

Effect of Zero-Valent Iron Nanoparticles on VOCs Removal from Air with a Modified Zeolite Bed

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Abstract

Volatile organic compounds (VOCs) are in categories of mankind and environmentally harmful materials. Some of VOCs are also carcinogenic and mutagen. Because of expanded application of these compounds as various domestic and industrial usages, prevention of environmental contamination of these compounds is a substantial issue. In this study, the effect of zero-valent iron nanoparticles application on a natural zeolite media, for VOCs removal efficiency was surveyed.

The Clinoptilolite zeolite after acidic amendment was used as a bed and coated with zero-valent iron nanoparticles. The particles were in size of 30-60 nm. The BTX compounds including Benzene, Toluene and Xylenes were applied as indices for VOCs pollutants. The obtained results showed a significant difference in removal of the pollutants whether by use of iron nanoparticles or not ($P=0.008$). The average removal efficiency without iron nanoparticles application was $43.31 \pm 24.84\%$, and by application of the nanoparticles it was $83.83 \pm 1.3\%$. Application of iron nanoparticles caused more complete decomposition of the pollutants up to 57.82%. According to the results, iron nanoparticles increased the VOCs removal efficiency of the zeolite and led to decomposing more amounts of pollutants in a unit volume of the zeolite. The amount of pollutants which completely decomposed to CO_2 is also increased.

Introduction

Volatile organic compounds (VOCs) are widely used in petrochemical products. The BTX are VOCs, including Benzene, Toluene and Xylene, which have harmful health effects such as anemia and carcinogenesis. The absorption properties of natural zeolites such as Clinoptilolite for VOCs are mentioned in various studies. The pervious researches declared also the increasing of transition metals oxidation- reduction property in nanoscales and decomposition of various compounds catalyzed by the transition metal, with this scales of size. Complete decomposition of VOCs will led to production of CO_2 and H_2O which is said mineralization. If the mineralization is not done properly, some organic intermediate compounds will be produced. In this study, we surveyed the effect of coating the natural zeolite, Clinoptilolite, with zero-valent iron nanoparticles in BTX removal from polluted air and its mineralization.

Material & Methods

1-2 mm diametric size zeolite grains were washed two times by 0.1N hydrochloric acid. Each washing operation took up to 6 hours to complete. It, then, rinsed several times with distilled water and dried at 180°C . The zero-valent iron nanoparticles were dispersed in distilled water by an ultrasonic set during 5 minutes and added to zeolite grains in a flask and was shaken for 24 hours and then gently dried at 80°C . The nanoparticles coated zeolites were placed in a furnace for 2 hours in 300°C for activation. The porosity and blank volume in zeolite were determined by water saturation test. A steel cylinder ($D=4.5$, $L=30$ cm) was used as reactor. The prepared zeolite was placed in the cylinder with the amount of as much as 200 g in each experiment. Polluted air with BTX was crossed through the reactor, and the pollutants concentration was measured in inflow and outflow. The air flow was 1.5 l/min, the sampling flow was 100 ml/min and sample volume was 2 l. Temperature of the reactor was set at 200°C during the experiment. The BTX sampling was carried out by using the charcoal tube that was extracted by CS_2 as a solvent. The samples were analyzed by a GC-FID. CO_2 concentrations were measured with CO_2 detectors and 100 ml sample as the detectors' instruction. All of the reagents used in this work were in lab grade.

Discussion of Results and Conclusions

The results declared that 93.94% of the applied nanoparticles were coated on zeolite grains, and it was 4.69 wt% of zeolite. Fig. 1 shows the zeolite grains with nanoparticles coating and without it.

The blank volume in nanoparticles coated zeolites (CZ) was 50.66% vs 51.34% for the not coated (Z). For 200 grams of each zeolite they were 231.84 and 235.86 ml, respectively. So, the retention times were 4.67s and 4.84s and the difference was negligible. The mean pollutants' elimination efficiency for the CZ was 83.83% vs 43.31% in Z. In table 1, the results of the removal process experiment are given in more details. The ANOVA test on these data showed a significant difference in pollutants' removal by the CZ and Z (p-value= 0.008). The CO₂ concentrations in inflow were the same, 500 ppm, but the outflow of CZ has higher concentration of CO₂. It was 625 ppm for CZ vs 525 ppm for Z. According to CO₂

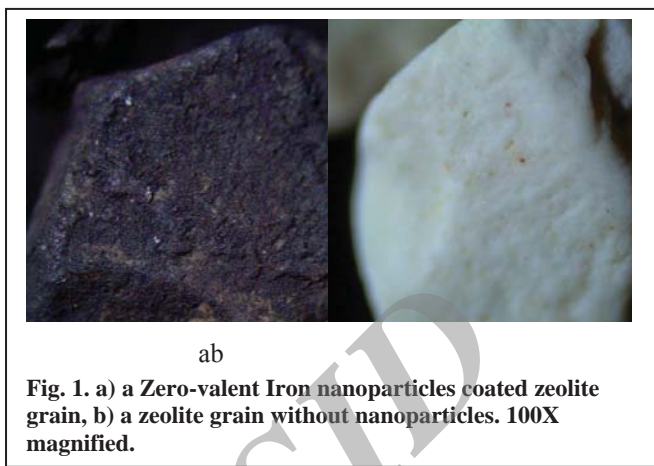


Fig. 1. a) a Zero-valent Iron nanoparticles coated zeolite grain, b) a zeolite grain without nanoparticles. 100X magnified.

concentrations and concentration of pollutants in inflow and outflow with regard to an air flow of 1.5 l/min during the experiments, the percent of pollutants mass which completely decomposed to CO₂ are calculated and are presented in Fig. 2. The standard deviation of pollutants' elimination in CZ is 1.31 whereas in Z it is 24.84. This reveals that, the elimination of pollutants in CZ is much against that for Z. These high and close pollutants' removal efficiencies in CZ cause it to be more reliable for elimination of different VOCs. Increased concentration of CO₂ in exhaust of CZ shows that the complete decomposition of the BTX in this one was higher than Z. Incomplete decomposition of the BTX may lead to some other organic compounds like Oxyphenyls or Formic, Oxalic and acetic acid or other organic compounds.

In Cz, with presence of zero-valent iron nanoparticles as reductants, the redox process can act more effectively in decomposition of the pollutants. The Fe⁰ atoms can donate electrons to reduction of the pollutants. This electron donation with presence of water vapor and heat can also result in production of OH[•] and H[•] radicals. Zhang in removal of VOCs by iron nanoparticles showed that, the iron nanoparticles by giving to electrons were converted into Fe²⁺. More oxidation of the Iron nanoparticles will produce Fe³⁺ that in presence of oxygen it makes Fe₂O₃ or Hematite. Combined application of zero-valent iron and copper oxide nanoparticles on a zeolite bed for BTX removal showed a complete decomposition up to 82.78% and average BTX removal of 56.98%. This is higher than that for the iron nanoparticles. However, the average BTX removal efficiency for the iron nanoparticles is higher. In another study, coating the zeolite with copper oxide nanoparticles decreased the BTX removal efficiency but it led to a little increasing of complete decomposition. According to these results, coating with nanoparticles decreased the pollution adsorption. The results of this study showed that the zero-valent iron nanoparticles have more ability for BTX removal and complete decomposition rather than copper oxide. In a study, TiO₂ nanoparticles on a bed of SiO₂ were applied for elimination of VOCs. The results of the study showed that the Toluene as an index of VOCs was eliminated by adsorption and catalytic decomposition processes. In the outflow, there were toluene, CO₂ and water vapor which are results of organic compounds' decomposition. Therefore, we can say that, in our work, the pollutants can be removed by those processes and the nanoparticles acted as the catalyst in pollutants' decomposition process and as excess CO₂ concentration of its outflow can prove the matter, in the CZ. So, according to the above discussions adsorption was the main mechanism of pollutants' removal in Z. But, in the CZ the main removal process was catalytic oxidation that could eliminate the pollutants with a similar rate where the adsorption did not show the same results.

Table 1. removal efficiency of Benzene, Toluene and Xylenes in a Zero-Valent Iron nanoparticles coated zeolite filter and a zeolite filter without nanoparticles coating.

	Benzene	Toluene	p-Xylene	m-Xylene	o-Xylene
Zeolite without nanoparticles coating	87.3±5.37	62.1±3.25	30.2±1.84	32.15±3.39	18.8±3.39
Zeolite with zero-valent Iron nanoparticles coating	82.54±4.3	83.89±1.99	83.14±0.91	83.61±0.58	85.99±1.68

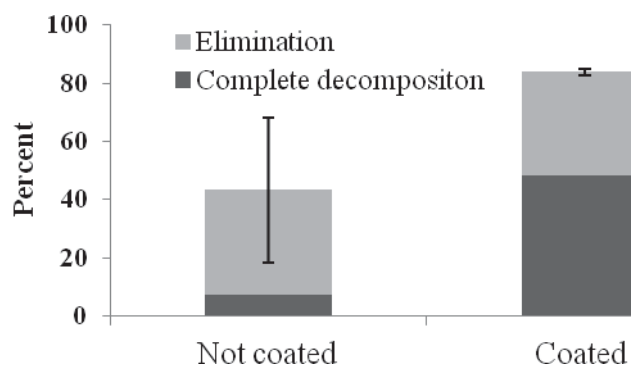


Fig. 2. Elimination and complete decomposition percent of BTX in Zero-valent Iron nanoparticles coated zeolite and the zeolite without coating.

Keywords: air pollution, Benzene, Toluene, VOCs, Xylene.

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