Pak. J. Agri. Sci., Vol. 45(4), 2008

EXTRACTING SILICA FROM RICE HUSK TREATED WITH POTASSIUM PERMANGANATE

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As an agro-waste material the rice husk is abundantly available is rice growing areas. In many areas rice husk after burning involves disposal problems because of higher quantities of silica present in it. Rice husk contains about 20 *per cent* silica, which is present in hydrated amorphous form. On thermal treatment the silica converts into crystobalite, which is a crystalline form of silica. However amorphous silica can be produced under controlled conditions ensuring high reactivity and large surface area. Leaching the rice husk with organic acids and alkalies removes the metallic impurities from its surface. How a dilute solution of potassium permanganate affects the rice husk is the subject of this research paper. The rice husk was treated with the dilute solution of potassium permanganate at room temperature and then analyzed by SEM, TGA and the ash by analytical treatment after burning under controlled temperature. The SEM results revealed that the protuberances of the rice husk were eaten away by the solution of potassium permanganate. Pyrolysis of rice husks showed that the thermal degradation of the treated rice husk was faster than the untreated rice husk where as analytical results confirmed the presence of more amorphous silica than untreated rice husk.

Keywords: Rice husk ash, potassium permanganate, cellulose, SEM, TGA, Amorphous silica

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INTRODUCTION

Approximately 20 *per cent* of the paddy is rice husk, which is obtained after separating rice, broken rice and bran. Increasing use of rice husk as a fuel in various industries produces a large amount of ash. The rice husk contains 80 *per cent* organic volatile materials and remaining 20 *per cent* silica. The rice husk ash (RHA) contains 85 *per cent* to 95 *per cent* amorphous silica. The chemical composition of the rice husk ash varies from sample to sample which may be due to the different geographical conditions, type of paddy, climatic conditions and type of fertilizer used [1].

Different types of combustion have one common characteristic; they all results in the oxidation of most of the combustible portion of the rice husk while leaving the inert portion. The inert portion is generally called ash or after gasification as char. The term "char" is referred to the un-combusted residue that has not been taken to a sufficiently high enough temperature to change its state, whereas the term “ash” implies that change of state has occurred. However when applied to RHA the term ash appears to be reserved for all processes apart from gasification irrespective of whether or not a change of state has occurred. In chemical analyses of various rice husks the term "ash" refers to the chemical constituents of the residue. The unburnt component is predominantly carbon which can be measured by reheating a sample of the ash in the furnace. The difference in the mass of the sample before and after heating is referred to as the “loss on ignition” (LOI). The LOI value is normally the same as that of the carbon content of the ash. The percentage of the carbon in RHA varies according to the combustion process.

The high silica content in the rice husk may be responsible for the residual carbon [2]. The silica in the rice husk is at the molecular level and is associated with water. It occurs in several forms such as quartz, cristobalite, tridymite, coesite, stishovite, lechatelerite, and opal, the latter two being amorphous [3]. For RHA as a marketable product, it should have more amorphous silica than crystal silica or should have high quality crystal silica that can be used as a filler in polymeric and ceramic composites. Two forms of silica dominate in combustion process, which are lechatelerite, an amorphous form, and cristobalite, a crystalline form. Amorphous silica of high purity, small particle size and high surface area has tremendous potential as an adsorbent and catalyst support in different chemical synthesis. In order to prepare amorphous silica of high purity, the treatment of rice husk with various chemicals before and after combustion was attempted by many authors [4, 5].

Mineral acid leaching of rice husk has been reported to be more effective than untreated rice husk for extraction of silica. Acids like HCl, HNO_3, and H_2SO_4 of varying concentrations have been used to remove metallic ingredients and found that the HCl is the most effective. Researchers also tried organic acids on RHA but it has been found that pretreatment of RH is better than post treatment [6]. The purpose of pretreatment is to reduce carbon contents in RHA. The pretreatment of rice husk with any organic acid does not improve the amorphicity of the RHA produced.

Pretreatment of rice husk with potassium permanganate

Treatment of rice husk with organic acids remove impurities present due to many reasons and have no contribution to enhancing combustion process. Boiling the RH with mineral acids for many hours to remove the minor impurities for commercial productions is not cost-effective either. In many commercial operations sufficient oxygen for combustion is more important than removal of impurities from the surface of rice husk.

In present study an attempt has been made to incorporate the potassium permanganate as an oxidizing agent to facilitate the combustion process. Potassium permanganate as an oxidizing agent is being used in pharmaceutical industry to oxidize functional groups such as aromatic side chain to carboxylic acids and organic sulfones. Potassium permanganate upon heating decomposes and liberates oxygen that can help in combustion of the rice husk. Keeping in view this characteristic it was planned to treat RH with various concentrations of potassium permanganate. The treated and untreated rice husks were examined by SEM and in thermal analyzer.

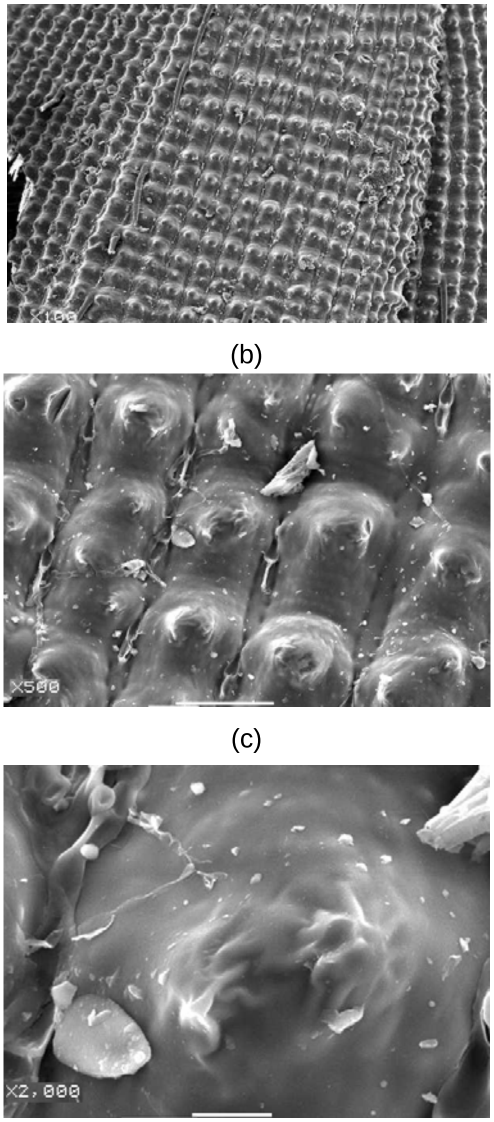
MATERIALS AND METHODS

The rice husk was collected from local rice mill during the milling season. The rice husk was first washed with deionized water for five minutes followed by drying in oven at 105 ^{0}C for 24 hours. A sample of 100 grams was treated with 0.08N solution of potassium permanganate for 30 minutes followed by drying in oven at 105 ^{0}C for 24 hours and designated as K1. The untreated rice husk was designated as R.

SEM analysis

The scanning electron microscope (SEM) images the sample surface by scanning it with high energy beam of electrons. The type of signals produced by an SEM includes secondary electrons, back scattered electron (BSE), characteristic x-ray, light, specimen current and transmitted electrons. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. Given high atomic number and sputter coating, gold produces high topographic contrast and resolution.

The rice husk samples were fixed on the glass plate with petroleum wax and then a thin film of gold was sprayed in a gold-depositing machine. The glass plate was also made conductive by using special conducting liquid. The results of the images are shown in Figs. 1, 2.


(a)

(b)

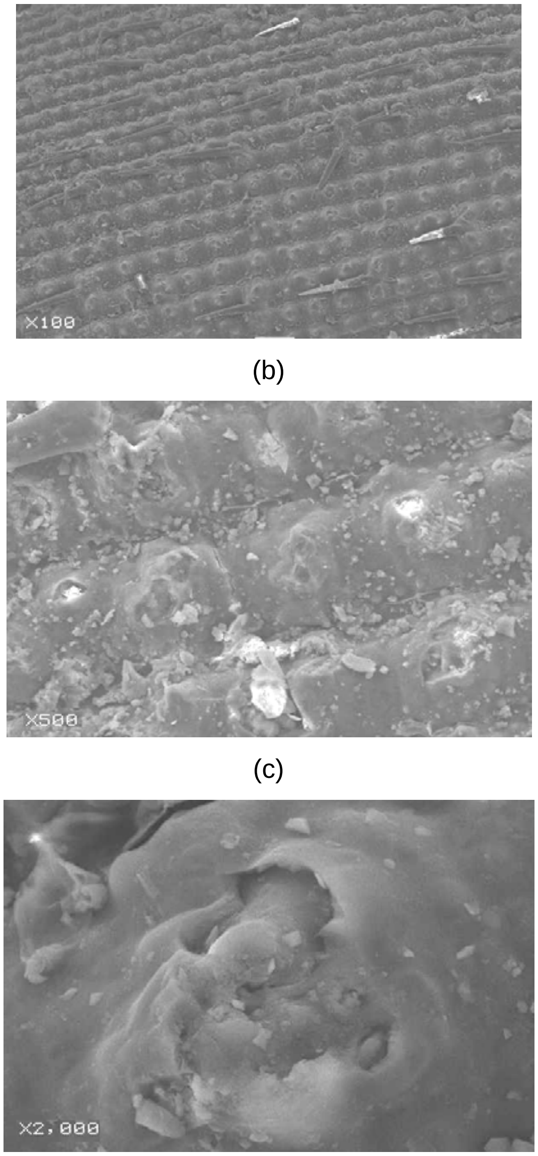
(c)

Fig. 1. SEM of untreated rice husk (R)
(a) X100 (b) X500 (c) X2000

Analysis (TGA)

The prepared materials K1 and R were ground separately and passed through 10 mesh sieve by a vibrating machine for 30 minutes before TGA. It is meant to establish the thermal behavior of materials. Weight loss against temperature was measured to establish the rate of thermal degradation. The tests were performed under nitrogen environment in differential thermal analyzer (TA instruments model Q 600). Nitrogen of 99 *per cent* purity was arranged through a British Oxygen Company. The purpose of

(a)



(b)

(c)

Fig. 2. SEM of rice husk treated with 0.08N solution of potassium permanganate (K1) (a)×100 (b)×500 (C)×2000

conducting the tests under nitrogen environment was to displace air in the pyrolysis zone. The gas was fed at a constant rate of 100 ml/minute. The temperature was raised at the rate of 10°C/minute from ambient temperature to 800°C. 20 mg samples of both categories were placed in platinum crucible and the weight loss against rising temperature was measured. The thermo-grams of K1 and R are shown in Fig 3.

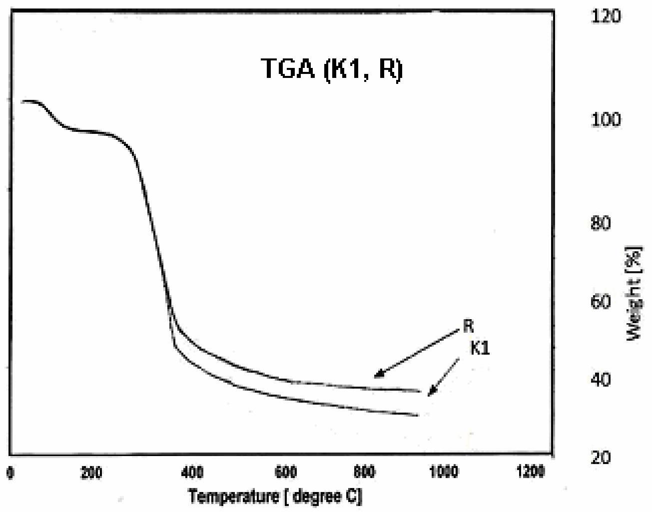


Fig. 3. Thermogravimetric analysis of untreated and treated rice husks. R for untreated and K1 is for treated rice husk

RESULTS AND DISCUSSIONS

The thermal degradation process can be divided into initial, active and passive zones. The weight loss up to 105°C may be attributed to the vaporization of light volatile matters and physically absorbed water. Major degradation takes place in the active zone that starts from 235°C and terminates at 380°C. In this zone decomposition of primary hemicellulose and cellulose takes place [7]. Passive zone that starts around 380°C and terminates at around 500°C is due to the decomposition of lignin. The slopes of curve in both zones differ and it may be deduced that the hemicellulose and cellulose are the main contributors in thermal degradation process while lignin gets converted into char that took longer time to decompose. It can be observed from Fig.3 that the thermal degradation of material K1 is faster than R in both active and passive zones under same conditions.

SEM images of both untreated and treated rice husks are different. The ruptured protuberances of treated rice husk are due to reaction with $KMnO_4$. It has been reported that $KMnO_4$ reacts with cellulose at room temperature [8]. The ruptured surface of the rice husk is due to the dissolution of cellulose in $KMnO_4$ solution. It may be concluded that the presence of potassium permanganate not only facilitates the oxidation of rice husk in active and passive zones but also reduces the cellulose contents in the rice husk. The reduced cellulose contents improve the thermal degradation activity in the active and passive zones.

Weight loss against temperature was calculated (for passive zone) from the indices obtained (Fig.3) and are shown in Table 1. It can be seen that the weight loss of sample K1 from 400°C to 800ºC is higher than that of R because of better degradation behavior of sample K1. Silica in each category was found same (19.8%) after LOI, therefore it can be safely concluded from Table 1 that the ratio of silica to ash is higher in category K1 comparing to R in above stated temperature range.

Table 1. Weight loss against temperatures obtained from TGA (Silica after (LOI)=19.8%)

Residual weights in %				
T(^{0}C)	**(R)**	**(K1)**	**Silica in (R)**	**Silica in (K1)**
400	47	42	42.12	47.14
500	43	37	46.04	53.51
600	40	35	49.50	56.57
700	39	33	50.76	60.00
800	37	31	53.51	63.87

To find out the percentage of amorphous silica, analytical technique has been used [9]. This technique involves the titration of $Ba(OH)_2$ solution against the paste of glycerol and Rice Husk Ash (RHA) by using phenolphthalein as an indicator. The RHA was prepared in tube furnace at 500ºC, 600ºC, 700ºC each for 90 minute before subjecting to analytical treatment. The results are summarized in Table 2.

Table 2. Amorphous silica obtained from treated and untreated rice husks at various temperatures

Temperature ^{0}C	**Amorphous silica in %**	
	K1	**R**
500	**85.2**	**82.2**
600	**79.5**	**75.6**
700	**62.3**	**58.2**

It can be observed from Table 2 that amorphous silica in both samples obtained is different at each temperature. In case of material K1 the conversion into amorphous silica is higher than material R. It can be deduced therefore that the treatment of RH with potassium permanganate produces more amorphous silica than untreated rice husk.

CONCLUSION

The rice husk was treated with 0.08N solution of potassium permanganate and then thermogravimetric analyses were performed under nitrogen environment. It has been observed that the pretreated rice husk thermally degraded faster than untreated rice husk in both active and passive zones. From the indices obtained from TGA it can be deduced that in passive zone the ratio of silica to ash is higher in K1 as compared to sample R. SEM results revealed that the protuberances of the rice husk were ruptured in reaction to potassium permanganate. Analytical result proves that the amorphous silica obtained, from 500^{0}C to 700^{0}C was higher in treated rice husk. It can be deduced that $KMnO_4$ has not only reduced the cellulose contents of the rice husk but also has acted as an oxidizing agent in thermal degradation process and generated more amorphous silica.

ACKNOWLEDGEMENT

The funding and support provided by University of Engineering and Technology Lahore Pakistan, is acknowledged.

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