

Aqua Regia as a Competitive Leaching Agent for Metallic Impurity Removal from Rice Husk

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ABSTRACT

Rice husk is widely recognized as significant biomass containing cellulose, lignin and silica. Usually, rice husk is combusted for energy purposes but it contributes to severe environmental pollution. Therefore, the integrated components of rice husk (i.e. silica) can be extracted and converted into value-added products. However, the metallic impurities must be removed before further extraction. Generally, rice husk is leached with conventional acids such as HCl and nitric acid, however, the present study has used aqua regia and compared the results with conventional acids. The leached rice husk samples were characterized using TGA, SEM and EDX. The results of the present work indicate that the aqua regia carries a significant leaching potential to remove metallic impurities from rice husk with 1 M and 2 M solutions removing more than 98% and 99% of impurities respectively. However, its brief chemical stability compels it to be prepared and used immediately.

Keywords: Aqua regia; leaching agent; rice husk

INTRODUCTION

Environmental problems, depletion and costs associated with the non-renewable energy sources have pushed the global trend towards exploiting renewable energy sources. On one hand, the burning of fossil fuels is satiating the energy demands but on the other hand, it is constantly polluting the environment with greenhouse gases and other pollutants. Coal, crude oil and natural gas are among such examples that are widely used for energy gains at the cost of the environment. For example, the combustion of coal releases CO₂, SO_x, NO_x as well as volatile organic compounds (VOCs). CO₂ results in the greenhouse effect, thereby causing global warming, whereas SO_x and NO_x may cause acid rain by reacting with the water and oxygen in the atmosphere (Nayak & Datta, 2021). Likewise, the VOCs react to form ground-level ozone or smog. Furthermore, the non-renewable energy sources are limited; hence their constant use is resulting in their depletion. Such continual usage and the expensive methods involved behind their transportation, mining and extraction are resulting in the increased level of their cost (Akhter, Soomro, et al. 2021; Zhu et al. 2020).

All these unavoidable factors have diverted global attention towards renewable energy sources. These sources are usually sustainable, environmentally friendly, abundant, and inexpensive. Among such sources, the agricultural crops and their biomass forms a significant portion. Biomass is an

organic matter acquired from plants and animals. Typically, the biomass of plant origin consists of numerous compounds that can be extracted as value-added products for diverse applications. For example, the rice husk, wheat husk, wheat straw and dry fruit shells contain cellulosic material, lignin, silica and metallic compounds (Santoso et al. 2020).

Rice is one of the major agro crops that is widely cultivated. China and India account for almost half of its global production (Nguyen et al. 2019). Such a huge production also results in the generation of massive rice husk. On a global scale, Pakistan is the 11th largest producer of rice. According to an estimate, in 2016, the total rice production in Pakistan was 6.9 million tons. One ton of rice paddy produces 220 kg of rice husk, hence 6.9 million tons will generate around 1.5 million tons of rice husk each year (Hamza Hasnain et al. 2021). Such an enormous generation of rice husk has led to environmental problems, mainly due to the way it is managed. For example, rice husk is either thrown off as a waste stockpile in an open atmosphere or burnt for energy. In both cases, it releases hazardous gases into the environment. For example, the open burning of rice husk generates rice husk ash as an end-product and produces greenhouse gases. Similarly, the open atmospheric microbial degradation of rice husk also contributes to environmental pollution. As a result, the rice husk ash still contains metallic impurities and usually ends up being dumped (Akhter, Zoppas, et al. 2021; Ozturk et al. 2017).

Therefore, to preserve the environment and extract the value-added product (silica) from rice husk, its metallic impurities need to be removed. If not, these impurities may result in much lower silica purity and also chemically interact with other compounds. The conventional method of removing the metallic impurities from rice husk is by leaching with acid. Typically, HCl and Nitric acids are used, however; the present study has also used aqua regia besides the conventional acids. Aqua regia, also known as Nitrohydrochloric acid, is a mixture of HCl and Nitric acid with a ratio of 3:1. Being the mixture of 2 strong acids, it has been shown to possess an impressive leaching capability for biomass (Bae et al. 2020), as demonstrated by the present work as well. Although, aqua regia stays briefly in its stable form, yet its leaching potential cannot be ignored. Therefore, the present work explores the leaching potential of aqua regia to remove impurities from rice husk and compares the results with conventional acids (HCl and Nitric Acids).

MATERIALS & METHODOLOGY

CHARACTERIZATION OF RICE HUSK

The surface morphology of rice husk was determined using Scanning Electron Microscopy FESEM JSM 6701F (JOEL) operated at 15 kV and 20kV. The thermogravimetric (TG) analysis was performed on a Perkin Elmer TGA6 instrument. Sample of 5 – 7 mg was heated at heating rates 20oC/min from 50°C to 900°C under nitrogen atmosphere with a flow rate of 20 mL/min. The metallic impurities in leached and unleached rice husk samples were determined using Energy Dispersive X-Ray (Model, JEOL JSM-7400F).

LEACHING ACIDS

A total of 3 acids; aqua regia, HCl and Nitric acid, were used in the present study. Each acid was prepared with solutions of 3 molar concentrations; 0.5M, 1M and 2M respectively. The prepared molar solutions of each acid were used for leaching rice husk samples (Azat et al. 2019; Bakar et al. 2016). Due to its unstable nature, the molar solutions of aqua regia were prepared right before the leaching experiments.

INITIAL WASHING AND DRYING OF RICE HUSK

Before preparing samples for leaching, 1 kg of rice husk was initially washed with distilled water several times to remove dirt and adhering impurities. The washed rice husk was then sun-dried for 5 hours, followed by oven drying at 110 °C for 24 hours. The drying ensured the complete removal of moisture from the rice husk (Askaruly et al. 2020).

LEACHING OF RICE HUSK WITH ACIDS

To prepare samples for leaching, the sun and oven-dried rice husk was divided into 18 samples (S1-S18), each of 50 g. Each rice husk sample of 50 g was mixed with 300 mL of distilled water in a beaker and magnetically stirred for one hour at 80 °C (Mirmohamadsadeghi & Karimi, 2020). Furthermore, 2 samples were leached with each molar solution of acids. Figure 1. Shows the experimental strategy performed in the present work, where as Table 1 indicates the classification of samples for leaching and % of impurities removed.

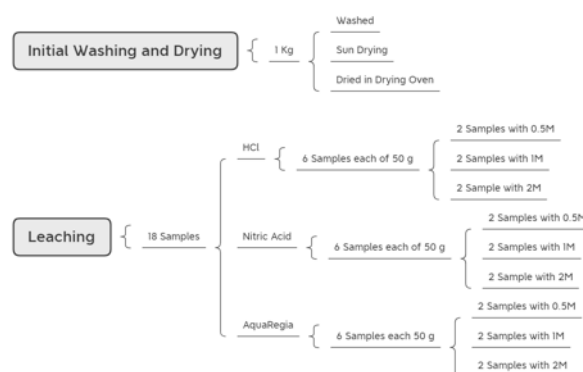


FIGURE 1. Experimental Strategy

RESULTS & DISCUSSION

THERMOGRAVIMETRIC ANALYSIS (TGA) OF RICE HUSK

The presence of organic components in the rice husk was determined by TG analysis. Figure 2. indicates the TG curves of acid-leached rice husks. It can be seen that, regardless of acid leaching, the first weight loss occurs between 50 and 150 °C, with a weight loss of 1 to 2 percent corresponding to the loss of water and other volatile chemicals. At temperatures ranging from 240 to 360 °C, the second stage demonstrates a rapid and significant weight loss. This is due to the heat degradation of hemicellulose and cellulose in the rice husk, which is a key organic component. Acid hydrolysis of hemicellulose and cellulose into smaller molecular weight molecules that are more readily thermo-degraded resulted in poorer thermal stability. The third stage indicates a weight loss of 26–31 percent, which can be attributed to lignin, a thermally more stable aromatic polymer that decomposes gradually between 370 and 600 °C. The noncombustible silica (16 percent, >600oC) makes up the majority of the ash residue.

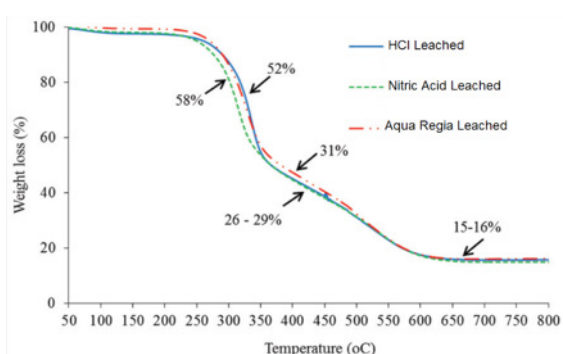


FIGURE 2. TGA Curves of HCl, Nitric Acid and Aqua regia leached Rice Husk

SEM ANALYSIS OF RICE HUSK

Figure 3 shows the morphology of leached and unleached rice husk. The unleached rice husk (a) indicates a much smaller pore size compared to leached samples. The leaching has resulted in increased pore size which is in agreement with the previous studies (Azat et al. 2019; Moayedi et al. 2019; Nuaklong et al. 2020). Apparently, the highest pore size was observed in the samples leached with aqua regia, followed by HCl and Nitric acid. This could be due to the metallic impurities being removed during leaching and the surface tension of acids. Furthermore, the amorphous structure can be attributed to acid delignification, hence the structural breakdown.

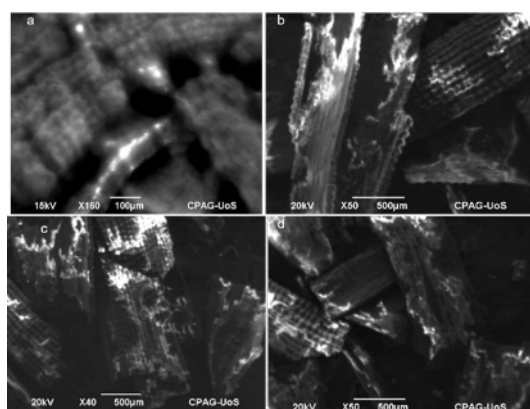


FIGURE 3. SEM Images of Rice Husk (a) Unleached (b) Aqua Regia Leached (c) Nitric Acid Leached (d) HCl Leached

EDX ANALYSIS

Energy Dispersive X-Ray analysis was conducted to determine the metallic impurities in acid leached and unleached rice husk samples. The acid leached samples were analyzed through EDX and the results were compared to the unleached sample to determine the percentage of impurities removed. Table 1. shows the impurities removal % of leached rice husk samples. Figure 4 shows the EDX results of the samples with the highest percentage of impurities removed. All the samples leached with 3 acids are compared in figure 5. As can be observed, 2 M nitric acid, 1 M and 2 M of HCl and Aqua regia were able to remove more than

98% of impurities. The highest impurities were removed by 2 M HCl with 99.56% and 99.48%, followed by 1 M with 99.16%. However, 2 M Aqua regia was significantly able to remove 99.06% and 99.02% of impurities, hence possessing a competitive leaching potential. Although aqua regia is a mixture of 2 strong acids yet its slightly lower impurity removal than HCl with the same molar concentrations can be attributed to its unstable nature. Furthermore, the lowest impurity removal % was observed in the samples leached with 0.5 and 1 M nitric acid respectively.

TABLE 1. Impurity Removal % of Leached Rice Husk Samples

Sample	Leaching Acid	Molar Concentration	Impurity Removal %
S1	HNO3	0.5M	96.21
S2		0.5M	96.91
S3		1M	96.98
S4		1M	97.2
S5		2M	98.73
S6		2M	98.81
S7	HCl	0.5M	98.02
S8		0.5M	98.17
S9		1M	99.01
S10		1M	99.16
S11		2M	99.48
S12		2M	99.56
S13	Aquaregia	0.5M	96.98
S14		0.5M	97.34
S15		1M	98.31
S16		1M	98.54
S17		2M	99.02
S18		2M	99.06

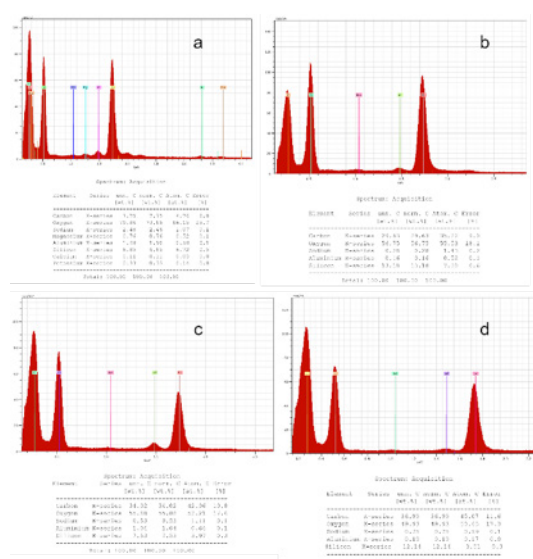


FIGURE 4. EDX Results (a) Unleached (b) HCl Leached (c) Nitric Acid Leached (d) Aqua Regia Leached

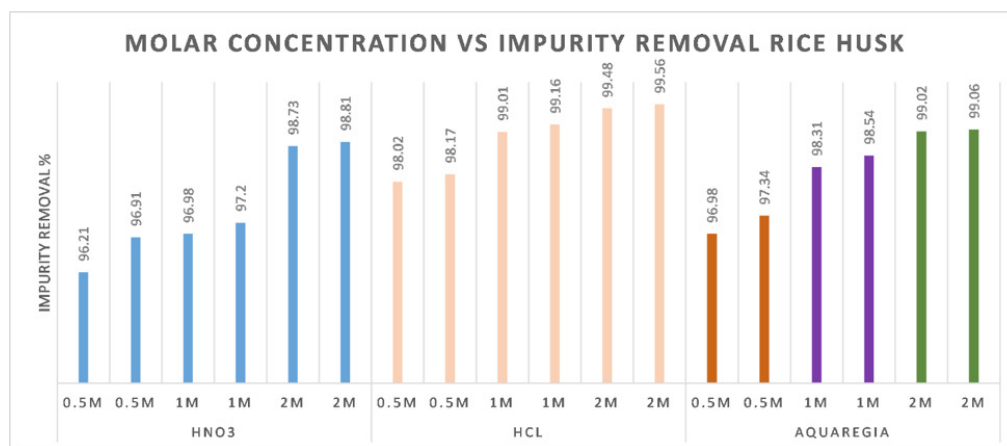


FIGURE 5. Impurity Removal Percentage of Rice Husk Samples Leached with Different Acids

CONCLUSION

Rice husk is shown to be of significant importance due to its composition. As biomass, it may contain various elements that can be extracted to produce value-added products, such as silica and lignin. However, the metallic impurities present in the rice husk can cause severe problems ahead. The impurities are usually removed via leaching with conventional acids such as HCl and nitric acid, however, the present study used aqua regia and compared its removal efficiency. It was found that aqua regia has a great leaching potential with 1 M and 2 M solutions removing more than 98% and 99% of impurities respectively.

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DECLARATION OF COMPETING INTEREST

None

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