

*Full Length Research Paper*

# **Equilibrium sorption isotherm for lead (Pb) ions on hydrogen peroxide modified rice hulls**

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**Modified rice hulls system for removing Pb (II) from aqueous solutions has been investigated. Rice hulls are agricultural waste product. The experimental condition was the modification of the rice hulls (sorbent) with different concentrations of hydrogen peroxide solution. The experimental results were fitted to the Langmuir and Freundlich isotherms to obtain the characteristic parameters of each model. The Langmuir isotherm was found to well represent the results. The maximum sorption capacities of various concentrations of hydrogen peroxide modified rice hulls were 2.57, 3.15, 5.15, 8.57, 10.97 and 11.88 mg/g for 0.1, 0.3, 0.6, 0.9, 1.2 and 1.5 M hydrogen peroxide solution respectively. It was noted that increasing the concentration for modification resulted in a higher metal uptake per unit weight of the modified rice hulls.**

**Key words:** Modified, Langmuir, Freundlich, hydrogen peroxide, rice hulls, lead.

## **INTRODUCTION**

Over the past 20 years, a number of legislations have come into force to control pollution. Problems associated with waste water disposal in developing countries and especially in Nigeria can be attributed to lack of adequate treatment/management policies coupled with ineffective legislation on the part of entrusted government agencies (Oboh and Aluyor, 2008). The sorption of pollutants from aqueous solution plays an important role in wastewater treatment since it eliminates the need for huge sludge-handling processes (Ho and McKay, 1999).

The high cost of water has prompted many industries to treat their wastewater. Wastewater includes contaminants like radiation materials, minerals or organic carcinogens. The transfer of contaminant from one medium to another e.g., the dumping of untreated waste directly into the river is no longer accepted (Hossein et al., 2005).

Lead is a typical toxic heavy metal with cumulative and non-degradative characteristics. Lead is fairly widespread in our society and probably is the most serious toxic metal. Evidence of harmful effects in adults is rarely seen at blood where lead levels are below 80 mg per 100 ml.

Human exposure to lead occurs through air, water and food. The passage of lead into and between these media

involves many complex environmental pathways. There is a long history of human exposure to abnormally elevated levels of lead in food and drink, due to practices such as cooking in lead-lined or lead glazed pots and the supply of water through lead pipes (Ho et al., 2002).

Rice hull availability depends on the type and size of the rice hull mills and their locations. Larger rice mills that are located in or close to urban areas will have more disposal problems with hulls compared with those located in the rural areas. In addition some rice mills operate only a few months out of the year, whereas others operate through out the year. Finally, restrictions on open pile burning affect the availability of hulls as well ([www.geroecology.org](http://www.geroecology.org), 2004). The waste to wealth approach to modern technology has lead to researches into ways of converting rice hulls in to more useful products (Akindahunsi and Alade, 2008; Ugheoke et al., 2008; Da Dosta et al., 2002; Arayapranee and Rempel, 2008); particularly as fillers (Sae-oui, 2002; Udonne and Aluyor, 2005) and as activated carbon (Okieimen et al., 2004)

## **MATERIALS AND METHOD**

Rice hulls were obtained from the rice market in Daleko, Lagos, Nigeria. They were dried in ambient temperature and then ground and screened through a set of sieves-the standard Tyler-sieves No. 80 and the 20–30 mesh fractions were

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retained. The sieved hulls were weighed and 200 g of it was placed in 4 L of 0.1 N sodium hydroxide. The slurry was stirred in a magnetic stirrer for 1 h at a rotation speed of 300 rpm and a temperature of 23°C, so that the hulls completely imbibed in the base. The resulting hulls, which is the base extract (BE) hulls were then poured onto a 40 mesh sieve and rinsed with distilled water, to remove the base from the hulls.

For modification, the BE hulls were mixed with various concentrations of Hydrogen peroxide in a ratio of 1.0 g of hulls to 7.0 cm<sup>3</sup> of Hydrogen peroxide. The various concentrations were 0.1, 0.3, 0.6, 0.9, 1.2 and 1.5 M. The hulls readily absorbed the peroxide and the ratio of hulls to peroxide used was to ensure that the hulls were completely imbibed in the liquid. The modified hulls were then washed and dried overnight.

This produced a uniform material for the complete set of sorption tests which was stored in an air-tight plastic container for all investigations. Analytical grade reagents were used in all cases. The stock solution of Lead (II) were prepared in distilled water using Lead Nitrate (Pb (NO<sub>3</sub>)<sub>2</sub>). All working solutions were prepared by diluting the stock solution with distilled water.

The experiments were carried out in the batch mode for the measurement of adsorption capabilities. The bottles with 500 cm<sup>3</sup> capacity were filled with 200 cm<sup>3</sup> of the synthetic wastewater, and 200 g of modified rice hulls (ground). The bottles were shaken for a predetermined period at room temperature in a reciprocating shaker for 2 h at 300 rpm. The separation of the adsorbents and solutions was carried out by filtration with Whatman's filter paper No. 4 and the filtrate stored in sample cans in a refrigerator prior to analysis. The residual metallic ion concentrations were also determined using an Atomic Absorption Spectrophotometer (AAS): model Philip PU 9100X.

## RESULTS AND DISCUSSION

The equilibrium sorption isotherm is fundamentally important in the design of sorption systems. Equilibrium relationships between sorbent and sorbate are described by sorption isotherms, usually the ratio between the quantity sorbed and that remaining in the solution at a fixed temperature at equilibrium. In order to investigate the sorption isotherm, two equilibrium models were analyzed. These included the Langmuir and the Freundlich isotherms (Ho, 2002).

### Langmuir isotherm

The Langmuir sorption isotherm (Langmuir, 1916) has been successfully applied to many pollutants sorption processes and has been the most widely used sorption isotherm for the sorption of a solute from a liquid solution. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the sorbent. It is then assumed that once a metal ion occupies a site, no further sorption can take place at that site. The rate of sorption to the surface should be proportional to a driving force multiplied by area. The driving force is the concentration in the solution, and the area is the amount of bare surface. If the fraction of covered surface is  $f$ , the rate per unit of surface is:

$$r_a = k_a C(1 - \phi) \quad (1)$$

The desorption from the surface is proportional to the amount of surface covered:

$$r_d = k_d \phi \quad (2)$$

Where  $k_a$  and  $k_d$  are rate coefficients,  $r_a$  is sorption rate,  $r_d$  is desorption rate,  $C$  is concentration in the solution, and  $f$  is fraction of the surface covered.

At equilibrium, the two rates are equal, and:

$$\phi = \frac{k_a C_e}{k_d + k_a C_e} \quad (3)$$

and

$$K_a = \frac{k_a}{k_d} \quad (4)$$

Since  $q_e$  is proportional to  $\phi$ :

$$\phi = \frac{q_e}{q_m} \quad (5)$$

The saturated monolayer sorption capacity,  $q_m$ , can be obtained. When  $\phi$  approaches 1, then  $q_e = q_m$ .

The saturated monolayer isotherm can be represented as:

$$q_e = \frac{q_m k_a C_e}{1 + k_a C_e} \quad (6)$$

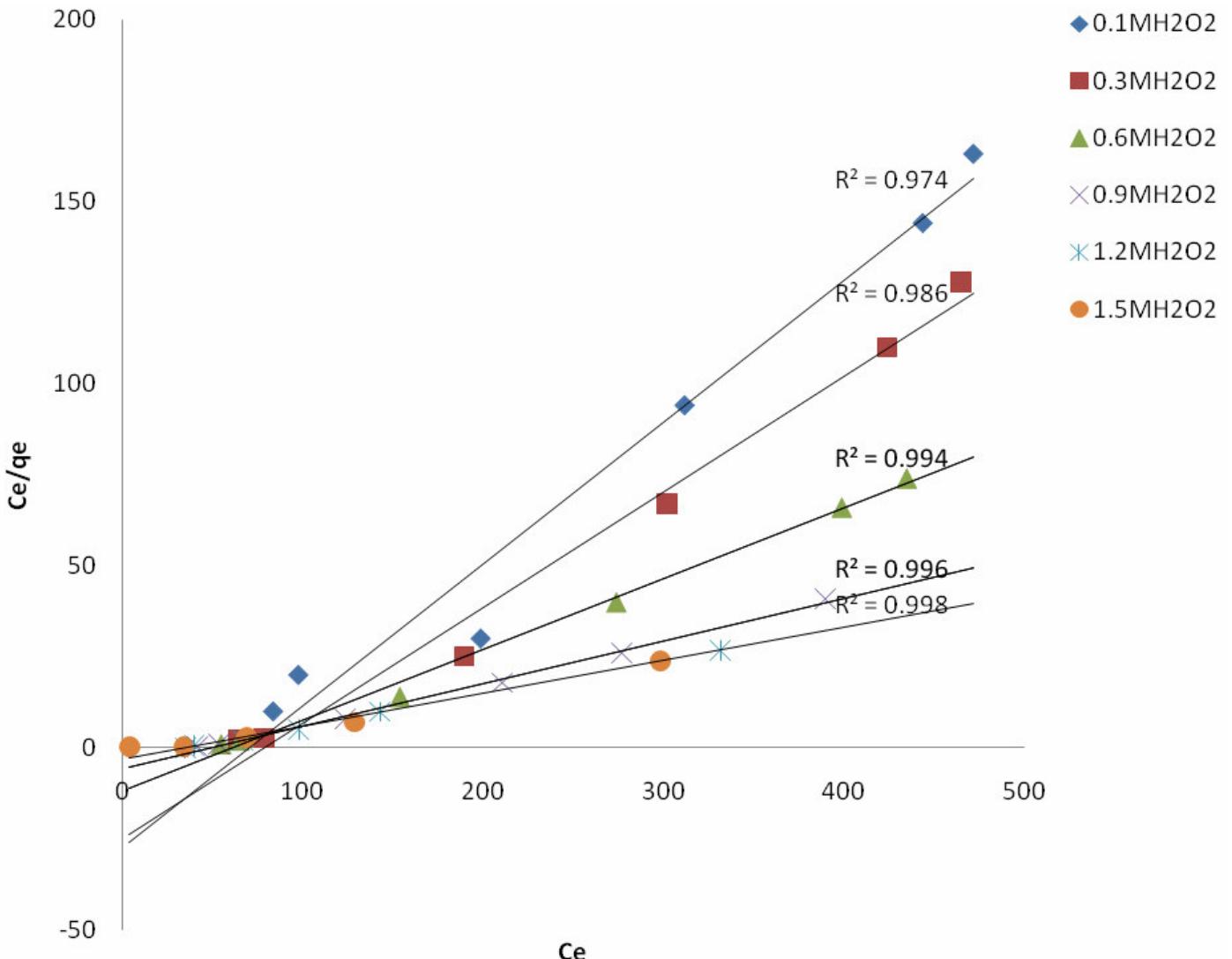
The above equation can be rearranged to the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{k_a q_m} + \frac{1}{q_m} C_e \quad (7)$$

Where  $C_e$  is the equilibrium concentration (mg/dm<sup>3</sup>);  $q_e$  is the amount of metal ion sorbed (mg/g);  $q_m$  is  $q_e$  for a complete monolayer (mg/g);  $K_a$  is sorption equilibrium constant (dm<sup>3</sup>/mg). A plot of  $C_e/q_e$  versus  $C_e$  should indicate a straight line of slope  $1/q_m$  and an intercept of  $1/K_a q_m$ .

### Freundlich isotherm

Freundlich studied the sorption of a material onto animal charcoal (Freundlich, 1906). He found that if the concen-



**Figure 1a.** Langmuir isotherm for  $\text{Pb}^{2+}$  on  $\text{H}_2\text{O}_2$  modified rice hulls.

concentration of solute in the solution at equilibrium,  $C_e$ , was raised to the power  $1/n$ , the amount of solute sorbed being  $q_e$ , then  $C_e^{1/n}/q_e$  was a constant at a given temperature. This fairly satisfactory empirical isotherm can be used for non-ideal sorption and is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \quad (8)$$

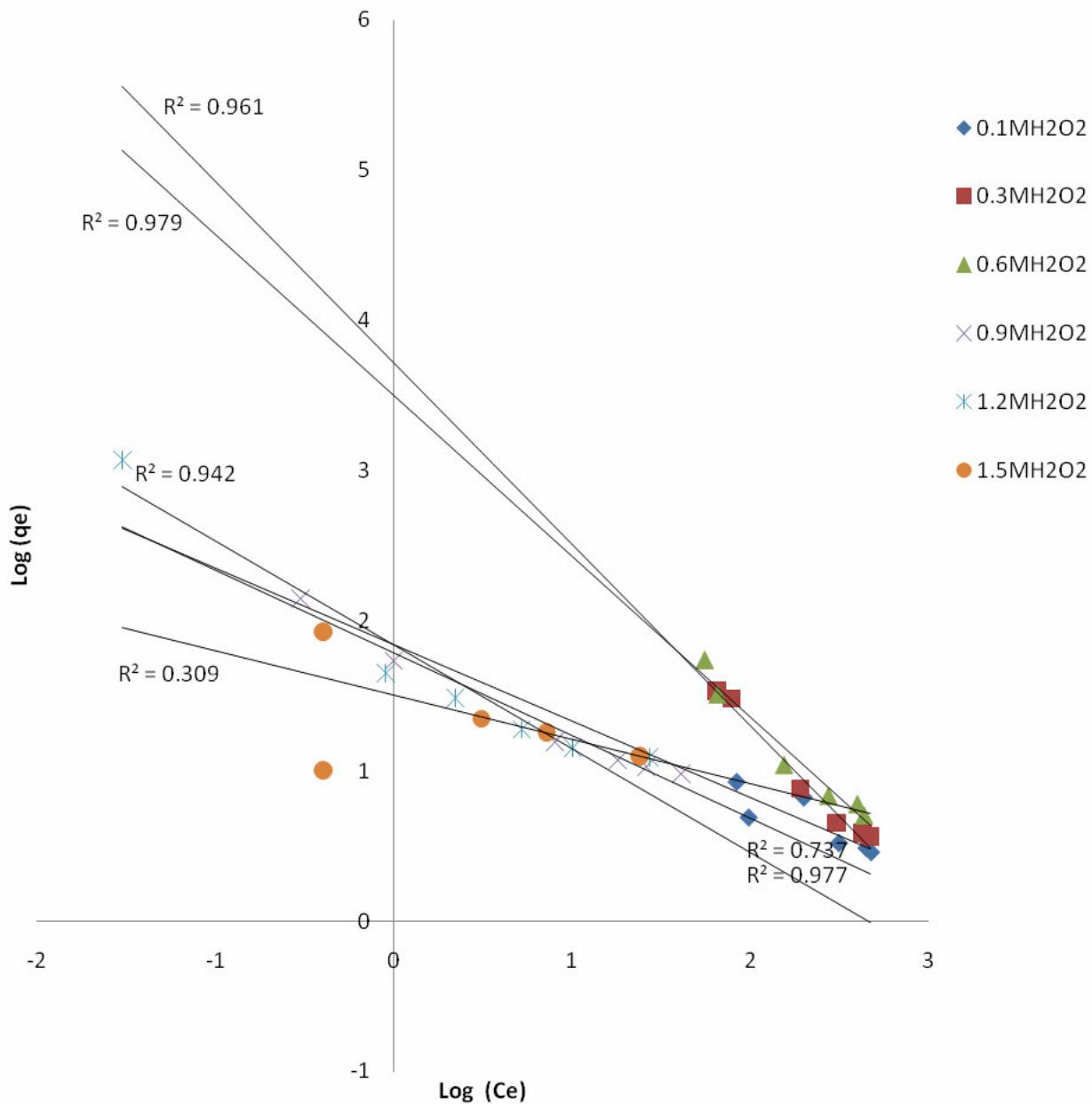
The equation is conveniently used in the linear form by taking the logarithm of both sides as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (9)$$

The application of the Freundlich sorption isotherm was

analysed and found not to in agreement as in the case with Langmuir and this can be seen when Figure 1a is compared with the corresponding Figure 1b. Table 1 shows the Langmuir and Freundlich sorption isotherm constants and the correlation coefficients.

Also, Table 1 show that as the concentration of hydrogen peroxide used for the modification of rice hulls increased the sorption capacity also increased which was 2.57, 3.15, 5.15, 8.57, 10.97 and 11.88 mg/g for 0.1, 0.3, 0.6, 0.9, 1.2 and 1.5 M of Hydrogen peroxide solution respectively. 1.5 M Hydrogen modified rice hulls had the maximum adsorption capacity of 11.88 mg/g which can be compared with the maximum lead (Pb) adsorption capacities of Hazelnut shell of adsorption capacity of 1.78 mg/g, Rice Husk of adsorption capacity of 4.0 mg/g and Barley Straw of adsorption capacity of 15.2 mg/g (Conrad and Hansen, 2007).



**Figure 1b.** Freundlich isotherm for  $\text{Pb}^{2+}$  on  $\text{H}_2\text{O}_2$  modified rice hulls.

**Table 1.** Isotherm constants for  $\text{Pb}^{2+}$  ions sorption onto various concentrations of hydrogen peroxide ( $\text{H}_2\text{O}$ ) modified rice hulls.

	0.1 M	0.3 M	0.6 M	0.9 M	1.2 M	1.5 M
<b>Langmuir</b>						
$q_m$ (mg/g)	2.57	3.15	5.15	8.57	10.97	11.88
$K_a$ ( $\text{dm}^3/\text{mg}$ )	-0.0141	-0.0127	-0.0163	-0.0206	-0.0276	-0.0407
$r^2$	0.974	0.986	0.994	0.996	0.998	0.979
<b>Freundlich</b>						
$K_F$ (mg/g)( $\text{dm}^3/\text{mg}$ ) <sup>1/n</sup>	69.17	5212.7	3147.6	66.88	69.36	31.72
$1/n$	-0.508	-1.206	-1.071	-0.550	-0.691	-0.295
$r^2$	0.737	0.979	0.961	0.977	0.942	0.309

**Table 2.** Specific surface areas of Pb<sup>2+</sup> for the various concentration of Hydrogen peroxide modified Rice hulls.

Concentration	q <sub>m</sub> (mg metal/g modified rice hulls)	S (m <sup>2</sup> / g modified rice hulls)
0.1 M H <sub>2</sub> O <sub>2</sub>	2.57	0.416
0.3 M H <sub>2</sub> O <sub>2</sub>	3.15	0.509
0.6 M H <sub>2</sub> O <sub>2</sub>	5.15	0.833
0.9 M H <sub>2</sub> O <sub>2</sub>	8.57	1.390
1.2 M H <sub>2</sub> O <sub>2</sub>	10.97	1.770
1.5 M H <sub>2</sub> O <sub>2</sub>	11.88	1.920

The ultimate sorptive capacity at high concentrations can be used to estimate the specific surface area, S, of hydrogen peroxide modified rice using the following equation and the results are shown in Table 2.

$$S = \frac{q_m N A}{M} \quad (10)$$

Where S is the specific surface area, m<sup>2</sup>/ g modified rice hulls; q<sub>m</sub> is monolayer sorption capacity, gram metal per gram modified rice hulls; N is Avogadro number, 6.02 × 10<sup>23</sup>; A is the cross sectional area of metal ion, m<sup>2</sup> which is 5.56 Å for Pb<sup>2+</sup>; M is molecular weights which is 207 for Pb<sup>2+</sup> (Ho et al., 2002).

The maximum specific surface area of hydrogen peroxide modified rice hulls towards Pb<sup>2+</sup> binding is 1.92 m<sup>2</sup>/g for the rice hulls modified with 1.5 M Hydrogen peroxide.

## Conclusion

Hydrogen peroxide modified rice hulls is able to sorb lead ions from aqueous. Increase in concentrations of Hydrogen peroxide for modification of rice hulls resulted in the metal uptake per unit weight of the sorbent. The experimental results were analysed by using the Langmuir and Freundlich and the correlation coefficients for fitting Langmuir equation was significantly better than the coefficients for the Freundlich equation. Sorption capacity increases with the increase in concentration of Hydrogen peroxide used for the modified rice hulls.

## REFERENCES

Akindahunsi A, Alade OO (2008). Exploiting the potentials of rice husk ash for construction in Nigeria. 2<sup>ND</sup> International Conference On Engineering Research & Development: Innovations. Pp. 1380-1384.

Arayapranee W, Rempel GL (2008). A comparative study of the cure characteristics, processability, mechanical properties, ageing, and morphology of rice husk ash, silica and carbon black filled 75: 25 NR/EPDM blends J. App. Polymer Sci., 109(2): 932-941.

Conrad K, Hansen HCB (2007). Sorption of Zinc and lead on coir. Bioresour. Technol. 98: 89-97.

Da Dosta HM, Visconte LLY, Nunes RCR, Furtado CRG (2002). Mechanical and Dynamic Mechanical properties of Rice Husk Ash-Filled Natural Rubber Compounds, J. Appl. Polym. Sci., 83: 2331-2346.

Freundlich HM (1906). F. u" ber die adsorption in lo"sungen. Zeitschrift fu"r Physikalische Chemie 57: 385-470.

Ho YS, Huang CT, Huang HW (2002). Equilibrium sorption isotherm for metal ions on tree fern. Process Biochem., 37: 1421- 1430.

Ho YS, McKay G (1999). Pseudo-second order model for sorption processes. Process Biochem., 34: 451-465.

Hosseini A, Naghipour D, Shahrokh N (2005). Center for Environmental Research, Department of Environmental Health Engineering, Tehran University of Medical Science Tehran, Iran.

Langmuir I (1916). The constitution and fundamental properties of solids and liquids. J. Am. Chem. Soc.38: 2221-95.

Oboh Ol, Aluyor EO (2008). The removal of heavy metal ions from aqueous solutions using sour sop seeds as biosorbent. Afr. J. Biotechnol., 7(24): 4508-4511.

Okieimen FE, Ojokoh FI, Okieimen CO, Wuana RA (2004). Preparation and evaluation of activated carbon from rice husk and rubber seed shell. Chem. Class. J., 191-196.

Sae-oui P, Rakdee C, Thammathorn P (2002). Use of Rice Husk Ash as Filler in Natural Rubber Vulcanizates: In comparison with Other Commercial Fillers, J. App. Polym. Sci., 83: 2485-2493.

Udonne JD, Aluyor EO (2005). An Assessment of Rice Husk Powder as Fillers in Rubber Compounding, J. Eng. Dev., 6: 178-186.

Ugheoke BI, Joshua MR, Ufodi RN (2008). The effect of processing techniques on the mechanical properties of rice husk polypropylene composite. 2<sup>ND</sup> International Conference on Engineering Research & Development: Innovations. Pp. 286- 291.

www.geroecology.org. (2004). Rice Hull or Husk uses by international Rice Research institute.