World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:3, No:6, 2009

Nitrogen and Phosphorus Removal from Livestock Wastewater by Zeolite Ion Exchange and Ionizing Radiation

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***Abstract*—**The ionizing radiation of livestock wastewater for the removal of nitrogen and phosphorus was studied in the presence of a natural zeolite. The feasibility of a combined process of zeolite ion exchange and electron beam irradiation of livestock wastewater was also investigated. The removal efficiencies of NH_4^+-N, T-N and T-P were significantly enhanced by electron beam irradiation after zeolite ion exchange as a pre-treatment. The presence of silica zeolite accelerated the decomposition rate of livestock wastewater in the electron beam irradiation process. These results indicate that the combined process of zeolite ion exchange and electron beam irradiation has the potential for the treatment of livestock wastewater.

***Keywords*—**Zeolite, electron beam, livestock wastewater, ammonia nitrogen, phosphorus.

I. Introduction

LIVESTOCK wastewater contains high-strength of nitrogen, phosphorus and organics. It is very difficult to treat by conventional wastewater treatment techniques. Raw livestock wastewater has high concentrations of ammonia which can reach values around 8000 mg NH_4^+-N/l. The presence of nitrogen in wastewater discharge is undesirable for several reasons. Free ammonia is toxic to many aquatic organisms, moreover, ammonium ion is an oxygen-consuming compound which depletes the dissolved oxygen in receiving water. In addition, all forms of nitrogen can be made available to aquatic plants and can consequently contribute to eutrophication. Furthermore, the presence of nitrite and nitrate ions in drinking water is a potential public health hazard.

Zeolites are three-dimensional microporous, crystalline solids with well-defined structures that contain aluminum, silicium and oxygen in their regular framework. The most common use for zeolites is as an ion exchange material in many applications. Zeolite has a high cation exchange capacity (CEC), and thus a high potential for an application for the removal of ammonia nitrogen from wastewater. And, zeolite has shown a great capacity for metal adsorption (Cu, Cd, Pb and Zn) and that property can be useful for removing toxics for microorganisms in the biological processes. Zeolite can be also useful as a microbial support both in aerobic and anaerobic processes of different wastewaters [1]. The ion exchange properties of natural zeolites are well known. Recycling and reuse of ammonium loaded zeolites as slow-release fertilizers have been studied, and the technique is well documented. Zeolite has also been introduced as an adsorbent in the advanced oxidation processes (AOPs) to increase the removal efficiency of a target compound. Chen et al. [2] have reported that the decomposition rates of organic compounds such as trichloroethene and 2-methylisoborneol during ozonation increase in the presence of silica zeolite, respectively.

Wastewater treatments using ionizing radiation such as gamma ray or electron beam have been studied, and the decompositions of many organic compounds in aqueous solutions have been reported. Since secondary polluted materials are not produced by ionizing radiation, it is also considered to be one of the promising methods. Electron beam radiation technology has been used to enhance the biodegradability of wastewaters containing various biologically refractory organic compounds such as textile wastewater, landfill leachate, paper mill wastewater, and effluent from a petroleum production [3-6]. Pospíšil and Múčka studied on the radiation removal of lead and PCBs in the presence of various sorbents including zeolite [7], [8].

In this study, the electron beam irradiation of livestock wastewater with a natural zeolite was carried out. Due to the specific properties of zeolite and its ability to act as a catalyst or an adsorbent, the intention was to investigate whether zeolite can act as a catalyst in electron beam irradiation/zeolite process or cause a synergistic effect in a heterogeneous mixture which can contribute to the overall effectiveness.

II. Experimental

The livestock wastewater was collected from a public livestock wastewater treatment plant located in Jeongeup, Korea. The natural zeolite, used as a heterogeneous catalyst, was obtained from Handu Co. Ltd., Korea, with mean particle diameter of 0.1, 0.5 and 2.0 mm, respectively. The chemical composition (%, w/w) of the zeolite was SiO_2, 70.30%; Al_2O_3, 13.60%; Fe_2O_3, 1.29%; CaO, 2.51%; MgO, 0.31%; Na_2O, 1.93%; K_2O, 3.17% ; ignition loss was 5.76% and the grain density was 2.04 g/cm^3. The radiation experiments were carried out by an electron accelerator (Model ELV-4, 1 MeV, 40 kW). The absorbed dose of a electron beam was measured

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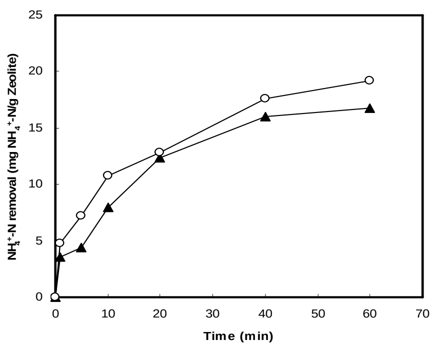
according to the dichromate dosimetry method of ISO/ASTM 51401-2003(E) [9].

The zeolite powder was added into each 200 ml glass bottle containing livestock wastewater, which then sealed, shaken for 2 h using a mechanical shaker, and then irradiated with an electron beam. Samples were taken and filtered through a 0.45 μm glass filter to obtain a filtrate. The changes in ammonia nitrogen (NH_4^+-N), total nitrogen (T-N) and total phosphorus (T-P) were determined by Standard Methods [10].

III. Results and Discussion

The trends of livestock wastewater treatment by zeolite adsorption and electron beam irradiation were showed at Fig. 1. As shown in Fig. 1(a)~(c), the removal efficiencies of NH_4^+-N, T-N, T-P were steeply increased for initial 10 minutes, and then gradually stabilized. After the zeolite treatment of 60 minute, 16.8 mg NH_4^+/g zeolite, 39.9 mg T-N /g zeolite and 10.3 mg T-P/g zeolite were obtained with zeolite adsorption (25 g zeolite/l) only, and they were increased to 19.2 mg NH_4^+/g zeolite, 44.2 mg T-N mg/g zeolite and 11.4 mg T-P/g zeolite with zeolite adsorption (25 g/l) and electron beam irradiation (20 kGy). Therefore, removal capacities of 14.3% NH_4^+-N, 9.7% T-N, 10.7% T-P were enhanced by the additional electron beam irradiation.

The effect of radiation can be combined with other processes, such as ion exchange and adsorption. Zeolite also behaves as an electron donor and as an acceptor of a moderate strength for the guest species depending on the adsorption site [11]. Ionizing radiation may generate charged dislocations on adsorbent surface and consequent adsorption of pollutant compounds from the solution occurs. This effect is called radiation adsorption. Irradiation may further cause a coagulation of finely dispersed adsorbent particles, which consequently may result in a generation of new centers of adsorption. Thus, following the capture of heavy metals or a radiolytic change of the adsorbent may occur. In this case, even synergistic effects are often observed [7], [8].



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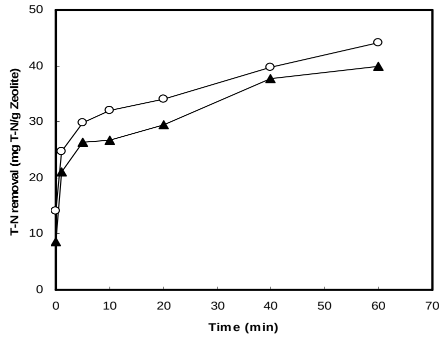

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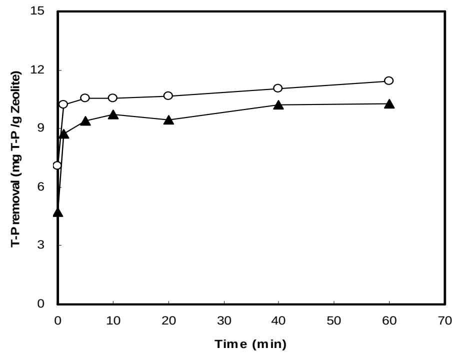

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Fig. 1 Livestock wastewater treatment efficiency by zeolite adsorption (25 g zeolite/l) and electron beam irradiation (20kGy), (a) NH_4^+-N (b) T-N and (c) T-P removal, ▲, zeolite adsorption only; ○, zeolite adsorption and electron beam irradiation

The effect of zeolite loading on the heterogeneous catalytic radiation of livestock wastewater was studied by varying the amounts of zeolite from 0 to 50 g/l. Fig. 2 shows the degradations of NH_4^+-N, T-N and T-P with 20 kGy of electron beam irradiation under various zeolite loadings. From Fig. 2, the removal efficiencies of NH_4^+-N, T-N and T-P increased to 28.2%, 33.6% and 65.9%, respectively, as the zeolite (0.5mm diameter) dose was increased from 0 to 50 g/L. Furthermore, when the 20 kGy of electron beam irradiation was applied after the zeolite adsorption, those of NH_4^+-N, T-N, and T-P were enhanced to 39.3%, 34.6% and 66.5%, respectively, as the zeolite dose was increased from 0 to 50 g/L.

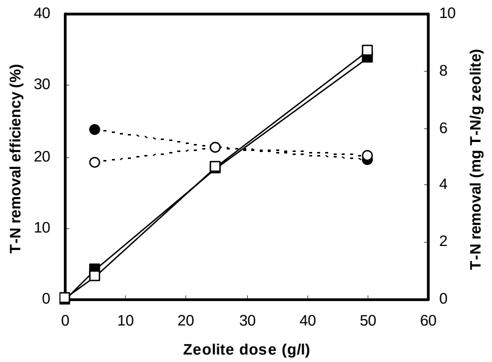
However, the trends of NH_4^+-N, T-N, and T-P removal capacities for 1 g zeolite doses were different from those of removal efficiencies. As the zeolite dose was increased from 5 to 50 g/L, the removal efficiency for 1 g zeolite dose decreased from 15.2 mg NH_4^+-N/g, 5.3 mg T-N/g and 1.4 mg T-P/g to 3.7 mg NH_4^+-N/g, 4.8 mg T-N/g and 1.0 mg T-P/g, respectively. When the electron beam irradiation was applied with the zeolite adsorption, the removal efficiency for 1 g zeolite dose also decreased, as the zeolite dose was increased. It can be inferred from these results that 5 g/L zeolite was an optimal dose condition for economical treatment.

In addition, the enhancement of removal efficiency by electron beam irradiation of livestock wastewater was highest for NH_4^+-N. Those for T-N, T-P were relatively insignificant. The NH_4^+-N ion exchange capacity increased from 15.2 to

32.8 mg NH_4^+-N/g. NH_4^+-N ion exchange capacity was enhanced by 2.3 times. Rho et al. [12] reported that the NH_4^+-N removal efficiency for unit zeolite mass was 7.116 mg NH_4^+-N/g. So, we can see that the NH_4^+-N removal efficiency for unit mass could be enhanced by the combination with electron beam irradiation.

Zeolite is a promising material for the simultaneous removal of ammonium and phosphate from wastewater. Zeolite can adsorb considerable amounts of phosphates to their hydrous oxides on Al structural sites [13]. Since zeolite is enriched with the oxides of aluminum, iron, and calcium, it may also emerge as a candidate material to purify phosphate-laden effluents. The mechanism of phosphate adsorption by Al^{3+}- and Fe^{3+}-zeolite may primarily be through ligand exchange. It is known that ligand exchange can take place even at very low initial phosphate concentrations [14]. Sakadevan and Bavor reported a P adsorption capacity of 2.15 mg/g for zeolites [15].

(a)



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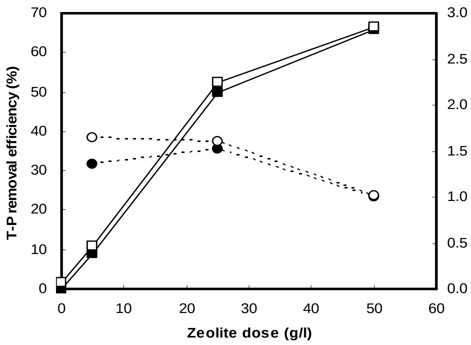

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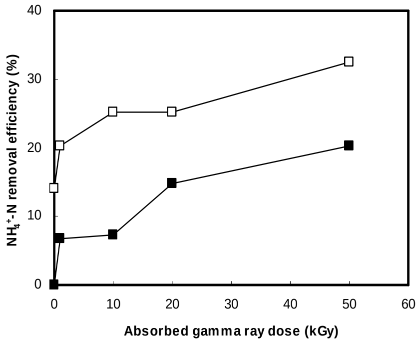
Fig. 2. Effects of zeolite dose on the electron beam irradiation of livestock wastewater, (a) NH_4^+-N (b) T-N and (c) T-P removal, ■, removal efficiency by zeolite adsorption only; □, removal efficiency by zeolite adsorption and electron beam irradiation (20kGy); ●, removal efficiency; ○, removal capacity per 1 g zeolite

The effects of electron beam irradiation on the zeolite adsorption of livestock wastewater were investigated over an absorbed electron beam dose of 0, 1, 10, 20 and 50 kGy with an initial zeolite loading of 25 g/L. From Fig. 3, the removal efficiencies of NH_4^+-N, T-N and T-P with electron beam irradiation increased to 20.3%, 0.5% and 2.0%, respectively, as the absorbed electron beam dose was increased from 0 to 50 kGy. Furthermore, when the zeolite adsorption was applied using 25 g/l of zeolite dose before the electron beam irradiation, those of NH_4^+-N, T-N, and T-P were enhanced to 32.5%, 18.3% and 53.0%, respectively, as the absorbed electron beam dose was increased from 0 to 50 kGy.

However, the effect of electron beam irradiation on the T-N, T-P removal was ineffective in spite of 50 kGy electron beam irradiation. They are enhanced when the zeolite treatment was carried out prior to the electron beam irradiation.

The effect of the addition of solid catalysts to enhance the AOPs such as ozone oxidation of organic wastewater has reportedly been observed [2]. They concluded that such effect is ascribed to the formation of OH radical from the decomposition of ozone at the surface of the catalysts. It was also reported that OH radicals produced in the bulk solution are trapped on the surface and the trapped OH radicals oxidize solutes after the irradiation has ended [16], [17]. We also considered that the effect of zeolite in enhancing the livestock wastewater treatment efficiencies by electron beam irradiation observed in the present study was also ascribed to the OH radical formation.



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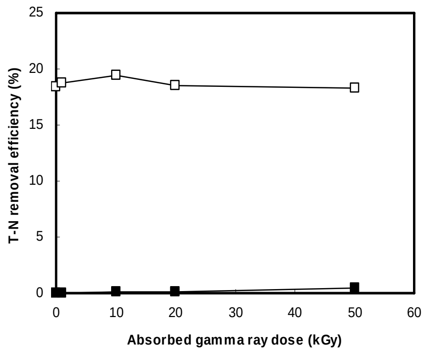

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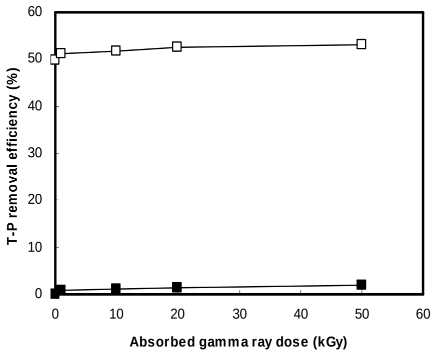

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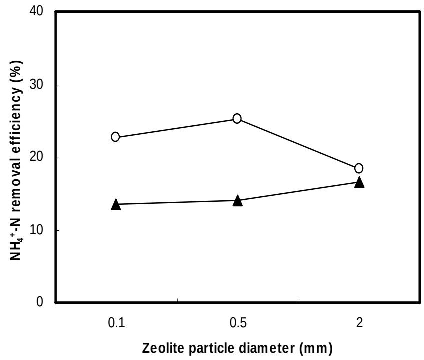
Fig. 3 Effects of absorbed electron beam dose on the zeolite adsorption of livestock wastewater. (a) NH_4^+-N, (b) T-N and (c) T-P removal, ■, removal efficiency by electron beam irradiation only; □, removal efficiency by zeolite adsorption and electron beam irradiation



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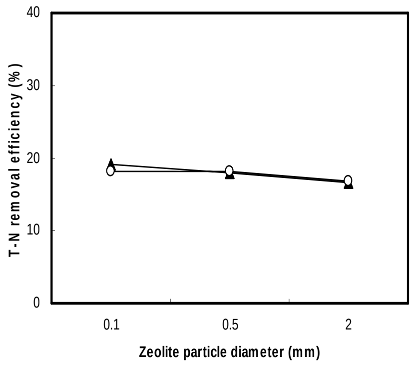

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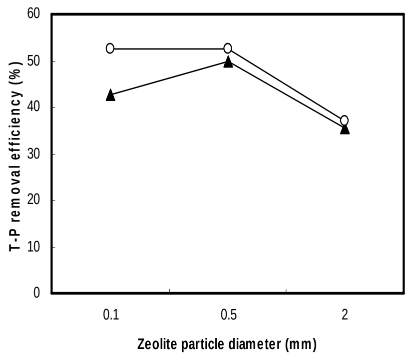

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Fig. 4 Effects of zeolite particle size on the treatment of livestock wastewater by zeolite adsorption and electron beam irradiation, (a) NH_4^+-N (b) T-N and (c) T-P removal, ▲, zeolite adsorption only; ○, zeolite adsorption and electron beam irradiation

Fig. 4 shows the removal efficiencies of NH_4^+-N, T-N and T-P by various particle size zeolite (0.1, 0.5, 2.0 mm). Generally, the specific surface area is increased as the zeolite particle size decreased, which is favorable as a catalyst [18]. However, the effects of zeolite particle size on the removal efficiency of NH_4^+-N, T-N and T-P were relatively insignificant. As the particle size of zeolite was increased from 0.1 mm to 2.0 mm, the removal efficiency of NH_4^+-N, T-N and T-P were 13.5~16.5%, 17.0~19.6% and 35.4~49.7%, respectively.

IV. CONCLUSION

Zeolite is generally used to remove the cationic ions from the aqueous solution, and the ionizing radiation technology is applied to treat the recalcitrant compounds from wastewater. In this study, zeolite adsorption and electron beam irradiation were applied simultaneously to treat the livestock wastewater which contained a high concentration of nitrogen and phosphorus compounds. As the amount of zeolite was increased, the removal efficiencies of NH_4^+-N, T-N, T-P increased, however, the removal capacities of NH_4^+-N, T-N, T-P for 1 g zeolite dose decreased. And as the absorbed electron beam irradiation dose was increased, the removal efficiencies of NH_4^+-N increased. However, the effect of electron beam irradiation on the removal of T-N and T-P was insignificant. Conclusively, we could find that the combination of the zeolite adsorption and the electron beam irradiation could be one of option for recalcitrant livestock wastewater.

ACKNOWLEDGMENT

This research was supported by Ministry of Education, Science and Technology of Korea. The authors deeply appreciate their financial support.

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