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ACTIVATED CARBON FROM RICE HUSK
Part - I. Activating Agent Selection

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The effect of different acidic and alkaline activating agents on the physical and chemical properties of activated carbons from high and low ash rice husk has been studied. The optimum deashing of rice husk was acheieved by leaching it with 1% sodium hydroxide solution. It was also observed that recovery in case of alkaline activating agents was comparatively better. It has further been noted that acidic and alkaline activating agents contribute best in developing micro and macro pores respectively. Among the different activating agents studied, zinc chloride has shown better results for high ash and potassium carbonate for low ash rice husk carbons.

Key words: Activated carbon, Rice husk, Activating agents, Ash content, Adsorptive properties.

Introduction

Rice is a major agricutural crop of Pakistan and paddy is grown to the tune of 4.1438 milion tons per annum [1] mainly in the provinces of Punjab and Sindh. The husk or hull accounts for about 20-23% of the whole rice [2]. Henceforth an approximate amount of 0.8288 million tons of rice husk is available in the country. It is rough in texture and abrasive in nature. It is not suitable for animal feed due to its low nutritive value. Because of its high ash and ligning contents, it is considered unsuitable for pulp and paper indsutry. Presently it only finds use as a fuel for brick kilns, chicken litter and animal roughage. The rest of the amount is presently being merely wasted and any large scale industrial use of this commodity is need of the hour.

In an earlier study [3], low ash acitvated carbon from rice husk was prepared by alkaline leaching of silica in high ash carbon obtained by low temperature pyrolysis in an inert atmosphere. This study has now further been extended and the avenue of 'chemical activation' has been explored to select an appropriate activating agent for high as well as low ash rice husk. A series of activating agents [4], both acidic and alkaline like zinc chloride, phosphoric acid, sodium carbonate and potassium carbonate have been used to study their effects on this particular raw material and henceforth being reflected in different physical and chemical properties of the finished product. As a result of this study, an appropriate activating agent has been selected for the preparation of activated carbon from high and low ash rice husk separately.

Experimental

Rice husk from a husking mill in the province of Sindh was collected, sieved and washed to free it from dirt and foreign materials. It was dried in an oven at 105° to a constant weight and refluxed with different concentrations of sodium hydroxide solution ranging from 0.1 to 7.5% for 4hrs. The leached material was then filtercrd on a buchner funnel and washed thoroughly with distilled water to neutral pH and then dried to a constant weight. The detailed chemical analysis of the original as well as each of the leached rice husk sample has been carried out and percentage yield of deashed husk established.

One kg of high as well as low ash rice husk (W_1) was mixed with 250 g (W_2) of zinc chloride, phosphoric acid, sodium carbonate and potassium carbonate dissolved in 700 ml of water in separate sets of experiments. However, in the case of zinc chloride treatment, water was premixed with 225g of hydrochloric acid. The chemically treated material in each case was dried in an oven at 110° for 24 hrs and carbonized in a S.S.vessel out of contact with air at a temperature of 700° for 2 hrs. Blank experiments without chemical treatment were also run under the same conditions. The carbonized material (W_3) was then refluxed with 0.1N HCl for 4 hrs, filtered, washed first with tap water to methyl red yellow (pH 6.3) and then finally with distilled water to free it from chloride ions and dried at 110° (W_4). The loss in weight, yield and activating agent recovery was calculated with the help of data generated during the process [5]. The ash, bulk and true density of these samples were determined by standard methods [6] and pore space per 100 g was there after calculated [7]. The iodine, methylene blue and molasses values of these samples were also determined [8,9]. The surface area of pores greater than 10, 15 and 28 Å contributing in iodine, methylene blue and mollasses adsorption respectively have been calculated [10,11].

Results and Discussion

The present study descirbes the influence of different activating agents on various physical and chemical properties of activated carbons prepared from high and low ash rice husk [12].

Table 1 describes the chemical analysis of the original as well as samples deashed with various concentrations of sodium hydroxide. It shows that ash and lignin reducing action of alkali is negligible initially and then increases rapidly. These approach to their minimum level at 1.25% alkali concentration., with a pattern of negligible decrease afterwards (Fig. 1). It also shows the drastically altering cellulose contents of leached R.H. with an increase in the percentage of alkali, attaining a maximum value of 72.51% at 1.25% concentration. Its furhter increase, however, has no pronounced effect on α-cellulose. Table 1 also gives the yield of different deashed R.H. samples and it shows a regular decrease with the increase in alkali concentration. In the light of chemical analysis of leached R.H. samples, it is evident that optimum deashing has been achieved at 1% NaOH concentration, which has been selected and being used in further studies.

Table 2 depicts different observations during the course of chemical activation with different activating agents. It shows that inthe case of activated carbons prepared from high and low ash R.H., the lowest loss in weight and henceforth highest yield is obtained in $ZnCl_2$, whereas activating agent recovery is on the lower side in both the cases, which may be due to its volatile nature [4]. It may also be noted here that for alkaline activating agents *viz.* Na_2CO_3 and K_2CO_3, % recovery is far higher (49-73%) than those of acidic ones (13-33%), contrary to that of yiled, which is comparatively lower in the case of former. As far as ash is concerned, $ZnCl_2$ has the highest ash reducing action, whereas K_2CO_3 also has a good ash reducing property only second to $ZnCl_2$.

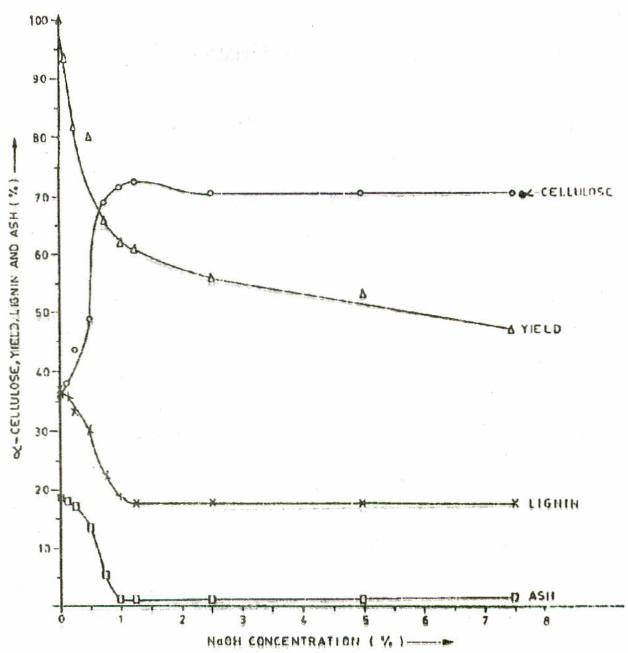

Fig. 1. Effect of NaOH conc. on α-cellulose, yield, lignin and ash contents of rice husk.

Table 3 describes different adsorption characteristics of activated carbons prepared from high as well as low ash R.H. It shows that highest acitivity in high ash carbons is obtained in $ZnCl_2$ activated sample (A_1), whereas low ash R.H. shows an entirely different behaviour and overall highest acitivity is

TABLE 1. CHEMICAL ANALYSIS AND YIELD OF ORIGINAL AND ALKALI LEACHED RICE HUSK.

S. No.	Sample code	NaOH (%)	Yield (%)	α-Cellulose(%)	Lignin (%)	Ash (%)	Extractive(%)	Pentosans(%)
1	A	0.00	100.0	35.88	36.38	18.90	1.16	21.21
2	B	0.10	94.0	38.01	35.90	18.04	1.09	22.35
3	C	0.25	82.0	43.66	33.14	17.26	0.98	23.02
4	D	0.50	80.0	48.81	30.26	13.75	0.73	23.97
5	E	0.75	66.0	69.05	22.46	5.57	0.65	24.25
6	F	1.0	62.0	71.75	18.69	1.25	0.58	24.67
7	G	1.25	61.0	72.51	17.51	1.23	0.52	25.50
8	H	2.5	56.0	70.25	17.35	1.22	0.33	24.62
9	I	5.0	53.4	70.45	17.25	1.22	0.34	24.00
10	J	7.5	47.2	70.07	17.24	1.21	0.37	24.23

TABLE 2. STUDIES ON VARIOUS PARAMETERS OBTAINED DURING CHEMICAL ACTIVATION WITH DIFFERENT ACTIVATING AGENTS.

S. No.	Sample code	Activating agent	Loss in weight(%)	Yield (%)	Activating agent recovery(%)	Ash (%)
1	A_1	Zinc chloride	55.0	45.0	33.2	37.34
2	A_2	- do -	60.5	39.5	14.0	4.35
3	B_1	Phosphoric acid	66.2	43.8	31.2	43.31
4	B_2	- do -	66.5	33.5	12.8	7.91
5	C_1	Sodium carbonate	66.2	33.8	48.8	41.42
6	C_2	- do -	68.7	31.3	62.8	8.02
7	D_1	Potassium carbonate	67.3	32.7	69.2	38.52
8	D_2	- do -	74.0	26.0	73.2	7.25
9	R_1	Nil	63.0	37.0	–	43.67
10	R_2	Nil	72.0	28.0	–	8.00

TABLE 3. ADSORPTION CHARACTERISTICS OF DIFFERENT ACTIVATED CARBON SAMPLES.

S. No.	Sample code	Iodine No. (mg/g)	Methylene blue No.(mg/g)	Molasses No. (mg/g)
1	A_1	391	48	83
2	A_2	478	18	106
3	B_1	106	8	68
4	B_2	335	10	80
5	C_1	69	8	121
6	C_2	29	7	112
7	D_1	103	9	162
8	D_2	621	38	165
9	R_1	117	4	70
10	R_2	52	2	72

TABLE 4. PHYSICAL CHARACTERISTICS OF DIFFERENT ACTIVATED CARBON SAMPLES.

S. No.	Sample code	True density (g/c.c)	Bulk density (g/c.c)	Pore space (per 100g)	Surface area of pores>10Å (m^2/g)	Surface area of pores>15Å (m^2/g)	Surface area of pores>25Å (m^2/g)
1	A_1	2.51	0.8167	82.60	349	137	40
2	A_2	2.55	0.6942	105.27	431	51	51
3	B_1	1.89	0.8262	68.13	83	23	33
4	B_2	2.00	0.7669	80.39	297	29	38
5	C_1	1.52	0.5694	109.83	48	23	58
6	C_2	1.43	0.5688	105.88	11	20	54
7	D_1	2.07	0.4763	161.64	80	26	78
8	D_2	1.68	0.4454	165.00	564	109	79
9	R_1	1.82	0.8002	70.02	93	11	34
10	R_2	1.67	0.7554	72.50	14	6	7

obtained in D_2-K_2CO_3 activated sample. The reason for this may be that, silica of high ash R.H. is further activated by the acid of the former resulting in its enhanced activity. Furthermore, in high ash R.H., appreciable amount of K_2CO_3 is utilized in its reaction with silica and henceforth results in poor activity which is not the case in low ash R.H. It has also been observed that samples activated with K_2CO_3 *viz.* D_1 and D_2 had a foamed appearance lacking mechanical resistance [13].

Table 4 shows different physical characteristics like true and bulk densities and thereafter pore space per 100 g of different samples prepared from high and low ash R.H. It also shows the surface area of pores greater than 10 Å (micropores), 15 Å (mesopores) and 28 Å (macropores), which gives a true picture of adsorptive capacities of these activated carbons towards the molecular species of iodine, methylene blue and molasses respectively [14]. It may be seen here that maximum pore space in high ash carbons is developed in sample D_1 with maximum macropore capacity. However, as far as micro and mesopores are concerned, sample A_1 is far better than B_1,C_1, and D_1. In low ash carbons, rather a clear picture emerges and sample D_2 with highest pore space (165 cc/100 g), has overall the most balanced micro, meso and macropore capacity, further confirmed by its better activity against iodine methylene blue and molasses as compared to other samples (Table 3).

A review of Tables 3 and 4 further shows that alkaline activating agents have a prominent effect in developing the macropores of these carbons, whereas in the case of acid activating agents, the contribution towards micropore is considerable. In unactivated carbon samples R_1 and R_2, the pore space is almost equal but the activity of R_1 (high ash) is slightly better than R_2 (low ash), which may be due to the higher prercentage of ash (43.67%) present in the former contributing towards its enhanced activity [15].

Conclusion

Rice husk may profitably be exploited as a potential raw material for activated carbon.

Zinc chloride and potassium carbonate are appropriate activating agents for obtaining active carbons from high and low ash rice husk respectively.

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