Clinoptilolite amendment to increase ammonium removal from landfill leachate in a clay loam soil

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Abstract
Municipal landfill leachate has been one of the major problems for the environment because of high organic substances, inorganic and heavy metal content and toxicity characteristics. Ammonium and organic substances are the most significant components of leachate in the long term. Land treatment is a cost-effective and environmentally sound method to reduce contamination or toxicity from waste waters before they can be released into the natural system. Clinoptilolite a natural zeolite, has been found very effective in removing ammonia from polluted waters. A soil column study was performed to investigate the zeolite effect on NH_4 removal from landfill leachate in a clay loam soil for duration of 12 weeks. Zeolite added to soil in three levels: 0%, 5% and 10% by weight. NH_4 concentration measured in the effluents at 1, 3, 5, 8 and 12 weeks. The results indicate that natural zeolite has a high potential for NH_4 adsorption and removal from wastewaters. Added Zeolite can improve soil removal efficiency, but the rates of application can be case sensitive depending on the soil and the type of zeolite and require a more accurate evaluation.

Key Words
Municipal landfill leachte, Clinoptilolite, NH_4 removal.

Introduction
Municipal landfill leachates are considered one of the types of wastewater with great environmental impact. The most critical aspects of leachates are linked to the high concentrations of several pollutants that can be divided into four main groups: dissolved organic matter, inorganic compounds, heavy metals and xenobiotic organic substances (Tengrui *et al.* 2007). Conventional processes for wastewater treatment include chemical precipitation, biological treatment methods and sorption processes. At present, heavy metals are not a major concern because average metal concentrations are fairly low. Ammonium and organics are the most significant components of leachate in the long term (Kjeldsen *et al.* 2002). Ammonium concentration in leachate can be found up to several thousand mg/L (Kargi and Pamukoglu 2003). Land treatment is a cost-effective and environmentally sound method to achieve treatment goals which is to reduce contamination or toxicity from waste waters before they can be released into the natural system or reused. In arid climates, it allows the use of wastewaters for irrigation and preserves higher quality water sources for other purposes. Soil matrix through passing of the wastewater, acts as a physic-bio-chemical reactor which can treat or stabilize pollutants of solid and liquid origin through degradation, adsorption, precipitation and utilization by crops (Idelovitch and Michael 1984).

Addition of soil amendments in order to improve the soils capacity for treatment of waste waters has been a challenging issue. Natural zeolite can offer environmental protection through sorption and binding toxic elements because of its extraordinary ion exchange capacities and water absorption. Due to its cost effectiveness and availability zeolite has been chosen for increasing soil adsorption capacity in the present investigation. Clinoptilolite, a natural zeolite, has been found to be very effective in removing ammonia from water because of its excellent ion exchange capacity since the 1970s (Wang *et al.* 2006).

Methods
The leachate applied in this experiment was taken from the Kahrizak Landfill which receives the municipal waste generated from Tehran, the capital city of Iran. The composition is given in Table 1. Soil texture used in the experiment was clay loam with 32, 32 and 36 percent of clay, silt and sand, respectively. The investigation was carried out in columns made of P.V.C. The dimensions of the columns were 16cm (diameter) by 50cm (height). Columns were packed with soil mixed with zeolite at three levels, which were 0%, 5% and10%, up to a height of 40 cm. Three replications were employed for each treatment. Leachate quantity was estimated based on 5cm height on the column surface. Experiment period was 12 weeks during

which leachate was applied in a cycle of one day per week. Influent was discharged over the columns in three stages within a 5 hour period. Effluent was collected after 24 hours at 1, 3, 5, 8 and 12 weeks intervals. Concentrations of NH_4 were measured in the influent and effluent in accordance with the method APHA 4500- NH_3. C (APHA 1998).

Table 1. The Composition of the applied landfill leachate.

Parameter	Unit	Value
COD	mg/L	60300
NH_3	mg/L	458.71
Total P	mg/L	110.58
pH	mg/L	4.4
EC	dS/m	19.41

Results

The removal efficiency and effect of the zeolite added to the column soils can be shown by comparison of NH_4 concentrations in the effluent (Figure 1). Average ammonium concentration in influent was 458.71mg/L during the 12 weeks.

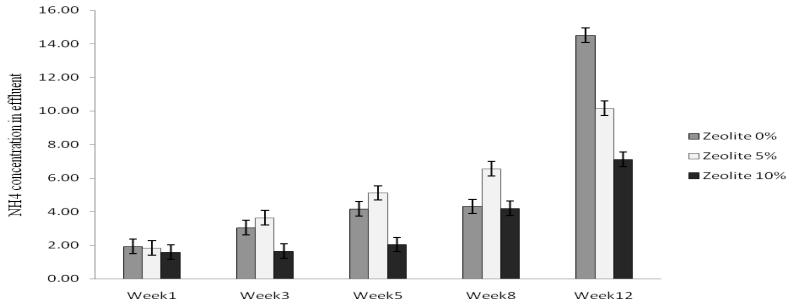

Figure 1. Concentration of ammonium (mg/L) in effluent for different weeks

As shown in Figure 1, soil has high potential to remove pollutants which has positive charge. Increasing trend of effluent concentration NH_4 means that soil capacity is restricted and its efficiency will be decreased. Zeolite addition had no significant effect in the first week. It reflects the basic removal capacity in the experimental condition which soil is responsible for it. Between weeks 3 to 8, unexpectedly, 5% zeolite showed less efficiency than 0% zeolite treatment, but 10% zeolite was significantly effective. At 8th week 10% zeolite's efficiency was equal to 0% zeolite. At 12th week, differences have been clear and zeoilite showed its effect. As indicated in Figure 1, ammonium concentration in 5% and 10% zeolite effluent rising with a regular trend but 0% zeolite treatment experienced a high increase in week 12 which caused significant difference between 5% and 10%zeolite.

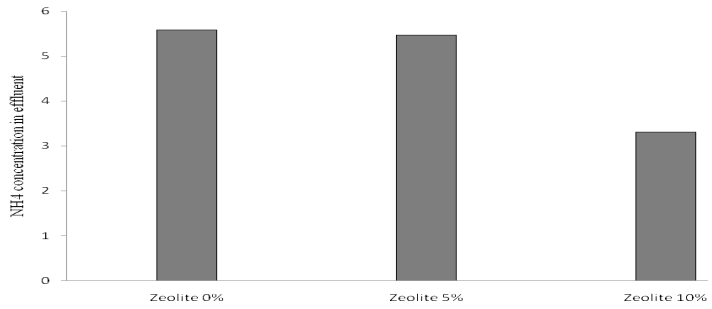

Figure 2. Mean of ammonium concentration (mg/L) in effluent during the experiment.

During 12 weeks, 0% and 5% zeolite showed no significant difference but 10% zeolite had a lower ammonium concentration (Figure 2). It is possible that, two different processes cause this result. Zeolite increases ammonium adsorption leading to a decrease of NH_4 in the effluent. In addition, zeolite can improve physical and biological condition in soils and prompt microbial activities, which degrade organic materials, and result in the release of more ammonium. The amount of released ammonium can neutralize the zeolite's effect for 5% zeolite, but it is perhaps less than the adsorption capacity provided by the 10% zeolite treatment.

Conclusion

Clinoptilolite, used in the experiment as an adsorbent is a natural zeolite with high potential for NH_4 adsorption and removal from wastewater. Its ability has been investigated for use in land treatment systems. Our results indicate that added Zeolite can improve soil ammonium removal efficiency, but the rates of application required can be case sensitive depending on the soil and the type of zeolite and development of criteria requires a more accurate evaluation.

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