www.amlett.com, www.vbripress.com/aml, DOI: 10.5185/amlett.2014.1018 Published online by the VBRI press in 2014

Metal decontamination from chemically modified rice husk film

S. K. Shukla[1]*, Nidhi[1], Sudha[1], Pooja[1], Namrata[1], Charu[1], Akshay[1], Silvi[1], Manisha[1], Rizwana[1], Anand Bharadvaja[1] and G. C. Dubey[2]

[1]*Bhaskaracharya College of Applied Sciences, University of Delhi, Delhi 110075, India*

[2]*Institute of Defense Scientists and Technologists, Dr. S. K. Mazumdar Road, Delhi 110054, India*

[*]Corresponding author. Tel: (+91) 11- 25087597; E-mail: sarojshukla20003@yahoo.co.in

Received: 26 August 2013, Revised: 29 September 2013 and Accepted: 18 October 2013

ABSTRACT

Finely grinded rice husk (RH) has been treated with different alkalis (NaOH, KOH, Na_2CO_3 and KCO_3) and a film was casted from obtained semi liquid product. The effect of various alkalis on physical properties like water absorption, swelling behavior, bulk density husk has been investigated. The morphology and chemical structure were studied by Infrared spectroscopy (FT-IR), Optical microscopy and thermogravimetry (TG) techniques. The results revealed the formation of homogenous film with partial crystalline nature with better thermal stability than RH and approx half bulk density. Further, the developed film was found suitable for metal (Cu(II) and As (III) decontamination from prepared aqueous sample upto 90 and 93 % with removal capacity 2gm per sq cm. Copyright © 2014 VBRI press.

Keywords: Rice husk; derived film; metal decontamination.

S. K. Shukla is currently working as an Assistant Professor at the Polymer Science Department, Bhaskaracharya College of Applied is Sciences, University of Delhi, India. He is born and brought at Gorakhpur, India and earned M.Sc. and Ph.D. degree from the D. D. U. Gorakhpur University, India. He has published and presented more than 50 papers and author of seven contributory chapters in books of International level. He is also recipient national and international awards for his scientific contributions. His major research interests are use of micro-analytical techniques in Chemical analysis, conducting polymers and biopolymers.

Rizwana is working as Associate Professor in Bhaskaracharya college of Applied Sciences, University of Delhi. She has published and presented many research papers in different journals and seminar. She is member of different scientific societies and presently her research interest is designing packaging technology.

Anand Bharadvaja is working as Associate Professor in Bhaskaracharya college of Applied Sciences, University of Delhi and obtained his Ph.D.degree from the University of Delhi. He is teaching Physics to undergraduate students at the Bhaskaracharya College of Applied Sciences, University of Delhi, India. He has many papers in his credit. His current area of research includes the study of conducting polymers, electron scattering using R-matrix approach. He strongly advocates the use of research methodology in education.

Introduction

Rich contents and huge accumulation of agro waste materials has created intensive research interest among the scientists to design and define waste management technology **[1-2]**. Rice husk (RH) is one of the potential agro-waste, available in large quantity in world as a waste from rice milling industries. Its composition is 35% cellulose, 25% hemicellulose, 20% lignin and 17% ash (mainly 94% silica, SiO_2 by weight) **[3-4]**. Further, due to lack of appropriate technology it left unused or simply burnt as a crude source of energy. The advantageous properties of RH are rich chemical contents, renewable nature, low density, nonabrasive properties and reasonable strength and stiffness [**3-5**].

In respond to the needs environmentally friendly composites, efforts has been made to prepare RH based composites with different polymers such as poly (lactic acid), poly butylene succinate (PBS), etc. These composites are finding wider acceptance to be used in automobile, industry, building profile, decking and railing products **[6]**. Kim et al. has prepared the rice husk and polypropylene composite. They investigated the effect of RH content on the thermal stability of thermoplastic polymers **[7-8]**. However, chemical changes in RH properties with chemical treatment has been not been studied as per our observations, while it poses tremendous affects the tensile strength and processibility of polymers **[9]**.

Another, important constituent of RH is silica, which has many potential applications as electronics materials and good adsorbent **[10-11]**. Selected efforts are reported to separate silica as well as to use RH in water purifications **[12]**. However, still RH is not fully commercialized and many as parameters like film forming ability are not reported **[13]**. Therefore, in continuation to our previous report **[2]**, this manuscript presents the development of a thick film after treatment of RH with alkali. The effect of alkali treatment on physic-chemical properties has been correlated with virgin RH. Thus, obtained film was studied for decontamination ability for toxic copper and arsenic metals along with its water adsorption behavior.

Experimental

Material

Rice husk from Kundan rice mill, India, sodium hydroxide, potassium hydroxide, sodium carbonate and potassium carbonate of AR grade from E-Merck were procured and used without any further purification.

Alkali treatment

The known weight of the RH was treated with different alkali solutions: sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3) at 100 ^{0}C individually for 30 min. The obtained solutions were rinsed several times with distilled water, until a neutral pH was observed in the drained water. Drying was carried out by placing the paste like material on a locally prepared glass mould at 120 ^{0}C for 10–12 h and film brown color thick film was obtained.

Chemical and morphological testing

PerkinElmer (RK-1310) FTIR spectrometer by making pellet with dehydrated KBr at 10 ton pressure, and Olympus optical Microscope with 10,000 magnification have been used for analytical purposes. However the Perkin Elmer Thermal (DTG-60) analyzer at heating rate 10 ^{0}C per minutes was used for thermal study.

Swelling studies

The above prepared films were cut into 1 cm X 1 cm square samples and dried at 100 ^{0}C for a period of 6 h to remove the moisture content. The dry weight of each sample was noted initially and immersed in 0.1 M solutions of NaOH. After a fixed time interval of 5 min, the samples were taken out, wiped carefully with filter paper and weighed. All the sample weights were taken in triplicate and their mean is reported. The experiment was continued till there was saturated absorption. The water absorption and expansion in thickness of the specimens were calculated by using eqs. (1) and (2)**[14]** The water absorption and expansion in the thickness were expressed as the mean values of the test results of three specimens, respectively.

$$\Delta m\% = \frac{m_2 - m_1}{m_1} \times 100 ------(1)$$

where m_1 is the mass of the dry specimens before and m_2 is the mass of the specimens after immersed in water.

$$\Delta T\% = \frac{h_2 - h_1}{h_1} \times 100 ------(2)$$

where h_1 is the thickness (mm) of the dry specimens and h_2 is the thickness (mm) of the specimens after water immersion.

Bulk density

The bulk density of film was determined by measuring dimensions and weight of five samples. Weighing was performed by using Shimadzu Corporation, electronic balance with least count 0.1 mg least count. The dimension measurement was conducted by using vernier caliper.

Metal removal capacity

In order to evaluate metal removal ability with above prepared RH film, solution of As(III) and Cu(II) was prepared by dissolving As_2O_3 in 1% NaOH and $CuSO_4$ in distilled water**[15]**. Further this solution was poured in a 100 ml beaker having a layer of RH film. The water was taken at different time (10 min. 20 min. 30 min) intervals by pipette and UV spectra has been recorded in reference to stock metal solution.

Results and discussion

Development of film

Separation and chemical characterizations: The alkali treatment of RH make the sodium salt of cellulose in the form of viscous liquid. The formation of sodium salt of cellulose and separated from other constituents like silica. Further, after neutralization with washing water and dil HCl produces cellulose with modified structure because of re-solidification process and generated cellulose and may be consider as regenerated form of cellulose. The scheme of chemical treatment is given in eqn. (3):

$$\text{Cellulose} \xrightarrow{\text{NaOH}} \text{Cellulose--Na} \xrightarrow{\text{HCl}} \text{Cellulose + NaCl} \quad \text{--------} \ (3)$$

Further, the proportionality of crystalline and amorphous nature is important for processing and other properties [**16**]. The physical appearance and flexibility of all film developed by treatment with different alkali has been checked and found that film developed from NaOH was suitable.

Chemical characterizations of film

The IR spectra of RH and developed film are shown in **Fig. 1**. The spectra is indicating peaks at 893 for C-O-C, β ($1\rightarrow4$) band due to amorphous nature and at 1430 for CH_2 due to crystalline nature in RH **[17]**. The peak intensity of amorphous character is sharply enhanced in developed film than RH, reveals the increment of amorphous character in developed film. The other observed i.r peaks in film are at 2854 cm^{-1} (CH_2) , 1090 cm^{-1} (pyranose ring) and 1265 cm^{-1} (C-O-C aryl-alkyl) and 1645 cm^{-1} (adsorbed water). Further IR peak at 3431 cm^{-1} in RH for hydrogen bonding is showing considerable shift at 3467 cm^{-1} in film due to effect alkalis may be due to hydrolysis **[18-19].**

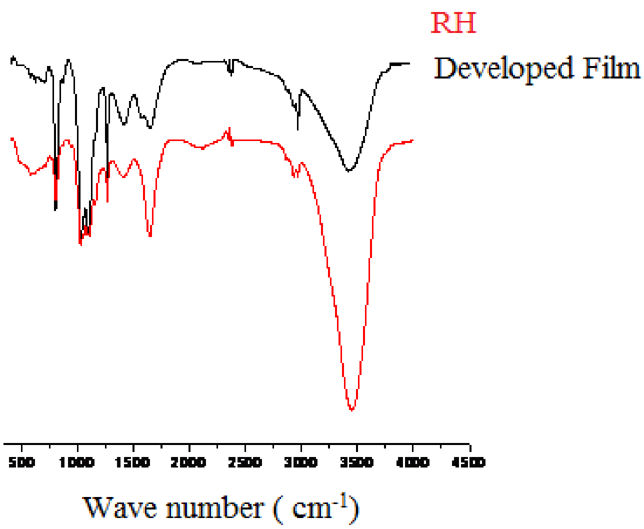

Fig. 1. IR spectra of RH and developed film.

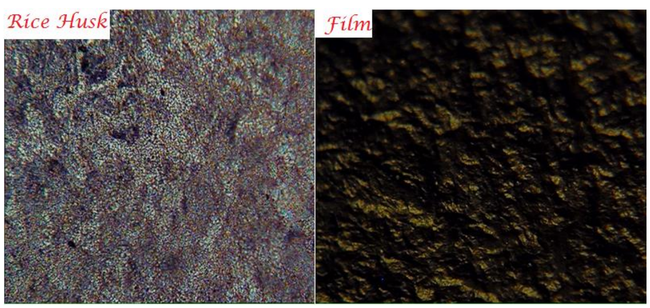

Fig. 2. Optical micrographs of RH and derived film cellulose.

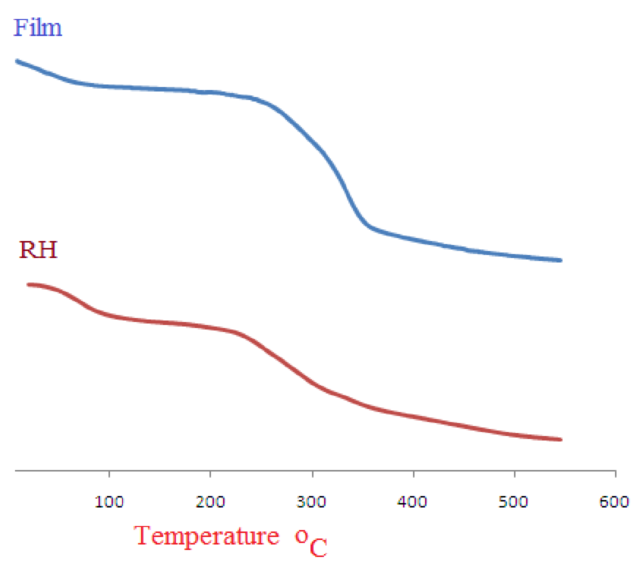

Fig. 3. TG curve of RH and developed film.

The surface photographs of obtained pure RH and cellulose film is shown in **Fig. 2**. The micrograph clearly indicates the compact, non planner structure of obtained film. This kind of film supports the better adsorption process. TG curve of RH and film is shown in **Fig. 3.** TG curve of prepared film is showing weight loss in two steps initially below 133 ^{0}C due to removal water molecules followed decomposition between 200 to 560 ^{0}C due to decomposition. However, develop Film is showing weight lesser below 133 ^{0}C associated with sharp decomposition till 400 ^{0}C with a weight loss 51%.It indicates the chemical treatment softens the matrix along with formation of some sort of linkage between different molecules after removal of silica, which increases stability.

Table 1. Physical properties of RH and derived film.

Properties	RH	Derived Film
Bulk Density	0.479	0.245
Moisture adsorption	153%	118 %
Swelling behavior	37 %	21.2 %

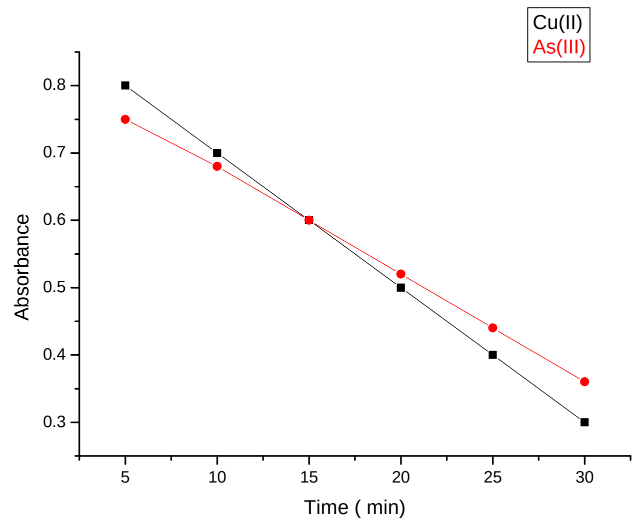

Fig. 4. Cu and As removal capacity of film.

Physical properties

The different observed physical properties are given in **Table 1**. It indicates that the prepared film having lesser bulk density, better flexibility due removal residual metal oxides. However, the compact nature of developed film is responsible for better moisture permeability behavior. These data supports the suitability of developed for different purpose like fabrication of packets.

Metal decontamination

The UV spectra of As (III) and Cu (II) solution recorded at different time interval after treated with developed film. The λmax for Cu(II) and As(III) were observed at 775 and 386 nm respectively. Further, the absorbance of spectra at λ max in continuously decreasing with increase in time. Which is because removal metal content from original solution. Thus, the graph between absorbance at λmax and was plotted with time and same is shown in **Fig. 4**. The graph indicates that prepared RH derived film is an effective sorbent for metal decontamination from water **[15]**. The comparison of maximum and minimum noted absorbance reveals the ~90% removal of As(III) and 93%

Cu(II) from water samples by developed film. . The adsorption capacity of the film for As(III) and Cu(II) is good than the most of unconventional sorbents **[20-21]**. In order to understand the efficiency of film the reduced quantity of metal was divided with area of film the results was found 2 mg per cm^2. Further the regeneration of sheet was evaluated by washing with hot water. We feel that A_S and Cu(II) were adsorbed on SiO_2 surface, due to the porous nature of cellulose present in RH and it also allow better absorption process due to capillary action and more surface area. The material are easy to regenerate and a better water purification method.

Conclusion

A film from RH with a better swelling behavior, thermal stability, and absorption behavior and bulk density has been developed. The obtained film has been used as adsorbent for metal removal because of its low cost, considerable better adsorption capacity. Further film was regenerated very easily by simple washing the film with hot water. The suitable adsorption mechanism for the efficacy of developed film in water decontamination has been also proposed.

Acknowledgements

Authors are thankful to University of Delhi, India for financial support (Innovation project: BCAS:104)**.**

Reference

1. Davis G.; Song J.H. *Industrial Crops and Products* **2006**, 23,147-161.
   DOI: 10.1016/j.indcrop.2005.05.004
2. Shukls, S. K.: Nidhi; Sudha; Pooja; Namrata; Charu; Akshay; Silvi; Manisha; Rizwana; A. Bharadvaja, A.; Dubey, G. C.; Tiwari A. *Adv. Mat. Lett.* **2013**, 4, 714-719.
   DOI: 10.5185/amlett.2013.2415.
3. Singh, A.; Rana R.K. *Adv. Mat. Lett.* **201**0, 1,156-163.
   DOI: 10.5185/amlett.2010.6134
4. Ishak Z. A. M. *eXPRESS Poly. Lett.* **2011**, 5, 569.
   DOI: 10.3144/expresspolymlett.2011.55.
5. Munaf E.; Zein R. *Environment. Technol.***1997**. 18. 359-362.
6. Rozman, H.D.; Yeo, Y.S.; Tay, G.S.; Abubakar. A. *Polym. Testing*, **2003,**22, 617–623.
   DOI: 10.1016/S0142-9418(02)00165-4
7. Kim, H-S. ; Yang, H-S.; Kim H-J.; Par H-J. *J. Therm. Anal. Cal*, **2004**. 76, 395.
   DOI: 10.1023/B:JTAN.0000028020.02657.
8. Rosa, S. M.; Santos E.F.; Ferreira C.A., Nachtigall S.M., *Mater. Res.* **2009**, 2, 533-538.
9. George, J.; Ramana, K.V.; Sabapathy, S.N.; Bawa A.S.., *World J. Microbiol. Biotechnol.* **2005**. 21.1323-1327.
   DOI: 10.1007/s11274-005-3574-0.
10. Sun, L.; Gong, K. *Ind. Eng. Chem. Res.* 2001, 40, 5861-5877.
    DOI: 10.1021/ie010284.
11. Rosa, G.; Gardea-Torresdey J.L.; Peralta-Videa J.R.; Herrera, I.; Contreras ,C.; *Bioresource Technology* 90 (2003) 11–17.
    DOI: 10.1016/S0960-8524(03)00099-3.
12. Kalapathy, U.; Proctor A.; Shultz, J.; *Bioresource Technology* 73 (2000) 257-262.
    PII: S 0 9 6 0 - 8 5 2 4 (9 9) 0 0 1 2 7 - 3.
13. Della, V.P.; Kuhn, I.; Hotza, D.; *Mater. Lett.* **2002,** 57, 818.
    DOI: 10.1016/S0167-577X(02)00879-0.
14. Shukla,S.K.; Deshpande,S.R.; Shukla, S.K.; Tiwari, A.; *Talanta* 2012, 99, 283–287.
    DOI: 10.1016/j.talanta.2012.05.052.
15. Rastogi, R.P.; Singh, N.B., Shukla, S.K.; *Ind. J. Eng. Mater. Sci*, 2011, 18, 390-392
16. Ciolacu , D.; Ciolacu, F.; Popa V.I., *Cellulose. Chem. Technology*, **2011**, 45, 13-21.
17. Moran, J.I., Alvarez, V. A.; Cyras, V.P.; Vazquez A.; *Cellulose*, **2008**, 15 ,149–159.
    DOI: 10.1007/s10570-007-9145-9.
18. Sharma A. K. ; Mishra A. K. ; *Adv. Mat. Lett.* **2010**,1,59-66.
    DOI: 10.5185/amlett.2010.4120.
    Singh, V.; Tiwari, A.; Sanghi, R. *Journal of applied polymer science*, **2005**, *98*, 1652-1662.
    Singh, V.; Tiwari, A.; Pandey, S.; Singh, S.K.; Sanghi, R. *Journal of applied polymer science*, **2007**, *104*, 536-544.
19. Kumar, A.; Negi, Y. S. ; Bhardwaj, N. K.; Choudhary V.; *Adv. Mat. Lett.* **2013,** 4(8), 626-631.
    DOI: 10.5185/amlett.2012.12482.
20. Horsfall, M. J.; Abia A.A.; Spiff A.I. *Afri. J. Biotechnol.* **2003**, 2, 360-364.
    ISSN: 1684–5315.
21. Popuri, S. R. ; Vijaya Y.; Boddu, V. M.; Abburi, K. *Bioresource Technology* **2009**, 100,194–199,
    DOI: 10.1016/j.biortech.2008.05.041.

