was less than 0.06 m/h (for this study conditions), reduction of water velocity was low, but increase of nitrate removal percentage was high. Also, the effect of water drainage velocity on nitrate removal was less than the availability of carbon source because nitrate removal percentage in the control column was less than that of all the other treatments while its water drainage velocity was less than that of all the other treatments (Fig. 3).

Statistical comparison in Table2 show that, the optimum percentage of barley straw is 20% and 30% for layered and mixed treatments, respectively. Among all the treatments, the column containing 20 percent of barley straw in the layered form (20L) has been the most effective treatment in removing nitrate from the soil columns. Also, nitrate concentration of drainage water was sensitive to the percentage of barley and the method of using it.

Ammonium Concentration

Variation of ammonium concentration in influent and effluent of treatments are shown in Fig. 4. The ammonium concentrations of the effluent in all the treatments have decreased with the passage of time. On the other hand, the study shows that a small amount of ammonium could be consumed under the anaerobic condition owing to the growth of anaerobic bacteria cells (Kettunen et al., 1996).

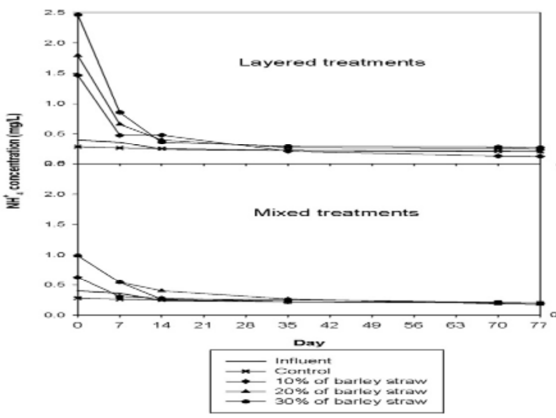

Fig. 4. Effluent ammonium concentrations in treatments during the experiment.

Furthermore, a recent finding demonstrated an interesting reaction in biological removal of nitrogen under low-oxygen concentration which is the biological conversion of NH_4^+ and NO_2^- to N_2(Li et al., 2006). Equations1 and 2 describe these reaction schemes:

$$NH_4^+ + 1.5O_2 \rightarrow 2H^+ + H_2O + NO_2^- \quad (1)$$

$$NH_4^+ + NO_2^- \rightarrow N_2 + H_2O \quad (2)$$

Table2 show that, there was no significant difference between the mixed and control treatments and no obvious difference between the layered treatments.

pH

The levels of pH in influent and effluent of treatments are shown in Fig. 5. However, the pH values didn't have a particular trend during the experiment, the effluent values almost followed the influent values, but the pH values of effluent were always less than those of the influents. These values fluctuated between 7.18 and 7.95, which are close to the pH of soil saturation extract.

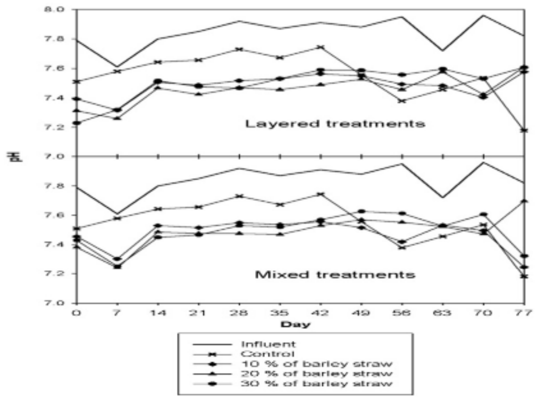

Fig. 5. Effluent pH values in treatments during the experiment

This may be due to the unexpected variation of the influent pH and soil buffering characteristics that did not allow dramatic changes in pH (Liu et al., 2002). Also, maximum nitrate removal by denitrification occurred in pH range of 7.2-8.4, that was about the pH of the soil (Songliu et al., 2009).The results showed that the best value of pH for denitrification is between neutral to a little alkaline. On the other hand, high acidic and alkaline environment was not fit for denitrification, and pH value played an important role in nitrite accumulation (Zhou et al., 2007).

The main reason was that pH influenced the enzyme activity of bacteria. Also, NO_2^- reduction is restricted by high pH levels, and too much nitrite accumulation brings about the poisoning of the microorganism (Liu, 2006). Furthermore, according to Table2, values of pH of drainage water were not sensitive to the percentage of barley and the method of using it. Also there was no significant difference between the mixed treatments, whereas there was a significant difference between some of the layered treatments in this respect.

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Table 2. The mean values of NO^{-3}, NH^{+4} concentrations and pH of the effluent in treatments

Treatment	10 L	10 M	20 L	20 M	30 L	30 M	Control
NO_3 (mg/L)	54bc	58b	39d	50c	40d	41d	71a
NH^+_4 (mg/L)	0.48abc	0.31c	0.6ab	0.43bc	0.75a	0.41bc	0.24c
pH	7.49bc	7.47bc	7.46c	7.49bc	7.5b	7.49bc	7.55a

* In every row, values followed by the same letters are not significantly different ($P<0.05$).

CONCLUSIONS

In this study, biological nitrate removal was investigated by applying barley straw in soil columns. Layered and mixed treatments were compared because mixing barley and soil in large volumes which is needed in underground drainage systems is sometimes difficult or impossible, costly and requires advanced equipment. Results proved all the treatments to be profitable. Also, the results showed that the optimum treatment with maximum nitrate removal efficiency (80%) was the layered treatment with 20% of barley straw. Ammonium concentration of the effluent decreased in all treatments with the passage of time but it was almost close to influent values. Furthermore, variation of pH levels of the treatments didn't show a particular trend during the experiment and almost followed the influent trend. So, the application of the barley straw in layering method is a practicable inexpensive solution to achieve higher nitrate removal efficiency compared to the mixing method. In this way, there is no need to be worried about the side effects and dangers of pH in effluent drainage water that can be used in artificially recharge systems or the reuse of wastewater as irrigation water

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مقاله کوتاه

کاربرد کاه‌جو جهت حذف نیترات از آب زهکشی

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واژه‌های کلیدی:
کاه‌جو
فیلترهای زیستی
آلودگی
کودهای نیتروژنه
آب زهکشی

چکیده-امروزه کشاورزان کودهای نیتروژنه را برای افزایش محصول به کار می‌برند. از سوی دیگر در زمین‌های کشاورزی اغلب کودهای نیتروژنه به سرعت در اثر آبشویی از دسترس خارج شده و موجب آلودگی منابع آب و خاک می‌گردند که به عنوان مهمترین منبع آلودگی نیتراتی گزارش شده است. همچنین استفاده مجدد از آب‌زهکشی به علت کمبود منابع آب خصوصاً در نواحی خشک و نیمه خشک ضروری است. اگرچه فیلترهای زیستی برای حذف نیترات از آب‌زهکشی مفید هستند اما بسیاری از تحقیقات نشان داده که آن‌ها به منبع کربن خارجی (اضافی) جهت تقویت دنیتریفیکاسیون نیازمند هستند. محققان بسیاری بر روی روش‌های مختلف مطالعه کرده‌اند اما بیشتر آن‌ها نیازمند تجهیزات و موادی هستند که مناسب مطالعات آزمایشگاهی می‌باشند. به طور مثال مخلوط نمودن این فیلترهای زیستی با خاک در مقیاس وسیع سیستم‌های زهکشی زیرزمینی بسیار مشکل است. بنابراین هدف این مطالعه توصیف پژوهش‌های آزمایشگاهی به منظور بررسی حذف نیترات با کاه جو در درصد-های مختلف به صورت مخلوط همگن و یا لایه‌لایه با خاک می‌باشد. نتایج نشان داد که روش لایه‌بندی برای حذف نیترات مؤثرتر بوده است. درصد بهینه اختلاط کاه‌جو در روش لایه‌بندی و مخلوط به ترتیب ۲۰ و ۳۰ درصد بود که هر دو تقریباً ۸۰ درصد نیترات ورودی را حذف می‌کردند. بنابراین کاه‌جو را می‌توان به صورت لایه‌ای به عنوان روشی مؤثر، امکان‌پذیر و ارزان جهت حذف نیترات به کار برد.