ACTIVATED CARBON FROM RICE HUSK
Part-II. Impregnation Ratio, Temperature and Time Influence

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The effect of variation of different parameters *viz*. impregnation ratio, temperature and time on the physical and chemical properties of activated carbons from high and low ash rice husk has been studied and optimum working conditions for their preparation established. Potassium carbonate (K_2CO_3)used as activating agent in low ash rice husk has been found to be effective in creating micro and mesopores, whereas zinc chloride ($ZnCl_2$) has given quite good results in developing macroporosity in high ash rice husk. It has also been found that although surface area of alkali activated products is higher but their yield is low as compared to acid ones.

Key words: Activated carbon, Rice husk, Chemical activation, Activating condtions.

Introduction

The major rice producing countries in the world are India, China, Pakistan and Indonesia [1]. Rice husk and rice bran are obtained during intial and final polishing of rice respectively. The husk or hull presently has meagre industrial uses and this situation demands an extensive R and D effort for economic uitliation of this important agricultural waste. It may benefit a community of irce producing developing countries.

Rice husk (R.H.) has the inherent disadvantage that it itself contains 17–23% of ash [2], which is highly undersiable in exploring its different uses on the basis of cellulosic content. In an ealrier study [3], an appropirate method for deashing rice husk by its alkaline leaching was described and deashing acheived of the order of 1% as in the leached meterial. In this study, a method for obtaining activated carbon from high and low ash R.H. by the mehtod of chemical activation was reported. An appropriate activating agent *viz*. Zinc chloride for high ash and potassium carbonate for low ash rice husk were also selcted among a variety of activating agents used in this tudy. This work has now further been extended and present study describes the influence of other variables like impregnation ratio of these selected activated agents, carbonization temperature and time on different physical and chemical properties of the finished product prepared from this particular raw meterial in its high and low ash form. As a result of this study, appropriate working conditions for obtaining powdered activated carbon from high as well as low ash R.H. have been established.

Materials and Methods

Rice husk was sieved, washed free of foreign meterials, dust etc. and dried to constant weight. Low ash R.H. was prepararcd by leaching high ash husk with 1% sodium hydroxide solution as described earlier [3].

(a) Variation in impregnation ratio. One kilogram of high as well as low ash R.H. were mixed with different percentages of activating agents (A.A.) *viz*. 0.5, 1.0, 1.5, 2.0kg of zinc chloride and potassium carbonate respectively predissolved in 500 ml of water. However, in the case of former, 225g of HCl solution was also added to facilitate the dissolution of zinc chloride. The chemically treated material in each case was dried at 110° for 24 hrs. The dried mass in each set of experiments was carbonized in a S.S. vessel out of contact with air at a temperatures of 550° for 2 hrs [4]. The carbonized materials were than refluxed with 0.1N HCl for 4 hrs, filtered and washed with tap and distilled water to free it from acid and chloride ions respectively and dried to constant weight. Different factors like loss in weight, yield, A.A. recovery and ash content were calculated by the process data [4]. The pore space of each of the sample was calculated by its bulk and true density measurements [5]. The adosrptive capability of these samples were determined against adsorbates of iodine, methylene blue and molasses [6,7]. The surface area of these carbon samples have been calculated by their methylene blue adsorption [8,9] by equation:

$$S = \frac{Xmax}{M} \, N.\sigma$$

where, N = Avogadro's no., M = Mol. wt. of adsorbate, Xmax = Max. uptake value of M.B., σ = 1.35 nm (flat)

On the basis of results obtained in each of the case, I.R. of 100% in high ash R.H. and 50% in low ash R.H. were found to be appropriate and were utilized in latter sets of expriments.

(b) Variation in temperature. In this set of experiments, impregnation ratio selected from previous study *viz*. 100% $ZnCl_2$ for high ash R.H. and 50% K_2CO_3 for low ash R.H. were utilized. The different temperatures used for cabonization

were 450, 550 and 650°. In each of the case, time was kept constant at 2 hrs. The samples were prepared, processsed and evaluated as described in the preceeding paragraph and in the light of the results, the temperature of 550° was found to be appropriate for onward expriments.

(c) Variation in time. In this set, impregnation ratio selected from part (a) and activation temperature selected from (b) for high and low ash R.H. separately have been utilized. However, the time of carbonization was varied as 1,2 and 3 hrs to select an appropriate time for activation. In the light of different physical and chemical properties of the finished samples prepared as described in (a), the time suitable for carbonization of high and low ash R.H. has been found to be 2 and 1 hr. respectively.

Results and Discussions

Three different sets of experiments were performed by variation of I.R. (R), activation temperature (T) and time (t) to establish optimum working conditions required for the preparation of powdered activated carbon from high and low ash R.H. by the method of chemical activation.

Among the different variable studied, it may be seen in Table 1 that increase I.R. of both activating agents (A.A.) geneally increase the percent yield. However,the alkaline A.A. has a lesser yield than acid A.A. It may be due to the reaction of K_2CO_3 with carbon of the raw material [10], also been confirmed by other authors [11]. Furthermore the percent yield in the case of latter is higher as $ZnCl_2$ removes hydrogen as HCl instead of loss of carbon as methane and other hydrocarbons during the process of carbonization [12]. As regards temperature and time, their increase adversely affect the percent yield of the finished product [4]. The activating agent recovery (R.R.) increases with the increase in I.R. of both acid and alkaline A.A. However, this increase in quite prominent in the former. The increase of temperature and time also furtchr affects the R.R. in case of $ZnCl_2$, which may be due to the evaporation effect of this particular A.A.[4]. However, in the case of alkaline A.A. *viz*. K_2CO_3 in low ash R.H. Table 1 shows that recovery in this particular case is comparatively higher than that of $ZnCl_2$, whereas the pattern of R.R. incrrease with the increase in I.R. and its proportional

TABLE 1. DIFFERENT PARAMETERS OBTAINED DURING CHEMICAL ACTIVATION.

Sample code*	Yield (%)	Ash content (%)	True yield** (%)	Reagent recovery (R.R.%)
HR_1	52.4	52.1	25.1	47.1
HR_2	53.0	49.9	26.5	58.3
HR_3	53.8	48.5	27.7	61.2
HR_4	54.0	46.9	28.7	63.0
LR_1	24.0	5.6	22.7	74.0
LR_2	24.6	5.1	23.3	76.2
LR_3	26.0	5.6	24.5	79.0
LR_4	26.9	5.2	25.5	81.1
HR_4T_1	54.0	48.6	27.8	67.5
HR_4T_2	53.8	48.5	27.7	63.0
HR_4T_3	51.0	48.7	26.2	57.5
LR_1T_1	24.5	5.7	23.1	72.0
LR_1T_2	24.0	5.6	22.7	71.5
LR_1T_3	23.6	5.6	22.3	71.3
$HR_4T_2t_1$	54.5	48.3	28.2	67.7
$HR_4T_2t_2$	53.8	48.5	27.7	63.0
$HR_4T_2t_3$	53.0	49.0	27.0	55.2
$LR_1T_2t_1$	25.5	5.3	24.1	79.0
$LR_1T_2t_2$	24.0	5.6	22.7	78.1
$LR_1T_2t_3$	18.0	5.3	17.0	77.8

*H = High ash, L= Low ash, R = I.R., T = Temp., t = Time

**Yield after ash correction.

TABLE 2. PHYSICAL CHARACTERISTICS OF DIFFERENT ACTIVATED CARBON SAMPLES.

Sample code	True density g/c.c.	Bulk density g/c.c.	Pore space per 100g	Surface area by M.B. adsorp. 1000 m^2/g
HR_1	1.2382	0.5942	87.53	446
HR_2	1.0818	0.5214	99.35	561
HR_3	2.0525	0.3573	231.16	563
HR_4	1.9321	0.3471	236.64	565
LR_1	1.7607	0.3572	223.16	1130
LR_2	1.7939	0.2858	294.16	392
LR_3	1.4398	0.2032	422.67	446
LR_4	1.7512	0.1850	483.44	452
HR_4T_1	1.1738	0.4282	148.28	564
HR_4T_2	1.9072	0.3814	210.00	565
HR_4T_3	1.1538	0.4405	140.32	565
LR_1T_1	1.5040	0.3854	192.98	789
LR_1T_2	1.760	70.3572	223.16	1130
LR_1T_3	1.5205	0.3813	196.49	378
$HR_4T_2t_1$	2.1828	0.4113	197.31	567
$HR_4T_2t_2$	1.9072	0.3811	210.00	565
$HR_4T_2t_3$	1.8641	0.3908	202.20	555
$LR_1T_2t_1$	0.8367	0.2855	296.61	1262
$LR_1T_2t_2$	1.7607	0.3572	223.16	1130
$LR_1T_2t_3$	0.7386	0.2830	218.00	1251

TABLE 3. ADSORPTION CHARACTERISTICS OF DIFFERENT ACTIVATED CARBON SAMPLES.

Sample code	Iodine No. (mg/g)	Methylene blue No. (mg/g)	Molasses value
HR_1	548	156.0	254
HR_2	601	196.0	931
HR_3	612	196.8	11066
HR_4	683	197.6	20750
LR_1	1045	395.0	249
LR_2	905	137.0	153
LR_3	811	156.0	140
LR_4	809	158.0	139
HR_4T_1	643	197.0	1745
HR_4T_2	683	197.6	20750
HR_4T_3	655	197.4	10375
LR_1T_1	1030	275.8	108
LR_1T_2	1045	395.0	119
LR_1T_3	821	132.0	104
$HR_4T_2t_1$	710	198.0	2603
$HR_4T_2t_2$	693	197.6	20750
$HR_4T_2t_3$	707	194.0	9600
$LR_1T_2t_1$	1340	441.0	145
$LR_1T_2t_2$	1045	395.0	174
$LR_1T_2t_3$	1310	437.3	131

decrease with the increase in temperature and time is the same described in the case of $ZnCl_2$ for high ash R.H.. Table 1 further shows that only the variable of I.R. of acid A.A. has an influence in reducing the ash content in the finished high ash samples which may be due to the ash reducing action of $ZnCl_2$ [13]. As regards pore space (Table 2), calcualted on the basis of relative densities, it is noted that it increases in either case with increase in I.R. The effect of change in temperature in both these cases is indentical and maximum pore space is developed at temperature of 550° and it initially increases and then decreases both in high and low ash samples. As far as the effect of variation in time on ultimate pore space of the finished samples is concerned. Table 2 shows that in high ash carbons maximum pore space is developed in 2 hrs time, whereas in low ash samples, 1 hr activation time is sufficient in creating maximum pore space. The surface area of these carbons has also been calculated on the basis of M.B. adsorption and it shows that only the alkali activated carbons at 550° have surface area more than 1000 m²/g. An overview of Table 2 further reveals that pore space developed in alkali activated carbons is comparatively higher than that of acid ones.

The effect of change in working conditions on the adsorptive properties of the resultant samples is quite prominent

(Table 3). In the case of iodine no., correlated with pores <10Å [14], increase in I.R. of acid A.A. in high ash R.H. increases the micropores. This rate of increase is however nominal whereas in low ash R.H. increase in I.R. of alkaline A.A. decreases the micropores. The effect of change in temperature on iodine no. like I. R. is identical in both the cases and maximum iodine adsroptive capacity is developed at a temperature of 550°. The effect of time in low and high ash carbons however not pronounced, clearly shows that activation time of 1 hr is quite sufficient in creating optimum microporosity. In mesopores (>15 Å), determined by M.B. adsorption, optimum activity is attained at an I.R. of 100% in high ash [15], whereas comparative lower I.R. of 50% is quite effective in creating optimum mesopores in low ash R.H.. The effect of change in temperature in developing transitional pores is not prominent in high ash carbons. However, in low ash, temperature of 550° has been found to be quite appropriate. As regards time, like microporosity, 1 hr time has been found to be quite sufficient in both the instances. In high ash carbons, molasses value (correlated with pores>28Å) increases with the increase in I.R. specially at higher I.R., whereas in low ash, alkaline A.A. has proven to be quite incapable of creating sufficient macropores space [3]. With refernce to temperature, maximum activity against large molecular species, however, nominal in low ash carbons, is obtained at a temperature of 550°. The effect of time on macropores is quite prominent in high contrary to that of low ash samples. However, in both the cases, samples obtained after crbonization time of 2 hrs have given maximum activity against molasses.

As a result of this part of study, appropriate working condtions have been established, which are 100% I.R., 550° temperature, 2 hrs time for high ash R.H. carbons and 25% I.R., 550° temperature, 1 hr. time for low ash R.H. carbons.

Conclusion

1. Alkaline activating agent (K_2CO_3) has been found to be effective in creating micro and mesopores, whereas acid activating agent ($ZnCl_2$) has given quite good results in developing macroporosity.

2. Low ash rice husk carbons, activated at a temperature of 550° by alkaline activating agent, have surface area more than 1000 m²/g as caculated by their methylene blue adsorption.

3. The yield in case of alkali activated products is comparatively low as compared to that of acid ones.

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