

# Decolourizing of Distillery Spent Wash Using Indigenously Prepared Cation Exchanger from the Agricultural Waste (Wheat Straw)

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## Abstract

During the last few decades, management of waste and its control has become one of the most critical environmental problems. Distillery spent wash have very high value of chemical oxygen demand (COD), low pH, high organic matter, suspended solids and dissolved solids. Containing nitrogen, high potassium along with obnoxious odour and dark colour. Cation exchanger prepared from wheat straw is used to decolourize the distillery spent wash (batch study). The average exchange capacity of the H<sup>+</sup> form of sulphonated wheat straw is found to be 1.89 meq/gm. The reduction in colour of distillery spent wash with indigenously prepared cation exchanger from wheat straw observed by varying the amount of cation exchanger (1-6g), contact time, agitation, dilution and particle size. The maximum % decolourization (50.25%) observed after (12hrs) at pH (4.4) with fine cation exchanger (5g) from wheat straw. Decolourization and % reduction in biological oxygen demand (BOD) (30.27), chemical oxygen demand (COD) (43.35), and total dissolved solids (TDS) (39.12) by cation exchange of wheat straw seems to be effective low cost method.

**Keywords:** *Sulphonated Wheat Straw (S.W.S.); cation exchanger; exchange capacity; physico-chemical properties*

## 1. Introduction

Water requirement to meet agriculture, domestic, industrial and other uses indicate that there is need

for regeneration of waste water. Several methods have been used for the removal of various contaminants from the surface water and wastewater from various industries. Various naturally occurring substances like clay [Wiegner 1931 – Grim, 1942], coal [Mittal et. al., 1989; Lafferty et. al., 1990; Kosaka 1952; Kunin 1958], wood [Lisovo et. al., 1986] and stones are used as water softener. Naturally occurring aluminium silicates [Bacon 1936] called zeolites act as an ion exchanger is used for the purification of water. Ion exchangers are large molecular weight insoluble polyelectrolytes having cross linked structure which contains ionic groups. Ion exchangers can be produced from synthetic materials like inorganic aluminosilicates, condensation products of phenol and formaldehyde and from cellulose materials like paper, wood, coffee leaves, rice husk and wheat straw can provide us a suitable alternate to treat various industrial effluent [Nawar et. al., 1989 – Mckay et. al. 1999]. Wheat straw is abundantly available in India, therefore the conversion of wheat straw i.e. an agricultural waste into cation exchanger and exploring the possibility of its use in water softening and effluent treatment is a meaningful proposition.

The distillery spent wash has high value of BOD, COD, low pH, high organic matter, high acidity, dark colour and high percentage of inorganic matter [Satyawati et. al., 2008]. In India, each distillery industry generates about 15L spent wash an extremely large volume with foul odour and dark

colour for one liter of alcohol generated [Chakrabarti 1980]. According to the data of All India Distilleries Association, about 1.6 million kiloliters of alcohol are produced per year by 309 distilleries in India [Chakrabarti 1980]. Effluent derived from the distilleries can provoke serious environmental impact in the neighbouring water bodies. Apart from the high organic content, distillery waste water also contains nutrient in the form of N, P & K that can lead to eutrophication of water bodies, however its dark colour hinders photosynthesis by blocking sunlight and is therefore affects the aquatic life [Krishna et. al., 2011]. Patil and Kapadnis used hydrogen peroxide, calcium oxide and soil bacteria to remove BOD and colour from distillery waste [Patil et. al., 1995]. Repin and Skvortsov recommended anaerobic bacteria and aerobic treatment of spent wash, followed by physico-chemical method for colour removal [Repin et al., 1995]. Gokarn, Oswal and Sankpal studied the use of Moringa-oleifera drumstick seeds for removing colour from distillery spent wash previously treated by anaerobic and aerobic means [Gokarn et. al., 1999]. Another attempt at colour removal by electrochemical means was done at laboratory scale by Sankpal, Dongare and Gokarn, Mahajani and Dhale used wet air oxidation to treat distillery spent wash to reduce COD as well as colour [Sankpal et. al., 1999-Dhale et. al., 2001]. Colour removal and COD reduction from spent wash was tried by Ramteke, Wate & Moghewith the help of pyrochar prepared from waste sludge of paper mills [Ramteke et. al., 1989]. Reduction of BOD, COD, and colour removed from diluted distillery spent wash by cation exchanger from wheat straw is an effective low cost method. Therefore, attempt has been made to treat distillery spent wash by indigenously prepared cation-exchanger from wheat straw before discharging into water bodies or on land. The aim of the present work was to study the absorption capacity of cation exchangers for colour removal from diluted distillery spent wash under different experimental conditions.

## 2. Material and Methods

### 2.1. Preparation of S.W.S. cation exchanger

The cation exchanger has been prepared after treating the wheat straw with  $C_2H_5OH$  to remove any alcohol soluble gradient. Then sulphonation with  $H_2SO_4$  of the wheat straw was done to obtain the sulphonated wheat straw (S.W.S.H<sup>+</sup>). The powdered material obtained was then washed with glass distilled water.

Then dried in the open air and dried product was graded and screened with mesh sieve of different porosity. The cation exchanger formed was then subjected to various studies viz. moisture content, ash content, volatile matter, carbon, hydrogen, sulphur, nitrogen, oxygen and exchange capacity (Table 1-2).

### 1.2. Treatment of distillery spent wash with newly formed cation exchanger from wheat straw

Distillery spent was collected from the distillery industry. Various physico-chemical parameters i.e. pH, acidity, free CO<sub>2</sub>, chloride content, DO, BOD, COD, EC, hardness & total solids were determined by standard methods after dilution (1:100) at 25°C for the assessment of pollution load [APHA 2012]. Chromatographic column (65×250 mm) was packed with S.W.S.H<sup>+</sup> (5g) and diluted spent wash (1:100) was passed through the column by controlling the flow rate (9-10 drops/min). The status of the diluted spent wash after passing through column was analyzed by following same parameter. All the chemicals used were of analytical grade double distilled water was used for all experimental work. All parameters were done in duplicate.

### 2.3 Decolourization assay

Decolorizing activity was expressed in terms of the % decolorization by the modified method described previously [Ho et. al., 2000]. Decolourization of distillery spent wash was determined by monitoring of decrease in absorbance at the maximum wavelength ( $\lambda_{max} = 350nm$ ) of each spent wash. A scanning spectrophotometer (double beam EI-1372) was used for absorbance measurement and recording of visible absorption spectra.

Decolourization activity was calculated as follows:

Decolourization (%) = [(Initial absorbance) – (Observed absorbance) / (Initial absorbance)] × 100. All assays were done in duplicate. All the colour removal experiments were carried out by agitating (150 rpm) the S.W.S.H<sup>+</sup> or without agitation with (100 ml) diluted spent wash at pH 4.4 and 25°C. Samples were centrifuged and the supernatant solution was analyzed for residual colour concentration. Effect of contact time (0, 2hrs, 4hrs, 24hrs, 48hrs, 72hrs, 96hrs, and 120hrs) on decolourization of diluted distillery spent wash (1:100) using (S.W.S.H<sup>+</sup>) (1g, 2g, 4g, & 6g) without

agitation was observed. Effect of amount of (S.W.S.H<sup>+</sup>) on decolourization of diluted distillery spent wash (1:100) at constant time (12hrs) and with constant agitation was observed. Effect of dilution (1:100, 5:100, and 10:100) with contact time (1hr, 2hrs, 4hrs, 6hrs, 8hrs, 12hrs, and 24hrs) on % decolourization of distillery spent wash using (S.W.S.H<sup>+</sup>) (4g) was observed. Effect of particle size (fine, medium & coarse) on decolourization of diluted distillery spent wash (1:100) using (S.W.S.H<sup>+</sup>) (4g) was observed.

### 3. Results and Discussion

Distillery spent wash is one of the most obnoxious waste and it has a high BOD, COD, dissolved solids and low pH. In view of the highly polluted nature of spent wash, different methods have been performed to treat the waste water of distillery. Conversion of wheat straw into cation exchanger is an indigenous approach for making use of agricultural waste for the tertiary treatment of distillery spent wash. Treatment of diluted distillery spent wash with H<sup>+</sup> form of S.W.S. is to reduce acidity, BOD, COD, EC, total solids, hardness, and decolourization etc. to such an extent that it can be used for irrigation after dilution (Table 3). The ability of the H<sup>+</sup> form of S.W.S. for decolourization of distillery spent wash was analyzed.

#### 3.1 Effect of contact time

At different time interval (0, 2hrs, 4hrs, 24hrs, 48hrs, 72hrs, 96hrs and 120hrs) an varying the amount (1g, 2g, 4g and 6g) without agitation. The maximum % decolourization was observed with 6g of (S.W.S.H<sup>+</sup>) after (96hrs) of contact time (36.88%) (Fig 1)

#### 3.2 Effect of amount

The effect of varying amount of S.W.S.H<sup>+</sup> (1g, 2g, 3g, 4g, 5g, 6g) on decolourization of distillery spent wash increases with increasing the amount of

(S.W.S.H<sup>+</sup>) and maximum increase is with (5g) (S.W.S.H<sup>+</sup>). After (5g) of (S.W.S.H<sup>+</sup>) it remains constant with increasing amount of (S.W.S.H<sup>+</sup>). Maximum % decolourization is (50.25%) with (5g) (Fig 2)

#### 3.3 Effect of dilution ratio

From contact time data, it has been revealed that initial decolourization after (1hr) of agitation is slow in all dilution (1:100, 5:100, 10:100) of distillery spent wash and the amount of decolourization increases with increase in contact time up to 12 hrs of agitation. Maximum % decolourization (49.48) is observed in (1:100) dilution spent wash. The graph of absorbance vs. time indicates the amount % decolourization increases with increase dilution ratio of the distillery spent wash (Fig 3). Similar observation was also indicated by other worker [Gong et. al., 2005].

#### 3.4 Effect of particle size (fine, medium and coarse form)

The experimental data obtained indicates that as particle size decreases (coarse, medium & fine) form of (S.W.S.H<sup>+</sup>) the % decolourization increases (27.46, 33.67 & 49.48). The relatively higher % decolourization increases with fine particle of S.W.S.H<sup>+</sup> after (12hrs) of agitation due to the fact that smaller particle yield higher surface area and hence greater maximum % decolourization takes place (Fig 4). Therefore, cation exchanger from agriculture waste i.e. wheat straw can be effectively used for the decolourization of distillery spent wash which can be used for irrigation after proper dilution. It can be easily regenerated by dipping them in (0.1dN) HCl for (24hrs). There is no storage problem. It will also solve the problem of disposal of agriculture waste as well as pollution effect of distillery spent wash on soil as well as in various water bodies.

Table 1: Proximate and ultimate analysis of SWSH<sup>+</sup>

Proximate analysis (as received basis)	% by mass	Ultimate analysis (on dry basis)	% by mass
a. Moisture content	9.78	a. Ash	4.15
b. Ash content	3.74	b. Carbon	42.98
c. Volatile matter	67.77	c. Hydrogen	6.09
d. Fixed carbon (by diff.)	18.71	d. Sulphur	Less than 0.01
		e. Nitrogen	0.43
		f. Oxygen	Remainder

Table 2: Physical Parameters of Different forms of SWS

S. No.	S.W.S. forms	Exchange capacity (meq/gm)	% of Moisture	% of Ash (out of 1 gm)
1.	H <sup>+</sup>	1.896	11.00	6
2.	Na <sup>+</sup>	4.201	10.04	11
3.	K <sup>+</sup>	4.175	14.00	9
4.	Ca <sup>2+</sup>	4.141	9.00	10
5.	Mg <sup>2+</sup>	4.094	15.00	9

Table 3: Physico-chemical parameters of Untreated and Treated effluent with SWSH<sup>+</sup>

S.No.	Parameters	Untreated effluent	Treated effluent with S.W.S. H <sup>+</sup>	% Reduction with S.W.S.H <sup>+</sup>
1.	pH	4.4	5.59	21.28
2.	Acidity methyl orange	5900	2900	50.84
3.	Acidity phenolphthalein	11400	9400	17.54
4.	Free CO <sub>2</sub>	5016	3136	37.48
5.	Chloride Content	3408	3124	37.67
6.	Dissolved oxygen (DO)	Zero	2.2	----
7.	Biological oxygen demand (BOD)	15000	10459	30.27
8.	Chemical oxygen demand (COD)	114400	64800	43.35
9.	Electrical Conductivity (EC)	0.33	0.20	33.33
10.	Total Hardness	12200	4814	60.54
11.	Permanent Hardness	6542	3404	47.96
12.	Temporary Hardness	5140	1410	72.56
13.	Total Solids	85,000	52000	38.82
14.	Dissolved Solids	80,160	48800	39.12
15.	Suspended Solids	4840	3200	33.88

\* All the values in table are in ppm except pH & conductivity (mS/cm).

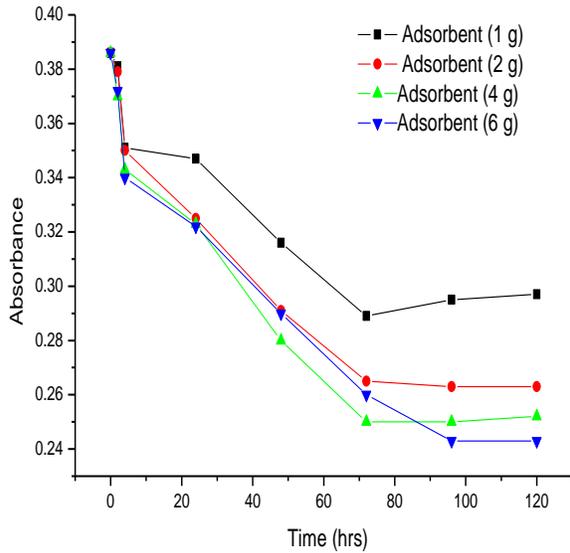


Fig 1: Effect of Amount of SWSH<sup>+</sup> on Absorbance Vs Time

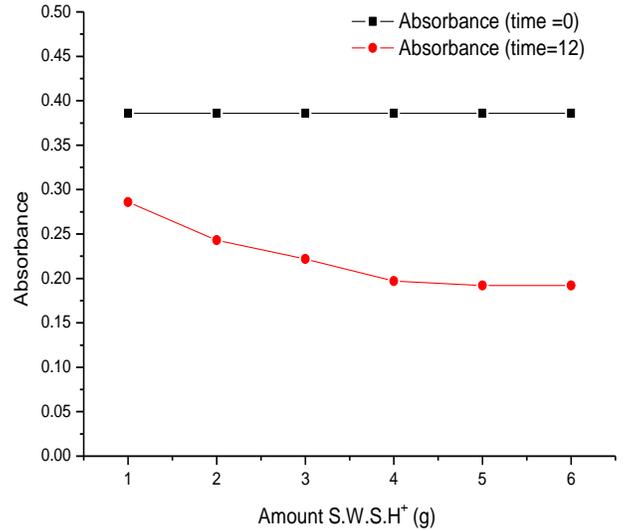


Fig 2: Effect of Effluent contact time with Adsorbent of SWSH<sup>+</sup> on Absorbance Vs Amount of SWSH<sup>+</sup>

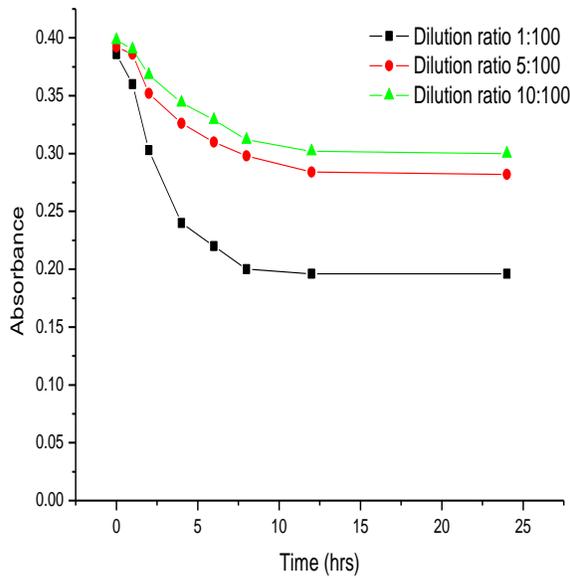


Fig 3: Effect of Dilution Ratio on Adsorbance Vs Time

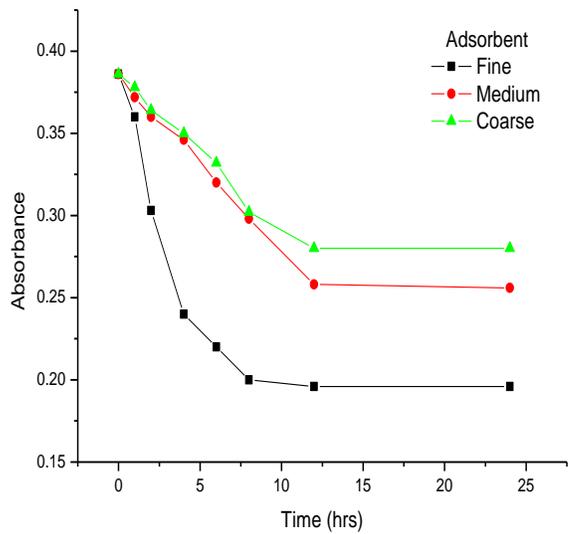


Fig 4: Effect of Adsorbent size on Adsorbance Vs Time

#### 4. Conclusion

The results of the present studies shows that the cation exchanger from agriculture waste i.e. wheat straw can be effectively used for decolourization of distillery spent wash in the diluted form. The complete decolourization can be achieved by using an appropriate amount of cation exchanger and time of agitation. Wheat straw is an agricultural waste material abundantly available in India at negligible rate. Therefore  $H^+$  form of S.W.S. is economical biodegradable and eco-friendly alternative for removal of colour and reduction of BOD, COD, and total dissolved solids from distillery spent wash.

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