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Pretreatment of the Distillery Spent Wash by Cation Exchangers prepared from the Agricultural Waste (Wheat Straw)

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ABSTRACT

During the last few decades, management for waste and its control has become one of the most critical environment problems. Distillery spent wash may be used as potential fertilizer for growing many crops after proper treatment. Conversion of wheat straw into cation exchanger is an indigenous approach for making use of agricultural waste for the production of cation exchanger. The cation exchangers from wheat straw can reduced the pollution load of distillery spent wash to such an extent that it can be successfully used for irrigation purpose or may be drained into various water bodies. The average value of exchange capacity of H^+ form of cation exchange from wheat straw is found to be 1.896 meq/gm. There is considerable reduction in various physico-chemical parameters such as pH, conductivity, total solids, acidity, total hardness, chloride content, BOD, COD, DO and metal ions Cu, Cr, Cd, Mn and Zn. This is suited for irrigation in Haryana.

Keywords: Sulphonation, erythrocyte homolyzates, physico-chemical, electrolytes.

INTRODUCTION

Today, the problem of adequate water supply for power generation, domestic and industrial purpose has become so acute in many areas of the world that several governments, individually or through UNESCO of the United Nations are studying the possible utilization of ion exchanger for sea water desalination, water softening and recovery of the water from sewage and industrial disposals. Keeping in view the chemist and manufacturing engineers have realized the importance of preparing new ion exchanger from industrial chemicals, agricultural wastes and other wastes. During the last few decades, management for waste and its control has become one of the most critical environmental problems. The process of removal of toxic chemicals is definitely a challenging task before Environmental Scientist and Engineer's. Various naturally occurring substances like clay, sand, coal, wood and stone are used as softening of water.[1-3]

Ion exchangers are large molecules water insoluble poly-electrolytes having a cross-linked structure which contains ionic groups. Ion exchangers can be produced from synthetic materials like inorganic alumino silicates, condensation products of phenol and formaldehyde and from cellular based substances like coffee lees, lignin, paper wood, natural brown coal etc. by sulphonation or oxidative treatment with nitric acid and phosphoric acid under different conditions. The ion exchanger from cellulose material can provide a suitable alternative, especially in India, being an agricultural country. Wheat straw is abundantly available in India and is presently being mainly used as cattle feed. Currently these agricultural wastes are being used as fuels but have very low calorific value and smokes of these wastes are disturbing our eco system. Therefore proper management of these wastes is a dire necessity. The conversion of wheat straw into cation exchanger and exploring the possibility of its use in water softening and effluent treatment is a meaningful proposition.

The process of alcohol production from molasses generally produces 8-15 liters of spent wash for every liter of alcohol generated in India. With 329 distilleries together produce 3.2 billion liters of alcohol per annum and spent wash is around 30-40 billions liters. These liquid is dark brown in color and has an unacceptable odour. The higher soluble salts contribute higher COD (80,000-120,000 mg/lt.) and suspended solids, especially organic solids contributes higher BOD values, making it unsuitable for direct disposal on land.[4-7] The Central Pollution Control Board (CPCB) in India has listed this industry among the 14 most polluting industries. Therefore, attempt has been made to treat the effluent of distillery spent wash by indigenously prepared cation exchanger from wheat straw before discharging into water bodies or on land. Disposal of distillery spent wash without any treatment will responsible for soil pollution and under ground water pollution.

Historical view

A significant development in the history of ion exchanger goes to the credit of Way and Thompson et.al, 1850 who found that water soluble fertilizer salt such as ammonium sulphate and potassium chloride which could not be easily leached out from the soil by the action of rain water which could be removed by ion exchanger.[8] In the years 1850-1854 Way reported the results of his extensive study of the phenomenon before the Royal Society of London. Way's work is extensively continued by Sestini et.al., 1873.[9] The ion exchange study of Gans in 1909 and 1913 were probably the first attempt to utilize ion exchanger for industrial purposes.[10] Adams and Holmes 1947 observed that certain synthetic resins are capable of exchanging ions. A pioneering work of Adams and Holmes was followed by D'Alelio in 1945 in the United State of America.[11] All current industrial and laboratory application of ion exchangers are based on such resins. Piontkovskaya et.al., 1972 prepared on alumino zeolite ion exchange resin for removing potassium ion from erythrocyte homolyzates.[12] Tatsuo, 1974 prepared ion exchange resin by the sulphonation of thermally plasticized anthracite which can be used for water softening.[13] Christopher, 1990 has found that the low rank brown coal used as an ion exchanger material.[14] At present a considerable quantity of material of the sulphonated coal type is being produced in the United State of America and Europe. Tokyo organic chemical industries limited has prepared activated carbon based ion exchanger. Brazilian coal (anthracite, lignites and peats) has been used for making cation exchangers by sulphonation under various conditions and may be used for water purification. A method for manufacturing of ion exchange from wool waste and feathers was presented by Wanda et.al, 1984.[15] The German sulphonic acid cation exchanger, Wotatit K is prepared from benzaldehyde 2-4 disulphonic acid and formaldehyde. There is much other type of sulphonic acid exchangers. Haagen,[16] Kosaka,[17] Oda[18] et.al, 1948–1953, Inaba, 1950.[19] Myers 1987 had discovered cation exchanger from isoprene polystyrene with H_2SO_4, $ClSO_3H$ as sulphonating agents.[20]

Apart from the synthetic materials cation exchanger can be produced from cellulose based substances like rice husk,[21] lignin, paper and wood etc. by sulphonation or by oxidative treatment with variety of oxidizing agents under different conditions.

MATERIALS AND METHODS

i. Preparation of Cation Exchangers from Wheat Straw.

Cation exchanger from wheat straw has been prepared by sulphonation with concentrated sulphuric acid under various conditions. The decomposition and introduction of sulphonic groups have been confirmed by analytical studies. The sulphonated product is washed and filtered. The filteration of the product was followed until the filterate was free from sulphonate ions. The washed product was dried in the open air and then analyzed.

ii. Preparation of Different Forms of Cation Exchanger from Wheat Straw.

The different forms of cation exchanger have been prepared. The pure hydrogen form of sulphonated wheat straw (S.W.S.) was prepared by passing HCl of constant boiling point, under a reflux condenser. The sodium form of S.W.S. was obtained maintaining a portion of the fine H^+ form of S.W.S. in contact with a large excess of saturated NaCl solution for 24 hours. After over night, the resin was washed with ordinary water and then with distilled water, until the resin was free from excess chloride and sodium ions. Drying of washed product was carried out in open air and analyzed. Magnesium, Calcium and Potassium form of S.W.S. were also prepared by the same method as in the case of alkali metal form by using their respective saturated salt solutions.

iii. Studies of Fundamental Properties of Cation–Exchanger.

The proximate analysis of wheat straw for moisture content, ash content, volatile matter, fixed carbon and ultimate analysis like ash, carbon, hydrogen, sulphur, nitrogen and oxygen have been got analyzed. The percentage for all the parameters have been determined and summarized in (table – 1).

Table-1- Proximate and ultimate analysis of wheat straw

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

The various physico-chemical properties of the cation exchangers formed were studied by following the standards methods. Density, ash content, moisture content, exchange capacity had been undertaken for different form of cation exchangers shown in (table – 2-5).

Table-2 Density of swollen fine H^+ form of S.W.S.

Solvent	Amount of SWS	Time of contact	Density
Water	1gm	10 min	0.8748
	1gm	24 hour	0.9167
	1gm	48 hour	0.9527
	1gm	72 hour	0.9934
	1gm	96 hour	1.0510
Benzene	1gm	10 min	1.2420
	1gm	24 hour	1.2675
	1gm	48 hour	1.2946
	1gm	72 hour	1.3180
	1gm	96 hour	1.3446
Acetone	1gm	10 min	1.1258
	1gm	24 hour	1.1538
	1gm	48 hour	1.1825
	1gm	72 hour	1.2105
	1gm	96 hour	1.2384

Table-3 Moisture Content of S.W.S. forms

S.No.	Cation – Exchanger	% of Moisture
1.	H^+	11.00
2.	Na^+	10.04
3.	K^+	14.00
4.	Ca^{2+}	9.00
5.	Mg^{2+}	15.00
6.	Wheat Straw	9.09

Table-4 Ash Content of S.W.S. forms.

S.No.	Cation – Exchanger	% of Ash (out of 1 gm)
1.	H^+	6
2.	Na^+	11
3.	K^+	9
4.	Ca^{2+}	10
5.	Mg^{2+}	9
6.	Wheat Straw	10

Table-5 Ion–exchange capacity of S.W.S. forms.

S.No.	Form	Exchange capacity (meq/gm)
1.	H^+	1.896
2.	Na^+	4.201
3.	K^+	4.175
4	Ca^{2+}	4.141
5.	Mg^{2+}	4.094

The results obtained were compared with the synthetic cation exchangers available in the market. The various factors affecting the exchange had also been undertaken. The factors like effect of particle size, effects of concentration of electrolytes on exchange, effect of solvents and effect of flow had been studied shown in (table – 6-9). Cost of the newly formed cation exchanger, its storage conditions and regeneration were also studied and compared with the already available cation exchangers.

(Table - 6) Effect of particle size on the exchange of S.W.S.

S.No.	Size	pH before	pH after	Decrease in the value of pH
1	Fine	8.0	5.4	2.6
2	Medium	8.0	6.0	2.0
3	Coarse	8.0	6.2	1.8

Table -7 Effect of electrolyte on the exchange of S.W.S., Monovalent salt NaCl.

S.No.	% solution	pH before	pH after	Decrease in the value of pH
1.	0.25	7.4	3.5	3.9
2.	0.5	7.4	3.6	3.8
3.	1	7.2	3.6	3.6
4.	2	7.2	3.6	3.6
5.	3	7.0	3.6	3.6
6.	5	6.9	3.6	3.3
7.	8	6.8	3.8	3.0
8.	10	6.4	3.5	2.9

Table -8 Effect of solvent on the exchange of H^+ form S.W.S.

S.No.	Solvent	pH before	pH after	Decrease in the value of pH
1.	Water	7.2	3.8	3.4
2.	Ethanol	7.2	4.2	3.0
3.	Acetone	7.2	4.8	2.4
4.	Chloroform	7.2	5.6	1.6
5.	Benzene	7.2	6.2	1.0
6.	Carbontetrachloride	7.2	6.6	0.6
7.	Hexane	7.2	6.9	0.3

Table - 9 Effect of flow on the exchange of S.W.S.

S.No.	Time (in sec.)	Volume of electrolyte	pH before	pH after	Decrease in the value of pH	% reduction
1.	155	20 ml	8.0	5.5	2.5	31.25
2.	330	20 ml	8.0	5.0	3.0	37.50
3.	500	20 ml	8.0	4.8	3.2	40.00
4.	615	20 ml	8.0	4.7	3.3	41.25
5.	900	20 ml	8.0	4.7	3.3	41.25
6.	1200	20 ml	8.0	4.7	3.3	41.25

iv. Pretreatment of Distillery Spent Wash with newly formed Cation Exchanger.

Distillery mill spent wash is dark brown color and has unacceptable odour. Due to presence of higher amount of soluble salts its COD level is very high. Due to presence of suspended solids, especially organic substances contribute higher BOD levels. Analysis of the spent wash indicates the presence of many nutrients including both major and minor nutrients. Discharged of untreated waste water of distillery will therefore create serious water pollution problems and toxicity to the aquatic life.

Various physico-chemical parameters of distillery mill spent wash were determined for the assessment of its pollution load. Chromatography columns were packed with newly formed cation exchanger from wheat straw and diluted spent wash of distillery mill was passed through these exchangers. The status of spent wash after passing through the exchanger was again determined in terms of same physico-chemical parameters.

The following parameters were studied by following the standard methods[22] pH, conductivity, total solids, dissolved solids, suspended solids, acidity (methyl orange, phenolphthalein), free carbon-dioxide, total hardness, permanent hardness, temporary hardness, chloride content, BOD, COD, DO and metals ion like Cu, Cr, Cd, Mn and Zn shown in (Table-10).

Table -10 Treatment of Distillery Effluent with H^+ form S.W.S.

S. No.	Parameters	Untreated Effluent	Treated Effluent With S.W.S.	% age with S.W.S.
1.	pH	3.97	3.59	9.57
2.	Acidity methyl orange	5900	2900	50.84
3.	Acidity phenolphthalein	11400	9400	17.54
4.	Free CO_2	50160	41360	17.54
5.	Chloride Content	3408	3124	8.33
6.	D.O.	Zero	0.22	----
7.	B.O.D.	15000	12459	16.94
8	C.O.D.	114400	84800	25.87
9.	Conductivity	0.33	0.26	21.21
10.	Total Hardness	12222	4814	60.61
11.	Permanent Hardness	6542	4444	32.06
12.	Temporary Hardness	5140	370	92.80
13.	Total Solids	85,000	62000	27.05
14.	Dissolved Solids	82,160	58800	28.43
15.	Suspended Solids	3240	3200	1.23
16	Metal ions			
a.	Cr^{2+}	366	266	27.32
b.	Cu^{2+}	40.7	20.1	50.61
c.	Cd^{2+}	2456	2419	1.50
d.	Mn^{2+}	1748	1721	1.54
e.	Zn^{2+}	1020	880	13.72

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

RESULTS AND DISCUSSION

Spent wash is a potential fertilizer containing most essential plant nutrient elements in liquid. The liquid is dark brown color having higher soluble salts which makes it unsuitable for direct disposal on land. Conversion of wheat straw into cation exchanger is an indigenous approach for making use of agricultural waste for the production of cation exchangers.

The average value of exchange capacity of H^+ forms of cation exchanger from wheat straw was found to be 1.896 meq/gm. It has been observed that the spent wash of distillery mill when treated with the cation exchanger from wheat straw show considerable reduction in various physico-chemical parameters such as pH, conductance, total solids, dissolved solids, suspended solids, acidity (methyl orange, phenolphthalein), free carbon-dioxide, total hardness, permanent hardness, temporary hardness, chloride content, BOD, COD, DO and metals ion like Cu, Cr, Cd, Mn and Zn.

The cation exchangers from wheat straw can reduced the pollution load of distillery spent wash to such an extent that it can be successfully used for irrigation purposes or may be drained into various water bodies. Spent wash is available at free of cost. Pre-treatment of the spent wash with cation exchanger from wheat straw can provide an opportunity to reduce cost of cultivation. Use of treated spent wash can improved carbon status and biological properties which intern provided better physical and biological properties of soil. Use of treated spent wash for cultivation not only increased yield of the crops at reduced cost but also solved the problem of management of agricultural waste and untreated spent wash which will directly disposed in the water bodies as well as on land. Treated spent wash is an excellent source of nutrients and has potential to replace chemical fertilizers.[23]

CONCLUSION

Contaminated soil with untreated industrial waste is an important issue and a challenging among the scientists and researchers. Pretreatment of the distillery spent wash with indigenously prepared cation exchanger show reduction in various physico-chemical parameters which are suited for irrigation in Haryana. Pretreated spent wash improved the soil fertility and amount of all the nutrients required for growth of the plants. It also solved the problem of storage of agricultural waste as well as spent wash of distillery mill.

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