ORIGINAL PAPER

Photocatalytic efficiency of molybdenum-doped zinc oxide nanoparticles in treating landfill leachate

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ABSTRACT

Among various techniques available for leachate treatment, nano-photocatalytic-based techniques have been considered as efficient. The photocatalytic leachate treatment using nanoparticles of zinc oxide doped with molybdenum oxide was performed in the presence of sunlight at a laboratory scale. The molybdenum oxide doped ZnO nanoparticles were synthesized. The properties of nanoparticle were analyzed by using FTIR, SEM, and XRD. Then the parameters such as pH (3, 5, 7, 9, & 11), concentration of nanoparticles (0.5, 1, 2 and 3 g/l), concentration of leachate with dilution (1:10, 1:25, 1:50 and 1:100), and contact time (15, 30, 45, 60, 90, & 120 min) were measured to determine the removal of COD and turbidity. The analysis indicated that nanoparticle size was appropriate and acceptable. Electron microscope images also showed that the nanoparticle shape was hexagonal. The optimum value of pH was 5. It was found that increasing the concentration of nanoparticles enhances the efficiency of the process, the concentration of nanoparticles from 0.5 to 2 g/l at 60 min of contact time, and the efficiency from 34.8 to 55.6%, and increasing in contact time decreases the COD and turbidity leachate. Enhancing the initial concentration of leachate reduces the treatment efficiency of landfill leachate.

Keywords: Doped, Nanoparticles, Photocatalyst, Zinc oxide

Introduction

Different types of organic and inorganic compounds can be generated by biological, physical, and chemical processes. These compounds can enter waste canals via rainwater penetration, resulting in leachate formation.[1] Landfill leachate is a strong sewage raising numerous environmental concerns as it contains a wide variety of organic and inorganic pollutants.[2] The pollutants in leachate could be dissolved or suspended.[3] Due to the variability of leachate properties, the most appropriate technique for the treatment of leachate directly depends on its specific properties. Generally, chemical compositions of landfill leachates could differ from each other since leachate composition can vary by type of the buried waste, landfill hydrology, climatic conditions, landfill age, and landfill design and operation.[4]

More than 200 types of organic compounds are known to exist in leachate. These compounds can be classified as circular hydrocarbons, two-ring compounds, aromatic hydrocarbons, alcohols, ethers, circular ethers, ketones, ethanol, acids, esters, phenols, phthalates, furans, and compounds containing nitrogen, phosphorus, sulfur, and silica.[5,6] Hence, leachate is known as a substance with extremely high environmental risks in many countries. Penetration of leachate into soil and groundwater aquifers causes soil and groundwater pollution due to the presence of various pollutants including hydrocarbons and heavy metals. Moreover, horizontal motion of

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leachate in urban landfill sites and its discharge from soil surface in low lands lead to the pollution of surface waters. Then if the water polluted by leachate is used with no monitoring, the prevalence of hazardous diseases will be highly probable.[5] Therefore, the proper management of leachate control is expected to highly reduce the potential risks of the landfill, groundwater, and surface water contamination.[7] Different methods can be used for the management of leachate, including recycling leachate into burial cells (local treatment), evaporating leachate, discharging it into urban wastewater refinery, and leachate treatment through different physical, chemical, and biological methods.[1,7]

One of the leachate treatment options is to use conventional methods in order to remove organic matters in landfill sites through coagulation, flocculation, oxidation, adsorption, and reverse osmosis.[7] Moreover, biological treatment is considered as a low-cost process for the removal of hazardous substances from leachate.[8]

Biological treatment processes are also effective for freshly produced leachates; however, they are ineffective for aged leachates of landfill sites (>10 years old).[4] Due to the presence of toxic and non-degradable substances in leachates, the exclusive implementation of biological treatment is not efficient for decomposition of organic matters so that it is of essence to achieve the required standards through physicochemical processes as pre-treatment, complementary treatment, or complete treatment.[9] In addition, the advanced oxidation processes (AOPs) can be used to reduce COD by converting organic compounds of leachate into simple final products (e.g. water and carbon dioxide) and to increase bio-degradability of treated wastewaters.[10]

There are many reports about the application of nanotechnology for treatment and the removal of pollutants from the environment.[11] Nanoparticles (NPs) can be used to treat and convert pollutants into non-toxic materials because of their small size, high surface area, crystalline shape, unique network ordering, and high reactivity.[12,13] In Iran, limited efforts have been made to control and treat leachate. In this regard, it is predicted that, with population growth and industrial development, the pollution caused by leachates will be one of the future environmental challenges in Iran. This study aimed to determine the efficiency of photocatalytic treatment of landfill leachate in Sanandaj, Iran, using molybdenum-doped zinc oxide NPs.

Materials and Methods

Chemical materials

The present study is a quasi-experimental study in laboratory-scale. ZnO, n-butylamine, NaOH, and HCl were purchased from Merck, Germany, and molybdenum oxide was obtained from Sigma, Germany. The leachate samples were collected from the landfill site of Sanandaj, Iran.

Synthesis of Mo- ZnO- nanoparticle

The hydrothermal method was used to synthesize Mo-ZnO NPs. In short, 2 N zinc oxide and 1 mol.% molybdenum oxide were added to a Teflon liner. Then 10 mL of sodium hydroxide (1 N) and 0.5 mL of n-butylamine were added dropwise under intensive mixing, and the liner was placed in a general-purpose autoclave for 12 h at 120 ºC. Afterwards, the synthesized material was removed from the liner, washed several times with distilled water, and dried at ambient temperature.[14]

Analysis of the experiments

The employed reactor was a batch system for which 250 mL beakers were used. The experiments were carried out in July and August at 12:00 to 14:00 with the highest light intensity (visible light 800 Lux, UV light 1.25 MW/cm^2) in 2015. During the experimental period, the sunlight intensity was measured by a CHY device Model 732 (Taiwan). In this study, the efficiency of organic material removal and leachate treatment were analyzed according to the analysis of chemical oxygen demand (COD) through a closed reflex method and turbidities of the samples were measured by an Aqualytic turbidity meter made in Germany.The efficiency of leachate treatment was calculated by Eq. (1):

$$R = \left[1 - \frac{C_f}{C_i}\right] \times 100 \quad (1)$$

where, C_f and C_i are the final and initial concentration of leachate in the samples, respectively.

Results and Discussion

Scanning electron microscopy (SEM) images of the zinc oxide NPs doped with molybdenum oxide and pure zinc oxide NPs are shown in Fig. 1.

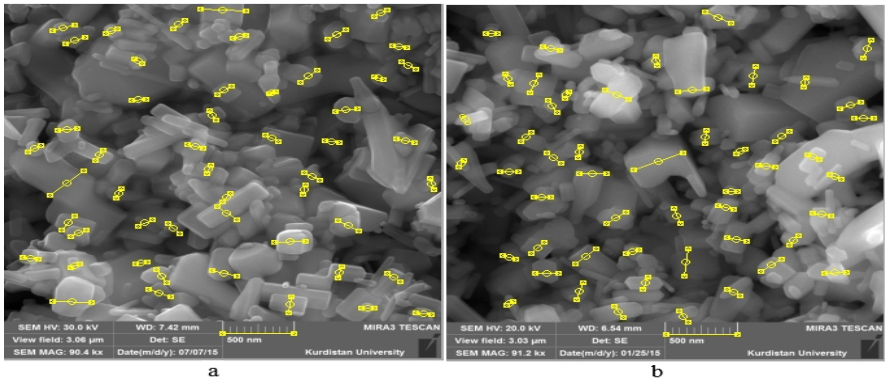

Fig. 1. SEM images of nanoparticles: a) 1.0% molybdenum doped ZnO and b) undoped ZnO

The size distribution of the Mo-ZnO NPs was determined based on the SEM images using Digimizer software and SPSS software version 21. The size distributions of Mo-ZnO NPs pure zinc oxide with its mean and standard deviation are shown in Fig. 2. The SEM images show hexagonal NPs that are completely separated from each other with no gluttony or agglomeration. Nevertheless, the mean size distribution and the associated standard deviation of Mo-ZnO NPs and pure ZnO NPs were 90.38, 38.828, 115.05, and 45.997 respectively, indicating that Mo-ZnO NPs are smaller than ZnO NPs with acceptable sizes.

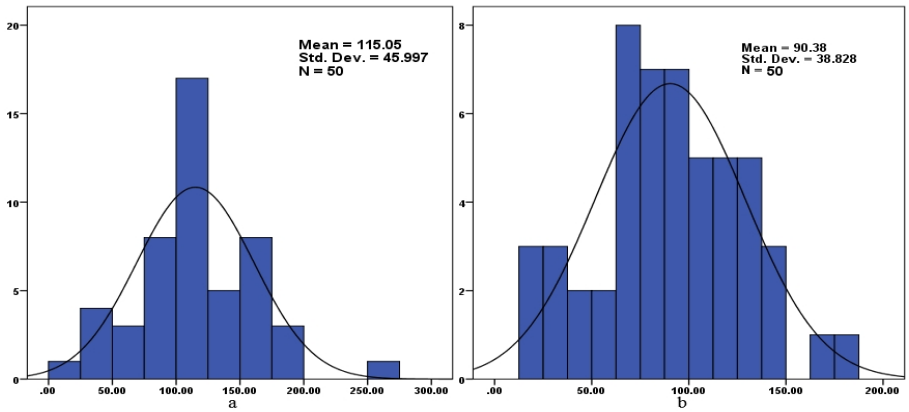

Fig. 2. Distribution of nanoparticle size: a) 1.0% molybdenum doped ZnO and b) undoped ZnO

X-ray diffraction (XRD) spectrum was used to verify the crystalline structure and purity of ZnO and the synthesized Mo-ZnO NPs (Fig. 3). The XRD spectra of Mo-ZnO and undoped ZnO NPs exhibit three main peaks of (100), (002), and (101), corresponding to the ZnO crystalline structure (JCPDS no.36-1451). According to the Miller indices, hexagonal structures of the NPs observed in the SEM images can be confirmed by the XRD analysis. Maximum peak intensity is related to the (101) plane positioned at $2\theta = 36.045°$.[15] XRD pattern of the Mo-ZnO sample has no additional peak, compared to the pure sample. Mo-ZnO peaks, however, have been slightly shifted, suggesting the presence of molybdenum.[16]

Fig. 4 shows FTIR spectra of undoped ZnO and Mo-ZnO NPs, with a strong band at 1300 cm^{-1} ascribed to C-H bond stretching of the amine groups. Moreover, N-H stretching vibrations at 3400 cm^{-1} are associated with the available amine groups. The amine groups are

the outcomes of adding n-butylamine as surfactant while synthesizing Mo-ZnO NPs. In a similar study, Mote et al. doped ZnO with chromium oxide and found similar results confirming the presence of N-H bonds at 3400-600 cm^{-1}.[17]

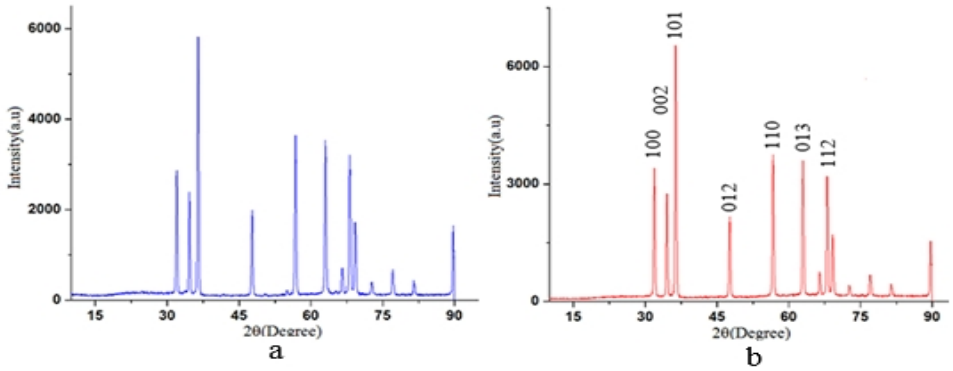

Fig. 3. XRD images of nanoparticles: a) 1.0% molybdenum doped ZnO and b) undoped ZnO

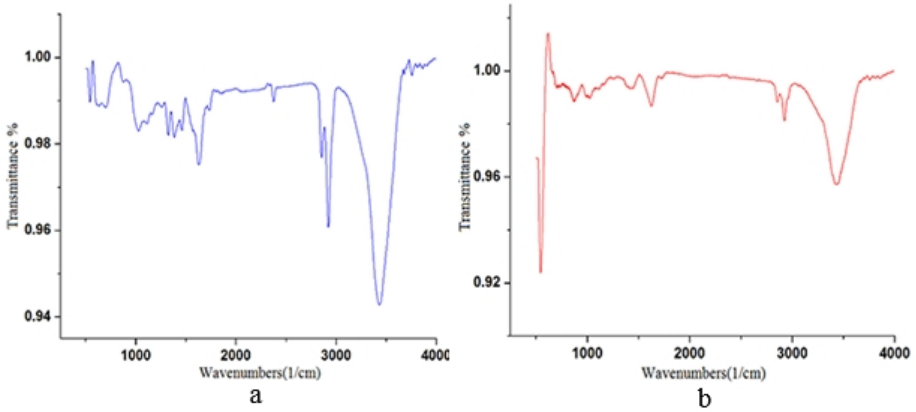

Fig. 4. FTIR images of nanoparticles: a) 1.0% molybdenum doped ZnO and b) undoped ZnO

Table 1 reports qualitative specifications of the raw leachate sampled from Sanandaj landfill site .

Table 1. Quality specifications of the raw leachate

Parameter	Value	Unit
pH	7.06	-
COD	8350	Mg/l
BOD	3100	Mg/l
TSS	2556	Mg/l
Conductivity	831.8	Ms/m

Effect of pH on the efficiency of leachate treatment

To study the effect of pH on the efficiency of photocatalytic degradation of the leachate sample, the sample was diluted with water (ratio 1:25). The pH values of the samples were set at 3, 5, 7, 9, and 11 and the NP concentration was 2 g/L. The samples were exposed to sunlight and sampled at 15, 30, 45, and 60 min. Then each sample was centrifuged at 4000 rpm for 10 min and the COD analysis was performed using the closed reflex method. The results are illustrated in Fig. 5.

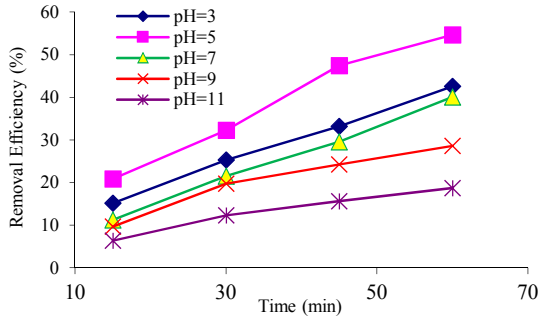

Fig. 5. Effect of pH on COD removal

The pH of the leachate solution has shown a complex effect on photocatalytic oxidation rate. These effects depend on the type of pollutant, photocatalyst surface charge,

ionization conditions, pk_a and electrostatic interaction between the surface of the catalyst and the pollutant.[10] The results of the pH effect showed that pH=5 has the highest impact on the COD removal. pH_{PZC} was found to be about 7.5 in presence of the ZnO NPs. In other words, the catalyst surface is positive at pH<7.5; therefore, the catalytic efficiency would be lower at pH values greater than pH_{PZC} due to the high alkalinity of the leachate and probable presence of carbonate and bicarbonate in the environment, which are known as radical hydroxyl consumers. By decreasing pH and eliminating alkalinity, the efficiency of the system was promoted gradually so that the highest efficiency was obtained at about 5. At pH<5, the efficiency of the system reduces as pH decreases due to the dominance of electron-hole mechanism instead of a mechanism of free hydroxyl radicals. There are similar results reported about the photocatalytic treatment of the leachate.[18,19]

Effect of nanoparticle concentration on the leachate treatment efficiency

To evaluate the effect of NPs dosage on the efficiency of leachate photocatalytic degradation , the leachate was diluted with distilled water (ratio 1:25). The pH level of the samples was set at the optimum pH of 5, and NPs dosage of 0.5, 1, 2, and 3 g/L were analyzed. The samples were exposed to sunlight and sampling was performed at 15, 30, 45, and 60 min. After running each experiment, the samples were centrifuged, and the COD analysis was performed. The results are presented in Fig. 6.

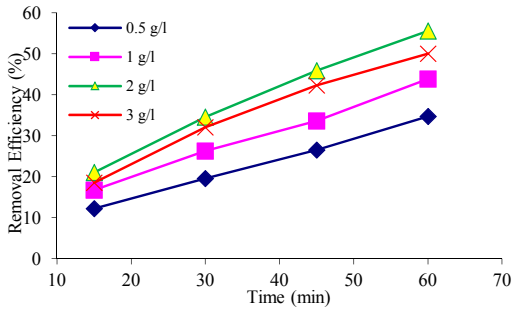

Fig. 6. Effect of nanoparticle concentration on COD removal

Increasing NPs dosage from 0.5 to 2 g/L at contact time of 60 min enhanced the process efficiency from 34.8 to 55.6%, whereas increasing NPs dosage from 2 to 3 g/L decreased efficiency from 55.6% to 50.1% after 60 min, suggesting a slight efficiency reduction. In addition, some other researchers have concluded that increasing NP dosage up to a certain level improves the efficiency while further increase in the concentration reduces catalytic efficiency due to the turbidity of the solution and reduction of light penetration.[20]

Effect of leachate concentration on leachate treatment efficiency

In order to investigate the impact of leachate concentration on the efficiency of leachate photocatalytic degradation, different concentrations of leachate samples were prepared using distilled water ratios of 1:10, 1:25, 1:50, and 1:100. The pH level of the samples was set at the optimum value of 5 and the optimum NPs dosage of 2 g/Lwas used. The samples were exposed to sunlight, and sampling was performed at 15, 30, 45, and 60 min. Then the catalyzed samples were centrifuged and the COD analysis was conducted. The results in Fig. 7 demonstrate that the efficiency of COD removal significantly promotes with reducing the leachate concentration.

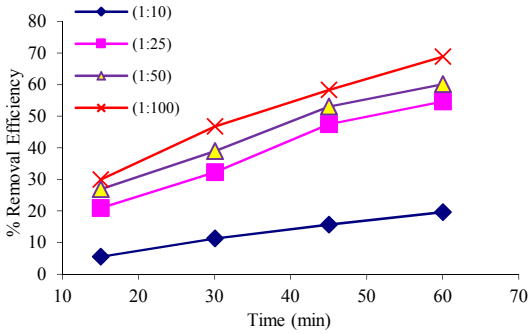

Fig. 7. Effect of initial leachate concentration on COD removal

When the dilution ratio was changed from 1:10 to 1:100, the removal efficiency increased from 19.6 to 68.9%. This result can be attributed to the fact that by elevating the initial concentration of leachate, more active surface sites of the catalyst are covered by the leachate compounds, which reduces oxidant production

and eventually leads to slow decomposition of the adsorbed compounds. In many studies on the treatment of various pollutants by ZnO based photocatalytic process and the application of ultraviolet light, decomposition efficiency was reduced with increasing the initial concentration of the pollutant.[21,22]

Effect of contact time on efficiency of leachate treatment

The effect of contact time on the efficiency of leachate photocatalytic treatment was explored by diluting the leachate with distilled water (ratio 1:25), adjusting the pH level of the sample at the optimum pH=5, and using the optimum NPs dosage of 2 g/L. The leachate solution was exposed to sunlight and sampled at the contact times of 15, 30, 45, and 60 min. Then the sampled portions were centrifuged and COD analysis was carried out. The obtained results (Fig. 8) showed that longer contact times enhance the efficiency of COD and leachate turbidity removal.

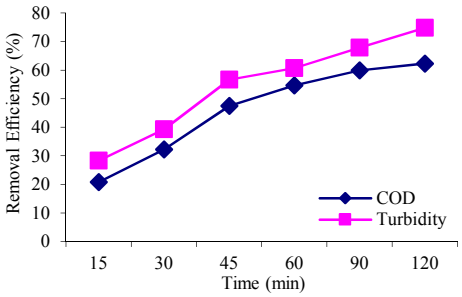

Fig. 8. Effect of contact time on COD removal and turbidity

It was observed that the efficiency increase was linear and significant up to 60 min, while efficiency changed negligibly from 60 to 120 min. It was also found that the efficiency of turbidity removal was higher than COD removal efficiency. The most important reason is that the pollutant concentration reduces periodically and when contact time is increased, the produced free radicals oxidize the leachate. Optimum contact time might vary depending on the chemical structures and stability of the contaminants.

Conclusion

In this study, photocatalytic degradation of leachate, sampled from Sanandaj landfills, Iran was performed using molybdenum oxide doped zinc oxide nanoparticles in the presence of sunlight. After synthetizing the nanoparticles, SEM, FTIR, and XRD techniques were performed to determine the specifications of the nanoparticles. The pH=5 was found to be the optimal level, resulting in the highest efficiency of COD removal; however, the efficiency of the photocatalytic process decreases under alkaline and acidic conditions. Moreover, increasing the nanoparticle dosage parameters and contact time improves the COD removal efficiency, whereas increasing the initial leachate concentration reduces efficiency. The results of this study demonstrated that the application of advanced oxidation method, along with Mo-doped ZnO nanoparticles and sunlight, provides a noticeable efficiency in leachate treatment.

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