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Short-term remediation of soil contaminated with landfill leachate using natural and microwave modified zeolite of the clinoptilolite type

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The experiment was conducted to evaluate the effect of raw and microwave modified zeolite application on leachate contaminated soils. Soils treated with 50ml leachate were amended with 0, 15, 25 and 35g zeolite per 300g soil. Chemical oxygen demand (COD) and ammonium of soil extract, soil pH and leaching toxicity were compared between soils treated with and without zeolite. The results showed natural and microwave modified zeolites were both effective to increase soil pH, eliminate COD and ammonium in soil extraction and decrease leaching toxicity of leachate polluted soils. Above observations were more likely attributed to biologic degradation reactions in zeolites relative to sorption reactions. Microwave modification was helpful for ammonium removal, but with no benefit for COD removal and toxicity eliminating. Furthermore, excessive zeolite application could induce negative influences on soils for both natural zeolite and its microwave modified forms. Therefore application dosages would act as an essential factor in remediation process.

Keywords: Soil remediation, Landfill leachate, Natural zeolite, Leaching toxicity, Microwave modification

INTRODUCTION

Waste leachates are residual liquids that are generated by water percolating through stored trash and thus dissolving and hydrolyzing organic and inorganic matter [1]. Improper methods of disposing MSW such as unlined landfill cause leachate migration resulting in pollution of soil system [2] and groundwater [3,4]. Considerable attention has been paid to landfill leachate pollution and many research studies have been carried out on this topic during the past decades. Electrical resistivity surveys were used to evaluate groundwater and soil pollution in landfill areas and indicated pollution risks posed by leachate [4,5]. The content and immobilization of Cd in leachate was analyzed with the method of leaching tests [6]. Smith and Senior [7] selected pH, electrical conductivity and copper as indicators and proved that high removal of pollutants from landfill leachate can be achieved by passage through a soil with a low attenuation potential. However, few reports were found to be focused on the approaches to remediation of leachate contaminated soils and biological impacts posed by leachate.

The natural zeolites have already found extensive applications to the environmental remediation and restoration [8]. The use of natural zeolites and their modified forms offer as advantages the low-cost, the availability in big quantities in many parts of the world, the good mechanical and thermal properties and the combination of high sorption capacity with the ability to modestly adjust the pH of the soil or the aqueous system. In addition, the natural zeolites, do not introduce additional pollution in the environment. Surface modifications such as heating, surfactant treatment, microwave irradiation etc., were usually used to promote sorption capacity or ion-exchange property [9]. Among various modified methods, microwave irradiation showed its advantages of notable promotion on the acidic and surface properties of zeolites as reported by González et al.[10]. Whereas little work was found about zeolite application on remediation of leachate contaminated soils in previous literatures. In this study, we attempted to adopt natural zeolite and its microwave modified forms as soil remediation materials.

Soil leaching toxicity is a typical indicator for migration properties of pollutants in soils to groundwater and surface waters, and simultaneously could be chosen as an effective indicator for effectiveness of soil remediation materials. Landfill leachate presents biotoxicity risks reasonably due to its content of heavy metals and persistent organic pollutants [11]. Our previous work suggested that high COD, ammonia and DEHP contents presented notable negative influences on microorganism growth [12]. In this study, tetrahymena pyriformis (TP) was chosen as leaching cute toxicity indicator due to its

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wide distribution in natural waters and good sensitivity to hazardous substances, which made it reasonable to be used to assess soil toxicity mobility and the risk of further pollution to waters.

In this paper, the emphasis is placed on remediation effectiveness of zeolites on selected parameters of leachate-polluted soils. The objectives of this study are to attempt the application of raw and microwave modified zeolites on leachate-polluted soils and to figure out their effectiveness on pH, COD, ammonium and biotoxicity of soil extract. Thus, a short-term incubation was conducted to simulate the dark environment in deep polluted soils and analyse the remediation mechanisms of zeolites on above representative parameters of leachate-polluted soils.

MATERIALS AND METHODS

Materials

Soil samples up to 20 cm below ground was collected from Maanshan Forest Park in Wuhan, China. The soil samples were dried in drying oven for 1 week and passed through 2 mm sieve before being used in incubation experiments. Typical chemical characteristics of the soil are measured from three samples and listed in Table 1. Leachate was collected from Changshankou Landfill in Wuhan, China. The indicators for leachate were determined according to MEPC [13] and are presented in Table 2. Natural zeolite was purchased from Xinyang, Henan Province and Table 3 summarizes the chemical composition of the zeolite sample used in the experiments. Besides, modified methods of zeolites are listed in Table 4. All types of zeolites passed through 1 mm sieve before being used in incubation experiments.

Incubation experiment

The soil was treated with 50 ml leachate per 300 g soil. According to Smith and Senior [7], enough leachate would significantly affect soil pH and we estimate 50 ml leachate per 300 g soil could reach the required level. The remediation was evaluated by repeated tests of chemical and biological soil properties (termed "indicators") in soils that were incubated for up to 35 days with three dosages (e.g. 15g, 25g and 35g) of zeolites treated with various micrwave conditions (Table 4). Similar modified method was proposed by Shang et al.[14].

The soil samples treated with zeolites and leachate were thoroughly mixed and watered. The soil was then transferred to glass beakers (Ø=12 cm, Height=7 cm) and in each beaker 300 g soil was placed. Treatments were arranged in a completely randomized design with three replicates per treatment. The treated soils were maintained at 60% water holding capacity with deionized water. All beakers were incubated without illumination to simulate the dark environment in deep natural soil.

Analysis of samples

Soil extract was obtained from each soil sample according to CMEP [15]. Chemical oxygen demand (COD), biological oxygen demand (BOD), ammoniacal nitrogen (NH_3-N), and pH were measured using standard methods [13] after 35-day incubation. All chemicals used for the analytical determinations were of analytical grade.

Tetrahymena pyriformis (TP) (generously provided by Institute of Hydrobiology, Chinese Academy of Science) was used as a probing indicator for biotoxicity assessment. Leaching toxicity experiments using protozoan TP were conducted with the method of the 24h-LC_{50} test (%) according to Tatara et al. [16]. TPs were tested in tissue culture plates containing 1 ml of test solution per sample. Test solutions consisted of six soil extract concentrations (6, 12, 25, 50, 75, and 100% of each soil extract) and a control with each replicated six times. TPs were incubated at 20°C for 24±1h, and the number dead was determined by visual inspection and probing the worms with a platinum wire under a dissecting microscope. This concentration response experiment was repeated three times for each zeolite type.

Table 1. Typical chemical characteristics of the soil.

Materials	pH	Organic matter (%)	Total P (mg/g)	Available P (mg/g)	NO_3^--N (mg/g)	NH_4^+-N (mg/g)	Available K (mg/g)
Soil	7.12	1.204	0.824	0.017	0.007	0.019	0.082

Table 2. Chemical characteristic of landfill leachate.

pH	SS (mg/L)	CODcr (mg/L)	BOD_5 (mg/L)	NH_4^+-N (mg/L)	Total Cr (mg/L)	Cr^{6+} (mg/L)	Hg (μg/L)	As (mg/L)
7.79	10700	38200	15200	1360	1.45	0.24	1.17	0.37

Quality control

All the glassware such as vials and bottles were first cleaned in an ultrasonic cleaner (20 KHz) assisted by liquor for 30min. Then they were further washed by tap water and deionized water for three times, respectively. Deionized water was obtained from a Millipore Milli-Q system (18.2mΩ cm). All chemicals used for the analytical determinations were of analytical grade. All parameters were measured with each replicated at least three times.

Table 3. Chemical composition of the natural zeolite (wt. %).

Composition	w%
SiO_2	67.25
TiO_2	0.17
Al_2O_3	7.82
Fe_2O_3	0.95
MnO	0.09
MgO	0.73
CaO	3.22
Na_2O	2.16
K_2O	3.84
H_2O	8.41
LOI	5.37

Table 4. Various types of zeolites for soil remediation.

Samples	Treatments
Control	No zeolite
NZ	Natural zeolite
MZ1	Natural zeolite+200W+3min
MZ2	Natural zeolite+500W+3min
MZ3	Natural zeolite+800W+3min

RESULTS AND DISSCUSSION

Soil pH

Soil pH of contaminated soils in the absence and presence of various types of zeolite is demonstrated in Fig. 1. Soil pH is a typical and important parameter and widely used for assessing soil quality [17] and remediation effectiveness [18,19]. Undoubtedly, suitable soil pH is close to the neutral value of 7. However, significant decrease was observed in simulated polluted soils with a pH value of 5.2 in the control samples, respected to initial value of 7.12 (Fig. 1). Similar results was obtained by Smith and Senior [7] that pH value decreased to below 5 in initial period of leachate irrigation. This observation may be attributed to organic acids occuring during the organic matter degradation processes within leachate [1], especially for leachate from anaerobic landfill due to lower content of inert COD [20], or the exchange of H^+ and Al^{3+} ions from the soil colloids by cations from the leachate [7]. The acid soil environment is unsuitable for soil biological activities and easily results in the increase of heavy metal mobility. Simultaneously, acid soil environment may cause serious damage to plant root.

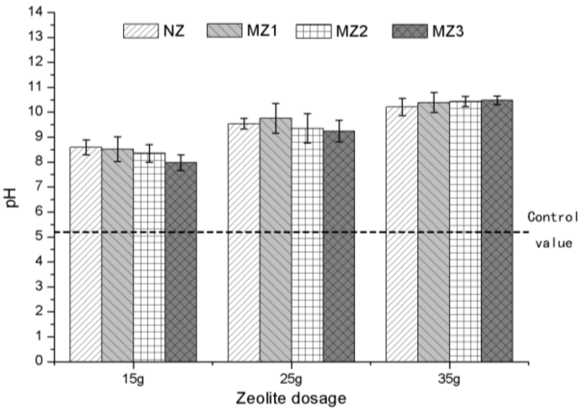

Fig. 1. Changes of soil pH in the presence and absence of zeolites.

With the addition of raw and microwave modified zeolites, notable pH increase was achieved with 36-day incubation and pH increased with the dosage of zeolite. It could be concluded that raw and microwave modified zeolites both increase soil pH in a short-term incubation. Our results show reasonably good agreement with other research reports. It has been reported that soil pH increased significantly with application of natural zeolites in lead-polluted soils [21], similar results were observed in wastewater treatment studies [22]. All above observations are probably attributed to the basic characters of ion exchange for natural zeolites and their modified forms. No regular changes are observed between raw and microwave modified zeolites on their effectiveness on soil pH. That means zeolite modification has no remarkable effect on their pH effectiveness. Consequently, raw and microwave modified zeolites are both effective to increase soil pH. Nevertheless, high alkalinity would undoubtedly induce negative influences to environment, therefore application dosages would act as an essential factor in remediation process.

COD removal of soil extract

High content of organic matter contained in landfill leachate puts a great threat on groundwater and surface water. Many experiments have been conducted to study the characters of leachate COD to find an effective approach to dealing with the complex wastewater (eg. [1,20]). While few studies are found to control the pollution of organic matters to soils from landfill leachate. COD of soil extraction for samples treated with various type of zeolites is presented in Fig.2. It can be seen that higher COD removal was achieved with zeolite application, especially for 15g-dosage group. Zeolites has been reported to be applied in remediations of organic matter polluted soils [23] and dealing with organic wastewater [24]. It should be noted that the studies above are focused on some solely or low content of organic pollutants in soils or wastewaters. When the objectives are some complicated and special pollutants, the effectiveness of zeolites is uncertain. Landfill leachate is characterized by its complicated compositions and high content of organic pollutants. Halim et al. [25] adopted zeolite as adsorbent to investigate the the adsorption effectiveness of COD in leachate, and found that zeolite was effective to decrease leachate COD mainly due to its adsorption property.

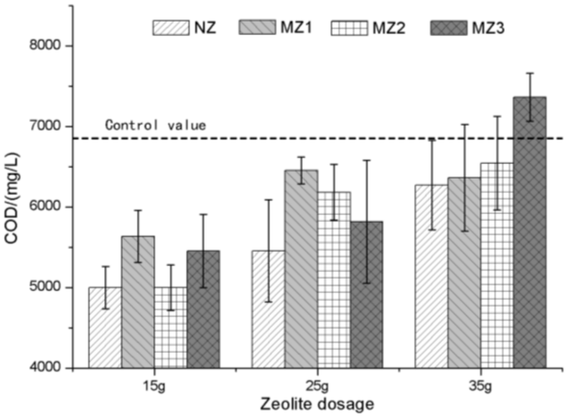

Fig. 2. Changes of COD in soil extract in the presence and absence of zeolites.

Fig.2 shows higher COD removal was achieved with zeolite application, but removal rate did not increase along with the increase of addition dosages. It was reported that zeolites are capable of sorbing into their cavities or channels different polar and non-polar inorganic or organic molecules [26]. If the COD removal was mainly attributed adsorption property of zeolites, the removal would be facilitated with the dosage increase. The results obtained in our study show a different trend for COD removal with the supposition above. As indicated in the literature zeolite was believed to act as two types of reactive media for contaminant removal [9]. Firstly, sorption reactions tend to be relatively fast, but eventually the maximum capacity of the medium will be reached, and there will be no further retention. The other media type is a degradation or transformation material. The contaminant will be transformed to a non-toxic compound after coming in contact with zeolites. Degradation reactions tend to be kinetically slow relative to sorption reactions, and but the reactions are persistent. Similar standpoints are found in other studies [8] that zeolite particles could act as good carriers of microbe, which increase the biological activity in contaminated soil or wastewater. In this study, COD removal was more likely attributed to degradation reactions in zeolites relative to sorption reactions and the observations may indicate microwave modification had no remarkable effect on degradation reactions . Meanwhile, excessive zeolite application is indicated to show negative influences on degradation reactions probably due to unsuitable soil pH.

Ammonium removal of soil extraction

Ammonia nitrogen pollution results in eutrophication of lakes and rivers, dissolved oxygen depletion and fish toxicity in receiving waters. Higher concentration of ammonium will cause a sharp decrease of dissolved oxygen and obvious toxicity on aquatic organisms. Negative effects occur in ammonium polluted soils similarly. Zeolites has been proved as a good remediation material for ammonium according to previous studies [27]. Ammonium of soil extraction for samples treated with various type of zeolites is presented in Fig.3. Significant decrease of ammonium was observed in most zeolite treated soils respect to the control soil. More ideal removal was obtained in the 15g dosage group comparing to 25g and 35g dosage groups..

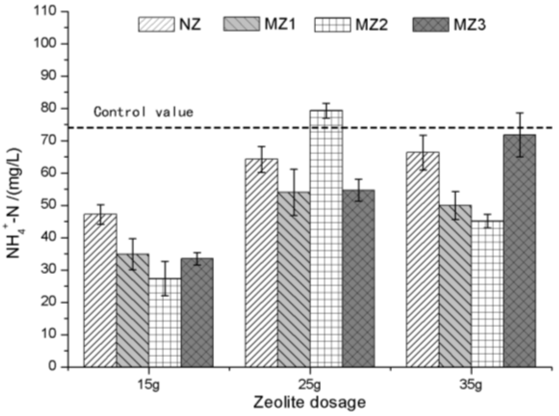

Fig. 3. Changes of ammonium in soil extract in the presence and absence of zeolites.

The removal mechanisms for ammonium probably are attributed to the three basic properties of zeolites: sorption, ion exchange and catalytic [26]. Fig. 3 demonstrated that the removal did not increase with the zeolite dosage added to soils. That leads us to believe the main mechanism was catalytic reaction rather than sorption and ion exchange because natural zeolite could adsorb ammonium steadily at a wide pH range [28]. As described in Section 3.2, zeolite particles could act as good carriers of microbe, which increase the biological activity in contaminated soil. Zaman and Nguyen [29] used conducted a field experiment to investigate the effects of zeolites on N_2O and N_2 emissions from a pastoral soil treated with urine or nitrate-N fertilizer. They found nitrifier-denitrification and denitrification acted as a significant role in ammonium removal in urine treated soils. Wang et al. [22] found that zeolite could increase pH to a 7.0~8.0 and thus fulfilled the conditions for anaerobic digestion in ammonium-rich swine wastes. In our study, it can be concluded that the catalytic impact of zeolite on biological activities is the main mechanism for ammonium removal in leachate contaminated soils. Excessive zeolite did not promote ammonium removal due to too high pH values as demonstrated in Fig.3. A previous study conducted by Milan et al. [30] demonstrated that a zeolite dose of 10g/L could contribute to process inhibition for ammonium removal in piggery waste. All above may explain the lower removal obtained in zeolite doses of 25g and 35g.

Moreover, modified zeolites show a more notable promotion effect on ammonium removal as showed in Fig.3, which may be attributed to the positive influences of microwave treatment on surface properties of zeolites [10]. It can be concluded that ammonium removal was attributed to nitrifier-denitrification and denitrification and microwave modification had positive effect on biochemistry reactions. Negative influences would occur with excessive zeolite application due to process inhibition for biological activities.

Soil leaching toxicity

Soil leaching toxicity is a typical indicator for migration properties of pollutants in soils to groundwater and surface waters, and simultaneously could be chosen as an effective indicator for effectiveness of soil remediation materials. Soil leaching toxicity for soil samples treated with various type of zeolites is demonstrated in Fig.4. Leaching toxicity was significantly lower in 15g and 25g zeolite dose groups, with LC_{50}s of about 62% and 50% respectively respect to the control soils of 32%. However, no notable decrease was observed in the 35g dose group. There has been some relative views in our previous work. Liu et al. [11] found that leachate toxicity decreased as landfill age increased and was dependent on ammonia concentration and COD with multivariate analysis. Liu et al. [12] suggested that high COD, ammonia and DEHP contents presented notable negative influences on microorganism growth. Heavy metals found in leachate (Table 2) are undoubtedly one of main toxic components and posed great threats on soils and natural waters near unlined landfills [31]. However, few studies are found to focus on decreasing biotoxicity or eliminating toxic pollutants from landfill leachate.

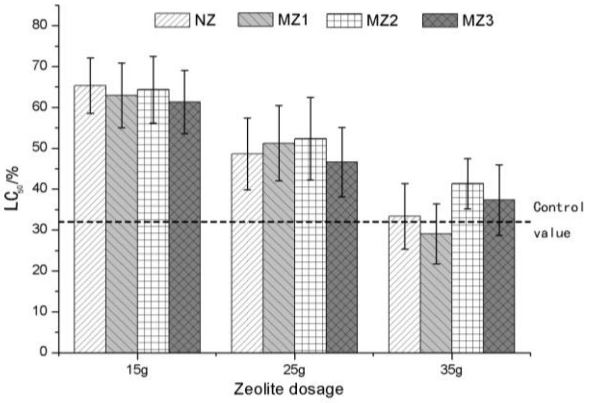

Fig. 4. Changes of leaching toxicity in the presence and absence of zeolites.

As demonstrated in Fig.4, leaching toxicity of leachate contaminated soils could be effectively decreased with suitable application of natural and modified zeolites. This may mainly be attributed to the catalytic property of zeolites. Other reports has been found to attempt to utilize zeolites for eliminating negative impacts of above pollutants. Burgess et al. [32] proved that zeolite could be effectively adopted to eliminate the toxic effects of ammonia in marine sediment in a laboratory scale. Shi et al. [33] studied the remediation effects of the lead-polluted garden soil by exogenous natural zeolite and humic acids, and found that the available fraction of lead compounds was reduced. Dercova et al. [34] proposed humic acids bound on zeolite reduced the potential toxicity of PCP to microbial community by lowering its bioavailability and thus facilitated its biodegradation. The results in this study has proved significant effectiveness of zeolites for COD and ammonium removal in soil extracts (Fig.2 and Fig.3). In fact, no notable decrease of leaching toxicity was observed in the 35g dose group. Strong basicity caused by excessive zeolite may explain the observations. As showed in Fig.1, pH values of above 10 were unsuitable for biological activities as described in Section 3.2 and 3.3. A previous study conducted by Milan et al. [30] demonstrated that high pH could contribute to process inhibition for anaerobic digestion in piggery waste. It can be concluded that proper dosage of zeolites could effectively reduced the leaching toxicity of leachate polluted soils and there was no significant difference between natural zeolites and its modified forms for toxicity removal.

CONCLUSIONS

A fundamental research had been carried out to explore the remediation effectiveness of natural and microwave modified zeolites for leachate contaminated soils. The influences of application dosage and mechanisms of pollutant removal were investigated. Conclusions were drawn as follows:

(1) Natural and modified zeolites were both effective to increase soil pH. But excessive zeolites would cause high alkalinity, which would induce negative influences to biological activities.

(2) COD and ammonium in soil extraction could be effectively eliminated with zeolite application, and this may be more likely attributed to degradation reactions in zeolites relative to sorption reactions.

(3) Leaching toxicity of leachate polluted soils also got high removal with proper dosage of zeolites. Impacts on toxic pollutants such as heavy metals and persistent organic pollutants may explain the observations.

(4) Microwave modification was helpful for ammonium removal, but with no benefit for COD removal and toxicity eliminating. Besides, excessive zeolite application could induce negative influences on soils for both natural zeolite and its modified forms.

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