



PREPARATION, CHARACTERIZATION AND APPLICATION OF RICE HULL-DERIVED ZEOLITES IN WATER TREATMENT

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ABSTRACT

This study aimed to prepare zeolite from rice hull, characterize the prepared zeolite and apply it in the removal of nitrate in water.

Pretreatment of rice hull before ashing was done using distilled water and 1M HCl. Purity of the rice hull ashes obtained in the process was verified by determining their percent carbon content. Using EDX, the alumina and silica ratios were calculated from the data gathered. SEM was used to determine the shape and pore size and XRD method to know the possible crystal lattice of the prepared zeolites.

The rice hull washed with water (RHA-W) has 21:16 (Si:Al) framework ratio while that acid-washed (RHA-A) 23:17 (Si:Al) which could mean that the Si-Al framework ratio of the samples are 1.3:1 and 1.4:1, respectively. SEM scans at 7500x magnification revealed that zeolites derived from RHA-W has bigger pore sizes (2 μm) compared to those derived from RHA-A with approximately 1 μm diameter. Using XRD spectroscopy, the rice hull-derived zeolites possible lattice was determined and both were not simple cubic crystals.

The trapping and exchanging capacity of the prepared zeolites were determined by treating a water sample with 69.0 ppm of NO_3^- and loading it with 0.2 g zeolite per liter of solution. Results show that the zeolite derived from RHA-W was able to decrease the concentration of nitrate in water by 99.11% while that derived from RHA-A by 99.26% while only 98.77% for the commercial zeolite.

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1. INTRODUCTION

Pollution is one of the major problems in the Philippines. Given that this country is surrounded by large bodies of water, good clean water is still rather scarce. Other than that, industrial and agricultural wastes greatly contribute in its contamination. Agrochemical runoff is also widespread in the Philippines and recent studies show that excess fertilizer use has already caused nitrates pollution in water bodies in agricultural areas in the country [1].

Another pollution that can pose hazard to humans is the rice hulls, the most common agricultural by-products that are difficult to dispose off [2]. When these hulls are burnt, they leave a powder mixture of carbon and silica which when inhaled can cause respiratory problems. Development of these silicon-rich by-products is being studied in the production of useful industrial materials so as to minimize disposal problems. The hulls are considered as a filler ingredient in cheap pet foods which serves as a source of fiber [3], as insulating materials [4, 5], as source of silicon carbide whiskers used to reinforce the strength of ceramic cutting tools [6], in the preparation of silica gel [7]. Modified rice hull as studied by Ong, et al. [8] was an inexpensive and efficient sorbent for the removal of ethylene blue. The rice hull ash as a good source of mesoporous silica used in the preparation of catalysts, inks, concrete hardening accelerator [9, 10], component of detergent and soaps and as a refractory constituent [11].

Zeolites are basically alumino-silicate minerals that are used in different applications depending on their structures. One of these applications is on water treatment where the zeolites likely usage is for pollution control that includes heavy metals and mineral filtration. Although zeolites can occur naturally under extreme conditions at a long period of time, synthetic zeolites can be prepared in the laboratory.

This study aimed to prepare and characterize rice hull-derived zeolite and apply it in the removal of nitrate in water. It specifically aimed to prepare zeolite from the pretreated rice hulls prior to ashing, determine the alumina and silica ratio content of the produced zeolite samples and its extra mineral contents by energy dispersive X-ray, characterize the different zeolite samples by X-ray diffraction method and scanning electron microscopy, and test the ability of the rice hull-derived zeolites in cleaning water which contains nitrates.

2. METHODOLOGY

2.1. Preparation of Rice Hull Zeolites

About 2 groups of 5 kg of rice hulls were treated separately with water and HCl. Approximately 50 g of the resulting rice hull ash were treated with 700 mL 6M NaOH. The resulting filtrates were labeled as the silicate solution. About 13 g of $\text{Al}(\text{OH})_3$ were dissolved in a mixture of 50 mL 6M KOH and 10 mL 6M NaOH and were stirred for 30 min. until a white homogeneous solution was obtained. The solution was filtered through a Whatman-40 ashless filter paper to remove some undissolved particles. The resulting solution was added to 150 mL of the silicate filtrate and about 1 mL triethanolamine was added. The resulting mixture was stirred for 1 hour until a thick gel formed. The mixture was placed in a pressure cooker for about 6 hours, after which the mixture was cooled for an hour. The mixture was filtered using a Buchner funnel to recover the residual gel. The gel was then washed three times with distilled water before drying in

an oven at 200°C for 2.5 hours. The gel was then deagglomerated by adding 150 mL 10% ethanol and was immersed in a warm water bath for an hour and then dried at 100°C in an oven for another 2 hours before analysis.

2.2. Characterization by Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX)

Different rice hull zeolite samples were analyzed by Scanning Electron Microscopy coupled with Energy Dispersive X-Ray apparatus. The surface morphology and mineral contents of the zeolites were obtained, respectively. Briefly, about a pinch of the zeolites, ground to pass through a 100 μ m sieve was mounted in the apparatus sample container and was sputter-coated with thin sheets of gold. Three different magnification images (1500x, 5000x, and 7500x) were obtained. Actual measurement of the particle size was carried out at 7500x magnification.

2.3. Characterization by X-Ray Diffraction (XRD) Method

Different rice hull zeolite samples were analyzed by X-Ray Diffraction. Crystallinity of the samples was determined. Briefly, about 100 mg of the dried rice hull zeolite were ground until a powder-like substance was obtained. The samples were mounted on the apparatus sample container. The HR-XRD Bede D³ system apparatus was set at an acceleration voltage of 40kV and a current of 30 mA and the samples are scanned at diffraction angle from 1 to 65°, 2 θ at a rate of 1 degree per minute.

2.4. Preparation of the Water Samples for Nitrate Filtration

Five hundred milliliters of the prepared water sample with concentration of 69 ppm nitrates were treated. An aliquot of the prepared sample was analyzed in UV-Vis Spectrometer for the anions to determine the matrix effect of the water sample. The treatments were composed of 100 mL of the prepared water samples containing 0.02g of a commercial zeolite and placed in a flask wrapped with aluminum foil to prevent penetration of light. Both Treatments 2 and 3 each treatment contained 0.1g of the different zeolites prepared from the earlier procedures: laboratory preparations of zeolites through water preparation (RH-W) and acid preparation (RH-A), respectively and were exposed to sunlight for 2, 3, and 4 hours in different Erlenmeyer flasks and were subjected to air bubbling. Ten (10) mL aliquots from each of the treated samples were subjected to spectrophotometric method to measure the concentrations of nitrates.

Each aliquot was filtered using Whatman-40 ashless filter paper. After filtration, the samples were preserved in the refrigerator and were analyzed not more than 48 hours after exposure using Spectronic 20 to determine the concentration of nitrates present in the treated solutions.

2.5. Spectroscopic Analysis of Nitrates (Brucine Method)

The determination of the amount of nitrate concentration during irradiation was analyzed using Spectronic 20 at 410 nm. A calibration curve was prepared using 1.0, 1.5, 2.0, 3.0, 5.0, and 10.0 ppm of nitrate standards. Exactly 719.54mg of Ca(NO₃)₂•4H₂O was dissolved in distilled water and was diluted to a 1-L volumetric flask up to the mark. This solution was labelled as 1000 ppm

nitrate solution. From this solution 100 mL was measured and placed in a 1-L volumetric flask and was diluted to mark. The resulting concentration was labelled as the 100ppm nitrate solution. From this solution, 1, 1.5, 2, 3, 5, and 10 mL aliquots were placed separately in 100mL volumetric flasks and were diluted to the mark. These solutions represent 1.0, 1.5, 2.0, 3.0, 5.0, and 10.0ppm nitrate solution, respectively.

About 10 mL of each of the standard solutions were pipetted into separate macro test tubes. Then, 2.0 mL of 30% NaCl was added to each tube and were placed in a cold water bath; 10 mL of 13N H₂SO₄ were also added in each test tube. The samples were cooled and were let to stand for a few minutes to undergo equilibrium. After the samples were cooled, 0.5 mL of brucine-sulfanilic reagent were pipetted and added to the solution. Then it was placed in a boiling water bath (100°C) for exactly 25 minutes. After that, it was transferred in a cold water bath until it reaches room temperature (20-25°C). The absorbance of the standard solution was recorded.

About 1 mL of the irradiated sample was diluted into a 10 mL volumetric flask up to mark. Then, the samples were treated following the procedure of the standard solution.

3. RESULTS AND DISCUSSION

3.1. Elemental Analysis of Zeolite

The Energy Dispersive X-Ray elemental data (Table 1) and spectra (Figures 1 and 2) showed that silicon was the most abundant element present in the zeolite. RH-W and RH-A have an element percent ratio of 23Si:17Al and 21Si:16Al respectively.

Table-1. EDX for the Rice Hull Ash Zeolites

Element	Element %		Standards
	RH-W	RH-A	
O	48.36	47.69	Quartz
Na	14.75	11.93	Albite
Al	15.99	17.08	Al ₂ O ₃
Si	20.90	23.31	Quartz
Total	100	100	(=2< Sigma)

Figure-1. EDX spectra for RH-W zeolite.

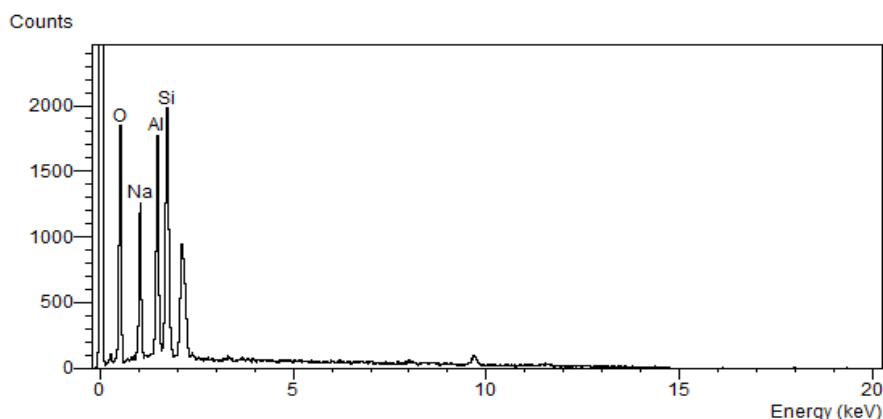
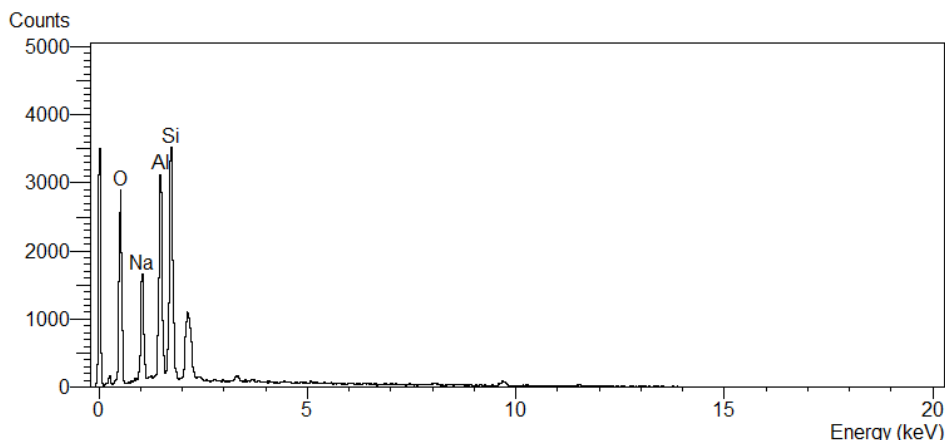


Figure-2. EDX Spectra for RH-A zeolite.



Based on the percent elements (Si, Al, O, Na) present in the sample, rice hull derived zeolites were closely comparable with Afghanite, Franzinite, and Liottite [12].

X-Ray Diffraction of Rice Hull Derived Zeolite

Figure-3. X-ray diffractogram of RH-A zeolite.

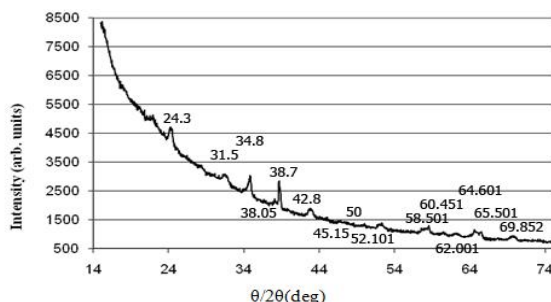
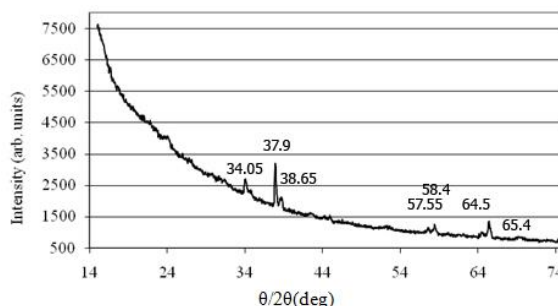


Figure-4. X-ray diffractogram of RH-W zeolite.



The XRD diffractogram for both rice hull samples were presented in Figures 3 and 4. The major peaks were served as reference guides for the determination of the crystal structure of the produced rice hull derived zeolites.

Indexing of the data by assigning Miller indices to the 2θ reflections and using the Bragg's equation showed that the crystal structure of the produced rice hull ash zeolites were not a simple

cubic crystal systems (simple cubic, body-centered, and face-centered cubic crystals). Results show that the product obtained in this experiment is of complex structures.

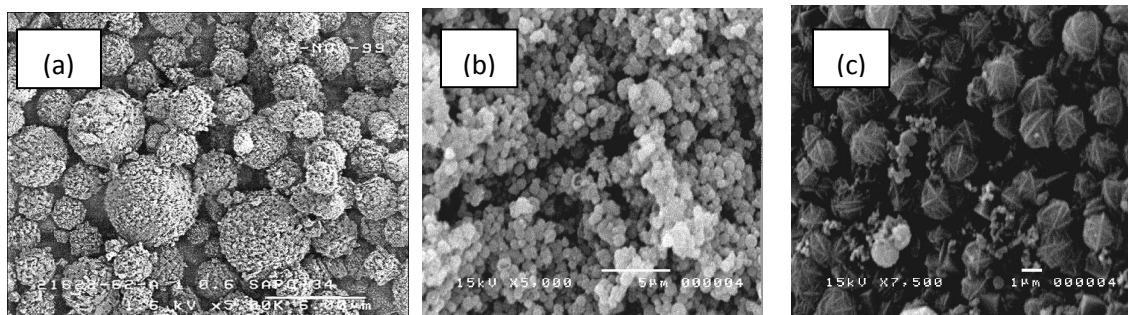
3.2. Surface Morphology of Rice Hull Derived Zeolite

The scanning electron microscope (SEM) microstructure revealed the surface morphology of the rice hull derived zeolite. Images were obtained at 7500x magnification and actual measurement of particle size showed 1 μ m for RH-A zeolite and 2 μ m for RH-W zeolite (Figure 5), respectively. RH-A zeolite has smaller pore size than RH-W. The slight difference in their sizes may have been influenced by the pretreatment procedure.

Treatment of the rice hull with an acid solution at the boiling temperature for several hours [De Souza, et al. \[10\]](#), removes a large fraction of the impure elements that would otherwise contribute to the formation of a glassy phase. The latter authors obtained silica with high specific surface area, *i.e.*, approximately 250 m²/g, and their transmission electron microscopy analyses revealed that the ultimate particle size of their silica powders was close to 10 nm. This specific surface area and ultimate particle size of the silica indicate that rice hull is a possible low cost source for nanosize silica powders, or at least a very reactive silica powder.

Moreover, the SEM shows that the rice hull-derived zeolites have smaller diameter sizes compared to the commercial zeolite having a 2.5 to 5 μ m diameter. This could explain why the laboratory prepared zeolites caused a greater reduction in the concentration of the nitrates in the water samples than that of the commercial zeolites.

Figure-5. SEM images of the (a) commercial zeolite, (b) RH-A and (c) RH-W zeolites at 5000x magnification.



3.3. Spectroscopic Analysis of the Nitrate-Treated Water Samples

The initial concentration of the mineral nitrate water sample was 69 ppm, the maximum residue limit of nitrates according to the World Health Organization. The concentration was observed to decrease greatly in all the treatments on the first two hours, and then slowed down as the time of exposure went on further. The loadings of 0.2g/L zeolite reduced the mineral nitrate contaminants in the solution effectively. Both RH-W and RH-A decreased the concentration of the nitrate pollutant by 97.03 and 97.22%, respectively, in the first 3 hours as compared to the commercial zeolite, with a 94.87% decrease. This result conforms with the study of [Burge and Halden \[13\]](#) who reported that anion-exchange can remove certain mineral nitrates from water. He

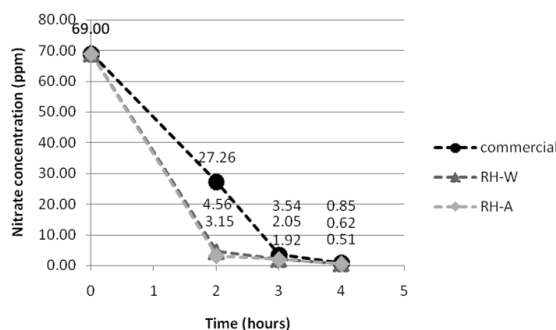
reported that the regeneration removal efficiency of mineral nitrates and perchlorates in water are calculated to be at 97% on average. Exposure of the zeolite-treated nitrate solutions under sunlight decreased the nitrate concentration in all treatments. Analysis of Variance revealed that the treatment means are significantly different at 5% level. DMRT further disclosed that RH-W and RH-A zeolites yielded a better removal of nitrate than that of the commercial zeolite.

Table-2. Nitrate concentration (ppm) at different collection periods.

Treatment	Nitrate Concentrations (ppm)				Treatment Mean*
	0 hr	2 hrs	3 hrs	4 hrs	
Commercial	69.00	27.26	3.54	0.85	10.55 ^a
RH-W	69.00	4.56	2.05	0.62	2.41 ^b
RH-A	69.00	3.15	1.92	0.51	1.86 ^b

* Numbers with the same letter designation means that those are not significantly different at 5% confidence level.

Figure-6. Nitrate concentrations of the zeolite treatments at different collection period.



The result could be attributed to the smaller pore sizes of the laboratory prepared zeolites. The nitrate molecules could have passed through the pores and were trapped in the small space in between the zeolite molecules. Also, laboratory prepared zeolites are more selective towards the nitrate molecules than the commercial zeolite.

4. CONCLUSIONS AND RECOMMENDATIONS

Based from the result of the experiment, the following conclusions are drawn:

1. the produced RHA zeolites have a higher silica ratio with respect to alumina;
2. the zeolites produced are not simple cubic crystals, thus of complex structures;
3. the crystal size of RH-W zeolites are twice as large than that of RH-A, thus pretreatment using 1M HCl removes a large fraction of the impure elements that would otherwise contribute to smaller specific surface area and ultimate particle size of the silica leading to smaller zeolite particles; and
4. the laboratory-prepared rice hull-derived zeolites are capable of removing mineral nitrates from water.

The analyses done were not enough to identify the specific zeolite that was produced. It is also limited to the use of EDX, SEM and XRD to determine the zeolite produced in the laboratory. It is therefore recommended that future works should include the following: determine the effect of pH and temperature as factors for producing rice hull ash zeolites; determine the capability of the produced zeolite in absorption by using Langmuir Isotherm; test the produced zeolites for other possible uses; and find suitable methods for reusing and disposing the used zeolite samples.

REFERENCES

- [1] R. Tirado, "Nitrates in drinking water in the Philippines and Thailand," *Greenpeace Research Laboratories Technical Note 10/2007*, 2007.
- [2] H. Akbar, "Production of low cost self compacting concrete using rice husk ash." Available from: <http://www.neduet.edu.pk/ICCIDC-I/Conference%20Proceedings/Papers/028.pdf>, 2003.
- [3] H. Watson, "Cereal in pet food. Dogs in Canada magazine." Available from: <http://www.hilarywatson.com/cereals.pdf>, November 2005.
- [4] P. A. Oliver, "The rice hull house." Available from: <http://www.thebiopod.com/pdf/ricehullhouse.pdf>, 2008.
- [5] J. Johnson, "Insulation and packing material made from rice hulls and fungus." Available from: <http://gadgets.boingboing.net/2009/05/14/insulation-and-packi.html>, 2009.
- [6] E. Mendoza, "Rice: A cradle to grave analysis." Available from: <http://bss.sfsu.edu/raquelrp/projects/Rice.ppt>, 2003.
- [7] R. B. Villamor, "Preparation and characterization of silica gel from sugarcane bagasse ash," Undergraduate Thesis, Central Luzon State University, Nueva Ecija, Philippines, 2008.
- [8] S. T. Ong, P.-S. Keng, A.-W. Chong, Siew-Ling, and Y.-T. Hung, "Tartaric acid modified rice hull as a sorbent for methylene blue removal," *American Journal of Environmental Sciences*, vol. 6, pp. 244-248, 2010.
- [9] M. F. De Souza, P. S. Batista, I. Regiani, J. B. L. Liborio, and D. P. F. De Souza, "Rice hull-derived silica: Applications in Portland cement and mullite whiskers," *Materials Research Journal*, vol. 3, April, 2000.
- [10] M. F. De Souza, W. L. E. Magalhaes, and M. C. Persegil, "Silica derived from burned rice hulls," *Materials Research Journal*, vol. 5, December, 2002.
- [11] V. R. Shelke, S. S. Bhagade, and S. A. Mandavgane, "Mesoporous silica from rice husk ash," *Bulletin of Chemical Reaction Engineering & Catalysis*, vol. 5, pp. 63 – 67, 2010.
- [12] C. Baerlocher, W. M. Meier, and D. H. Olson. *Atlas of zeolite framework types*. 5th Ed., Available from: <http://www.iza-structure.org/databases/books/Atlas5ed.pdf>, 2001.
- [13] S. Burge and R. Halden, *Nitrate and perchlorate removal from groundwater by Ion exchange*. Livermore, California: University of California. Available from: <http://www.clu-in.org/download/contaminantfocus/perchlorate/LLNL1.pdf>, 1999.