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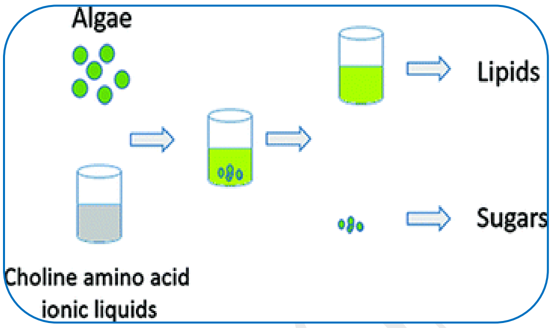
CLARIFICATION OF SUGAR SOLUTION USING IONIC LIQUID TREATED BIOMASS



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ABSTRACT:

The color removal of raw sugar is important step of sugar manufacturing. In addition to current methods of color removal, our objective is to provide alternative, better and more efficient method for the removal of unwanted color, turbidity and suspended solids. As cationic polymers are used as good decolorizing agents, attempts have been made by grafting laboratory made cationic liquids on certain plant residues such as rice husk, and passing the raw sugar solution through the beds of this grafted rice husk. Rice husk was chemically treated to delignify and then it was stirred with Cationic Imidazole and Pyridine ionic liquids for fixing the ionic liquids to the rice husk. Scanning electron microscopy (SEM) was used to measure the porous structure of rice husk after delignification and after grafting the ionic liquid. The decolorization done by phosphotation followed by the grafted rice husk was around 95%. It was better than an combination with ion exchange which is 90%. The decolorization shown by PAC and GAC is very poor comparativelywhich shows that adsorption process fails to decolorize sugar solutions with a high degree of efficiency. .This treated rice husk was used for the removal of color from raw sugar by varying its concentration from 0.25 to 1 gm in 50 cc of 50 brix solution for 30 min. The maximum color removal was in range of 90 % using only 1 gm of the treated rice husk. During decolorization there was no change in the polarization of melt. As these cationic liquids contain N, CHN (carbon, hydrogen, nitrogen) analysis of untreated and treated sugar solutions with grafted rice husk was done to check for cationic liquid leakage and N present in the solution was found to be absent. Thus this method doesn't involve the use of any direct addition of chemicals to the melt as in traditional methods and is eco-friendly and just involved the use of biomass which is readily available, cheap, and economically attractive.

KEYWORDS*: color removal , cationic liquids , sugar manufacturing.*

INTRODUCTION :

The challenge of raw sugar production is to produce marketable raw sugar of consistency high sugar recovery by the removal of color, turbidity and suspended solids from aqueous solutions. Refining processes such as affinationfollowed by carbonation/phosphotation remove significant amounts of color.An additional color removal step is needed ahead of the final crystallization stage to ensure that the white sugar product always meets the product color specification. The additional color removal process is almost always adsorbent based, using bone charcoal, powdered carbon, granular carbon or ion exchange resins.

Granular Activated Carbons (GACs) used in water, wastewater treatment and sugar decolorization are largely derived from bituminous coal which is non renewable. The versatility of coal based carbons can be seen in their ability to remove toxic organic compounds from industrial and municipal wastewater and potable water. The long term availability of coal and its long term environmental impact and potentially increased cost has prompted researchers to consider renewable resources such as agricultural by-products and food wastes as alternative feedstocks. Various types of low cost adsorbents suggesting the application of sawdust and orange peels for the water and wastewater treatment have been reviewed [1].

Rice straw based GACs have been evaluated for their ability to decolorize sugar or remove metals and low molecular weight organic compounds from solution [2,3]. There have been studies in using sugarcane bagasse for the removal of sugar colorants. GAC's have been developed for the removal of colorants found in raw sugar with bagasse based carbons without employing a binder [4,5]. While binders like sugarcane molasses, sugar beet molasses and corn syrup for making activated carbon for sugar decolorization have been employed [6]. Surface modified bagasse was also used to remove colorants and metals from water.Based on these concepts, rice hulls carbon have been investigated for sugar decolorization[7].

Most refinery regard color as most important raw sugar quality parameter as the removal of color is key function of a refinery and is high cost procedure regardless of method employed. In effective processing, having knowledge of total color and nature of colorants and distribution of colorant between the syrup film and the crystal is of utmost importance.

Color in the raw sugar is not a simple compound but a heterogeneous complex mixture. The key plant pigments may be low molecular weights (MW< 1000) and Indicator Value (IV) between 5 to 40 as they are highly ionized at high pH, in the form of flavonoids, chlorophyll and phenolic compounds which supply around 30 percent of the entire raw sugar colorants and usually removed in the refinery. Phenolics may react with amines or iron to produce more highly colored compound. Besides there are intermediate MW colorants i.e. ADP with MW 1000-2500 and IV(3-5) and polymeric colorants like caremels and melanoidinswhich are high molecular weight factory produced colorants with MW > 2500 and IV (1-2) which are responsible for about 70% of the raw sugar color [7] . These colorants are considerably harder to remove as they persist during the refining process and exhibit preferential inclusion into the growing sugar crystals

Dedini DRD process includes syrup clarification by phosphotation followed by ion exchange [8] giving 52% decolorization. SAT process has been used which involves the addition of polyamines which are cationic polymers followed by Ultrafiltration to produce sugar with color ranging from 80 – 200 IU, besides reducing scale formation by 75% and increase in pan capacity by 30% [9].Development in Membrane Technology have been such as to cope up with the demanding requirements of a sugar mill viz. the ability to handle high temperatures varying suspended solids characteristics while still achieving good separations at high flux rates and reasonable cost ceramic, stainless steel and polymeric membranes are used. High temperature around 90^{o}C is used to ensure that no microbiological loss or fouling occurs. An average color removal of 14% occurs from clear juice using ultra filtration. However commercial applications have been hindered because of the benefits of crystallized sugar quality have not out weighed the increased processing costsassociated with membrane applications[10]. Cationic polymers, which have a strongly basic centre coupled with long hydrocarbon chain have be used to pull out the anionic colorants by electrostatic attraction followed by their precipitation due to the long hydrocarbon chain. They are being used as decolorizing agents in the sugar industry[11].Laboratory synthesized cationic surfactants are being used for the removal of dyes from the effluents[12-14].As cationic polymers are being used in the sugar industry it was thought of fixing a cationic polymer on to the bed of rice husk and treating the solution with it for sugardecolorization.

2. MATERIALS AND METHODS

Rice husk was brought from a local rice mill. The two Cationic Gemini Pyridine and Imadazole based cationic liquids(CL) were synthesized in our laboratory as per the method [13-17]. Ionic liquids are characterized by its tendency to absorb at surfaces and interfaces. They have been used successfully for removal of synthetic dyes from waste waters and hence they have been tried as potential adsorbents for removal of raw sugar color. Raw sugar was brought from Chadha Sugar Mills, Kiri Afghana and it had the following characteristics given in Table 1 and their scheme of preparation of the

Cationic liquids is given in Figure 1. The cationic liquids are basically surfactants which have a hydrophilic head with the N of the Imadazole of the pyridine ring holding a positive chargeand a hydrocarbon chain and physically exist as liquids.The process has been carried out by treating the raw sugar melt to phosphotation followed by passing it through the beds of grafted rice husk or GAC, PAC or Cationic and Anionic Resins.

Table 1 Raw Sugar parameters

S. No.	RAW SUGAR	Value
1	Brix	99.80
2	Pol	96-97
3	Purity	94-95
4	Colour	400-600 IU

Figure. I Scheme for the preparation of the Cationic Ionic Liquids

Where X = Cl, Br and R = $CH_3(CH_2)_4$, $CH_3CHCH_3(CH_2)_2$

Imadazole Based Cationic Ionic Liquids

R = CH_3, CH_3CH_2

Pyridine Based Cationic Liquid

2.2 Treatment of the Rice husk

30 g rice husk was ground to pass through 20 mesh screen. It was refluxed at 40 ^{0}C with 2 N NaOHsolution in 2 litre flask for 4 to 5 hours. Then it was repeatedly washed with distilled water to get a clear solution. The material was dried and refluxed with 0.1 N H_2SO4acid. The treated rice husk was washed with distilled water 5 times and then kept overnight in the oven for drying at 60 ^{0}C. After drying 20 g of the treated rice husk was taken and was fixed with cationic ionic liquids (1 g) one at a time by stirring for 4 hours. This ratio of 20 :1 biomass: cationic liquid was standardized by using both higher and lower amount of CL per 20 g biomass and this ratio was found to be the best. After fixing the rice husk, it was washed with distilled water so as to remove the excess of the ionic liquid ascertained by conductivity measurements. It was dried over night at 60 ^{0}C

2.3 Method of determining color.

A 50 Bx raw sugar solution was prepared, and 50 ml solutions were used for decolorization. The sugar solution was treated with the given amount of treated rice husk for 30 minutes by stirring using magnetic stirrer at 20 ^{0}C. The color of the initial sugar solution and decolorized sugar solution were determined using standard ICUMSA method GS1/3-7(2005). (This ICUMSA method includes filtration as part of the color measurement.) The percent of sugar decolorization was calculated using the following expression,

$$\% \text{ of color removed} = \frac{\text{IU (initial)} - \text{IU (after treatment)}}{\text{IU (initial)}} \times 100$$

3. RESULTS AND DISCUSSION

a) Sugar Decolorization

Phosphatation was carried out on the prepared solution of raw sugar melt by treating it with 2g/100 ml CaO and neutralizing it with phosphoric acid to a pH of 7.2. This solution was further treated with Powdered Activated Carbon (PAC), Granular Activated Carbon (GAC), Ion Exchange Resinsand graftedrice husk to check the efficiencies of the methods adopted by the industry vis a vis the new method. . The process was carried out in two ways. In one procedure the raw sugar solution was passed through beds of 1.5 cm approx 2g and 2.5 cm approx 3.5 g in a funnel.The results are given in Table 3, 4 and in the second procedure different amounts of grafted rice husk (1-2.5 g) was stirred in the solution for variable time of 15 mins to one hour. The results are reported in Table 5. The CHN analysis of sugar solutions treated with ionic liquid treated rice husk was done to check the percentages of carbon, hydrogen and nitrogen in the raw sugar solution for checking the leakage of ionic liquid residue from treated rice husk to raw sugar solution. The results are given in Table 6. It can be seen that the initial percentage of nitrogen in raw sugar solution was nil and after treating it with ionic liquid treated rice husk the percentage of nitrogen remained zero in the solution. This confirms that nitrogen group which was present on the grafted rice husk doesn't leak into the raw sugar solution. The treatments were also carried out with PAC, GAC, Ion Exchange as these are the normal treatments been done by the industry for decolorization and the different process efficiencies have been determined. All the results have been represented by PI charts to show effective treatments for different processes. i.e. Figs. 1 &2 for PAC treatments, Figs. 3&4 for GAC treatments, Fig. 5 for Ion Exchange, Figs. 6 &7 for imidazole based cationic liquid grafted rice husk bed and Figs 8 & 9 for pyridinebased cationic liquid grafted bed.

It can be seen from Figs. 1,2,3& 4 that phosphotation removed approx 50% of the color. Even after two passes through the beds of PAC and GAC about 33 to 34% of the color still remains. However maximum color removal is done in the first pass. The results in Figure 5 obtained following decolorization with ion exchange resins are much better with 14% color removal by cation exchange and 11% removal by anion exchange, with still 25% of the color remaining. Figures 5,6,7,8 show that for treatment with Imadazole and Pyridine grafted rice husk are the best as the color remaining is hardly about 12 %.especially with Imadazole based grafted rice husk and for 1.5 cm l bed in case of pyridine based grafted rice husk. As colorants are anionic in nature they have been pulled out from the solution by electrostatic attraction, the process being instantaneous. The Maximum decolorization was about 88 % by stirring 1 gm rice husk with 50 ml raw sugar solution for 30 min. But the decolorization decreased with the increase of adsorbent dose, although it should have increased. This may be due to the fact that the sites overlap and the time is short for effective decolorization.

b) Adsorbent Surface Chemistry

Rice husk: Rice husk was treated with sodium hydroxide to remove the hemicelluloses which opens up the internal structure of biomassand increases the surface porosity and adsorption capacity. Moreover it also helps in the removal of the natural color of rice husk. The increase in porosity was confirmed through the SEM images of rice husk before & after treatment. This is elucidated through the SEM images of rice husk in Figure 1.1 and 1.2

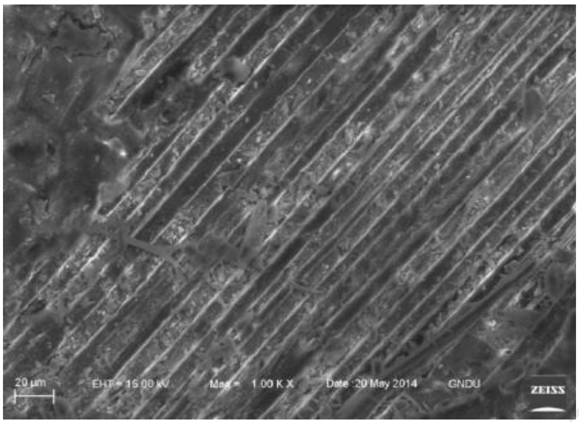


Figure 1.1 SEM of Rice husk

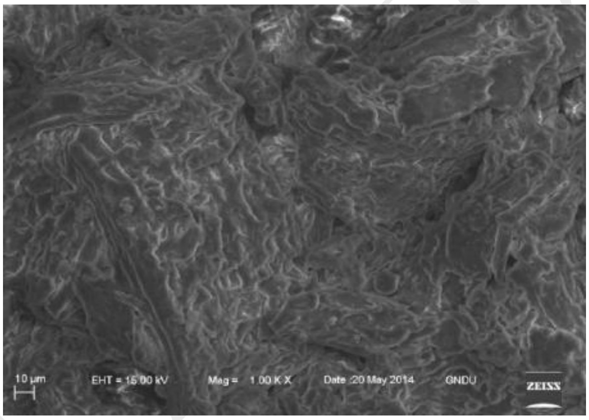


Figure 1.2 SEM of alkali treated Rice husk

The adsorption capacity of rice husk was enhanced using cationic liquids as it introduces more extractive sites on delignified rice husk. The morphology of the treated rice husk is shown in the SEM image in Figure 1.3.

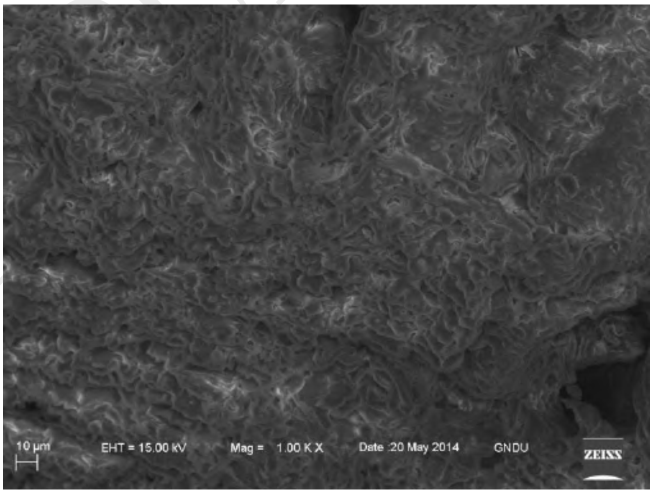


Figure 1.3 SEM of rice husk treated with ionic liquid (pyridine), which resulted in the increased porosity

Table 2 Decolorization Results by PAC & GAC

Original raw sugar sample(brix 49.15)	Colour	% Decolorization
Initial Color	563	
Phosphatation	280	50
PAC-1st stage (1.5 cm bed)	221	61
PAC-2nd stage (1.5 cm bed)	188	67
PAC-1st stage (2.5 cm bed)	227	60
PAC-2nd stage (2.5 cm bed)	191	66
GAC-1st stage (1.5 cm bed)	210	7
GAC-2nd stage (1.5 cm bed)	178	22
GAC-1st stage (2.5 cm bed)	219	4
GAC-2nd stage (2.5 cm bed)	185	19

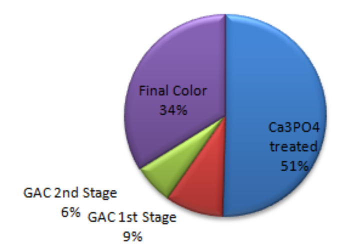


Fig.1 Color Removal Profile-PAC (2.5 cm bed)

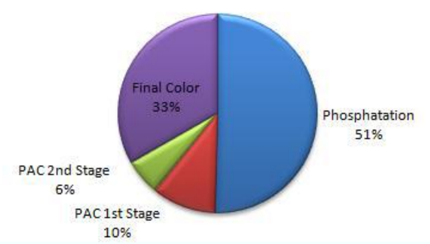


Fig.2 Color Removal Profile-PAC (1.5 cm bed)

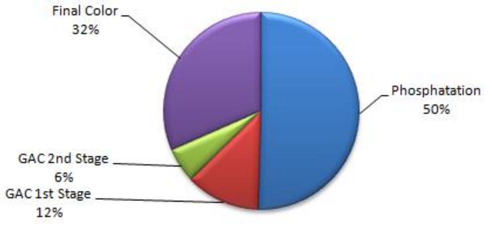


Fig.3 Color Removal profile-GAC (1.5 cm bed)

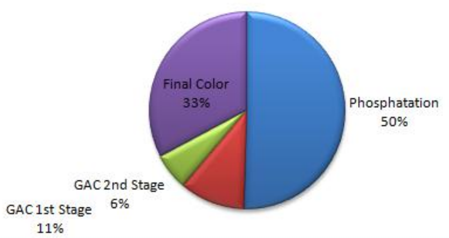


Fig.4 Color Removal profile-GAC (2.5 cm bed)

Table 3Decolorization Results by Ion Exchange & Imidazole Treated Rice Husk

Initial Color	563	
Phosphatation	280	50
Cation exchange	171	70
Anion axchange	65	88
Imidazole treated Rice Husk- 1st Stage (1.5 cm bed)	61	89
Imidazole treated Rice Husk- 2nd Stage (1.5 cm bed)	54	90
Imidazole treated Rice Husk- 1st Stage (2.5 cm bed)	80.5	86
Imidazole treated Rice Husk- 2nd Stage (2.5 cm bed)	54	90

Fig.5 Color Removal Profile-Ion Exchange

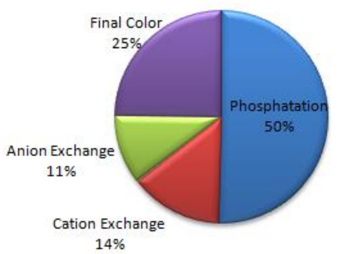


Fig.6 Color Removal Profile-Imidazole treated Rice Husk (1.5 cm bed)

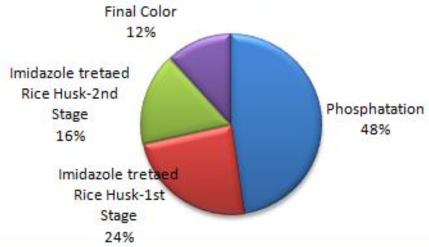


Fig.7 Color Removal Profile-Imidazole treated Rice Husk (2.5 cm bed)

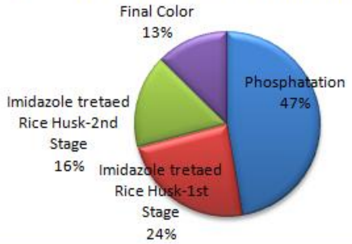
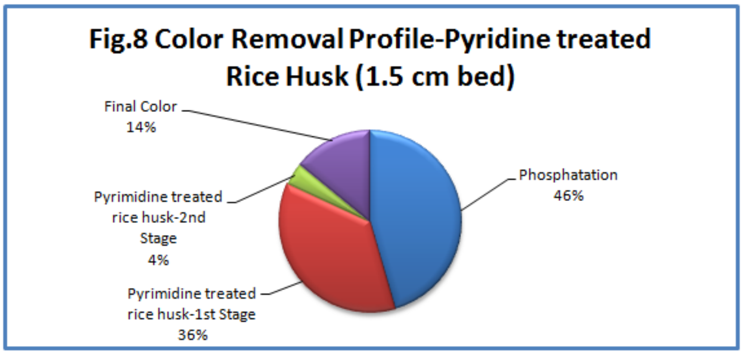
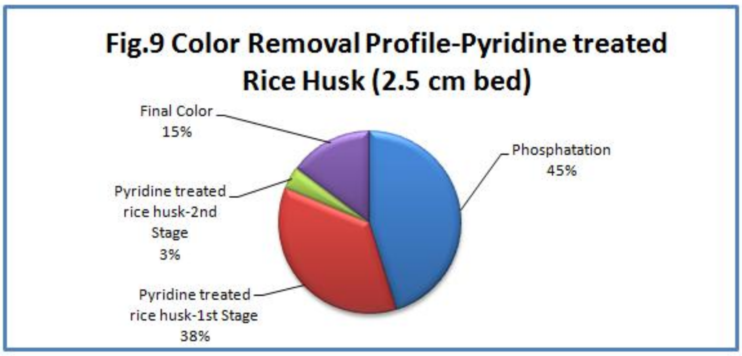


Table 4 Decolorization Results by Pyridine treated rice husk

Original raw sugar sample(brix 49.15)	Colour	% Decolorization
	563	
Ca3Po4 treated	275	51
Pyridine treated Rice Husk-1st stage (1.5 cm bed)	45.15	92
Pyridine treated Rice Husk-2nd stage (1.5 cm bed)	36.12	94
Pyridine treated Rice Husk-1st stage (2.5 cm bed)	83.23	85
Pyridine treated Rice Husk-2nd stage (2.5 cm bed)	67.12	88





To study the effect of high adsorbent dose as a function of time, the experiment were run using 1to 2.5 g adsorbent dose at various intervals of time by stirring it in the as shown in Table 5.

Table 5 Effect of adsorbent dose as a function of time

Quantity		Stirring (15 min)		Stirring(30 min)		Stirring(60 min)	
		Colour	RDS	Colour	RDS	Colour	RDS
1	1 gm	53.6	46.2	51.8	46.2	49.7	45.9
2	1.5gm	57	46.2	50.4	46.2	49.8	46.0
3	2.5gm	67	46.2	55.0	46.2	50.1	46.1

Table 6 CHN results of Rice husk treated raw sugar solution

Sample	Nitrogen%	Carbon%	Hydrogen%	Sulphur%
Before treatment	0.00	11.62	10.21	0.00
After treatment	0.00	10.91	10.17	0.00

It was observed that optimum de-colorization was at the time interval of 30mins without any reduction in RDS. 60 mins interval consequently resulted in the reduction of RDS. This lead to the conclusion that a balance of time and quantity of rice husk used is necessary to carry out the decolorization of sugar solution.

c) Regeneration

Reuse of ionic liquid treated rice husk was checked using treated rice husk for re use of raw sugar solution again and again. It was found that upto fifth pass there was no significant decline in color removal efficiency of the treated biomass. Sixth pass onwards color removal efficiency showed a negative trend. Hence, it is confirmed that color removal of upto two cycles can be achieved by one dose of treated biomass.

Table 7 Reuse of treated biomass

S.no.	Colour(IU)
First Pass	93
Second Pass	89
Third Pass	94
Fourth Pass	94
Fifth Pass	95
Sixth Pass	110
Seventh Pass	121

CONCLUSION

The chemically treated adsorbents are successful in removing the color from raw sugar solutions.This technique of color removal doesn't involve the direct addition of ionic liquid into the raw sugar solution otherwise it would have resulted in the increase of non sugars in the solution. This method employed the color removal through solid state electrostatic attraction. The brix of the sugar solution was maintained at 50 bx for the ease of experimental procedure and to minimize the effects of increased viscosity at 64-65 bx.

The optimum dose of imidazole treated rice husk for color removal is 1 gm for 50ml solution which resulted in the removal of 93 %color approximately. Also the experiments on resuse of treated rice husk show that color removal of upto five cycles can be achieved by one dose of treated biomass.

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