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Tertiary Treatment of Sugar Mill Effluent from Indigenously Developed Cation Exchanger from Agricultural Waste Wheat Straw

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Abstract – Recycling and reuse of industrial effluents in agriculture is not only helpful for conserving the water for irrigation, also the plant nutrients. So it is essential that the amplifications of the use of industrial effluents in the crop field and their effect should be assessed before recommending for irrigation. The treated effluent did not cause an adverse effect on physico-chemical properties of soil. Waste water from sugar mill is properly treated and could be successfully used for irrigation, it is possible to prevent river waste pollution and also to augment already scare irrigation water resources. Utilization of agricultural waste i.e. wheat straw for large scale production of SWS ion exchanger is the need of the hour and exploring the possibility of its use in the treatment of various industrial effluents and use of treated effluents for irrigation is a meaningful proposition. Heavy Metal Analysis of Marigold Plant Irrigated with Treated Sugar Mill Effluent with SWS at Varying Dilution (Cu 0.135-0.278)

Key Words – Wheat Straw, BOD, Physico-Chemical, Zinc, Post-flowerin, DTPA

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INTRODUCTION

Industrial pollution is a global concern due to continue economic growth, green revolution, urbanization, increasing population growth rate are creating enormous stress and threat to the limited fresh water resources.[1] The indiscriminate disposal of liquid waste, solid waste, toxic substances, garbage and other wastes by human community and industries, induce an even greater concern for water resources.[2-3] It is estimated that nearly 70% of our water sources are polluted. The expansion of industry and subsequent increase in the amount of industrial waste has led to considerable environmental problems in all industrialized countries. The indiscriminate disposal of industrial and sewage effluents on agricultural lands is becoming a major source of heavy metal contamination in irrigation soil and in ground water.[4-5] All varieties of cation and anion exchangers nowadays available are imported from other countries. Ion exchange India Limited, which is in collaboration with some other manufacturer in UK, is the major supplier of exchangers. There is hundreds of industries viz. sugar, food, beverages, textiles, dyes and chemicals etc. use these exchangers either at one or the other stage. These can be successfully employed for the removal of heavy metals and these reducing the pollution load of industrial effluents and domestic waste water. India is an agricultural country, so there is a huge quantity of agricultural waste in the form of wheat straw, rice husk; pea nut skin, bagasse, coconut fibre etc. are available.

Tens of millions of tons of toxic or otherwise hazards materials enter the environment every year. They cause cancer, delayed nervous damage, mutagenic changes etc. Once the waste water containing toxic substances enter into the environment, it spreads in a very complex way and may be converted into other substances which have different effects.[6]

The ion exchanger process is a strong alternative to reduce pollution load in waste water. The conversion of wheat straw into cation exchanger, developed in our laboratory constitutes an indigenous approach for making use of agricultural waste for the production of cation exchanger. Waste water from paper mill, sugar mill, distillery and metal industries has been treated by using cation exchanger from wheat straw before discharging into water bodies or on land. This treated water is used as potential fertilizer for growing various crops. It will reduce the fertilizers cost and thus benefit farmers by decreasing the cost with no adverse side effect on physical, chemical and biological properties of soil when used at the level recommended. Wheat straw is abundantly available in India. The conversion of wheat straw into cation exchanger and the use of treated water for cultivation of various crops are beneficial as it constitutes a good source of nutrients and has potential to replace chemical fertilizers. Recycling and reuse of industrial waste water after treatment with cation exchanger from wheat straw in agriculture is not only helpful for conserving the water for irrigation, also the plant nutrients. So, it is essential that the implification of the use of treated industrial effluents in the crop field and their effect should be assessed before recommendation for use in irrigation. The treated effluents of various industries did not cause any adverse side effect on physico-chemical and biological properties of soil. If the treated waste water of different industries located in Yamuna Nagar and Jagadhri could successfully use for irrigation then it is possible to prevent Western Yamuna canal pollution and also to augment already scare irrigation water resources.

The major limitation is that the technologies include the high cost of resins, the extent of regeneration of resins and the chemical stability of synthetic resins. An estimated cost of sulphonated wheat straw on the basis of the raw materials comes out to be low as compare to synthetic exchanger. Hence it is economically viable alternative to synthetic resins. The treated effluents had a potential to be used as a fertilizer for growing various crops in the field.

LITERATURE REVIEW

Currently India is generating about 18004 mm^3 of waste water per day of which 20% is treated in various treatment plants. Sugar industries discharge a large quantity of liquid and solid waste.[7]

The side products produced in sugar industries are utilized as raw material in various distilleries. Every litre of alcohol produced about 15 L of waste water named as spent washor distillery effluent are discharged into running water or on land directly. About 10 to 11 billion litre of spent wash is produced annually in India with 329 distilleries which together produced 3.2 billion litre of alcohol per annum. The liquid is dark brown in colour and has unacceptable odour. The high soluble salts contribute for its higher COD (80,000-120,000 mgl^{-1}) and suspended solids, especially organics contributes for higher (30,000-40,000 mgl^{-1}) making it unsuitable on land. The quality of liquid waste generated and the practices followed by the industries are governed by the Central Pollution Control Board in India. Spent wash is a potential fertilizer containing most essential plant nutrients in liquid as no other commercially available fertilizer provides such a complete source of nutrients. Sugarcane (Saccharum officinarum L.) is a globally important cash crop.[8-10]

Sugar industries in India, for example, generate about 1 kL of wastewater for one ton of sugar cane processed. Therefore, a sugar industry with a capacity of 2500 tons crushed per day (TCD) will generate about 450 mL of wastewater in a running session of 6 months. Sugar mills consume around 2 kL of water and generate about a kL of wastewater of per ton of cane crushed. The effluent is generated from the floor washing wastewater and condensate water, sugarcane juice, syrup, and molasses contained therein.[11]

The sugar mill effluent has a BOD of around 1500 mg/L, and it appears clean initially.[12]

Sugar mill effluent contains considerable amount of potentially harmful substances including soluble salts and heavy metals such as Fe, Cu, Zn, Mn, Pb. The long-term use of this sugar mill effluent for irrigation must be discouraged, as this improper wastewater usage results in the contamination of soils and crops.[13]

The spent wash contains plant nutrients P, K, S in higher concentration. In addition C, N, Fe, Cl and some other elements are also present and hence it can be very well utilized as a source of irrigation on agriculture after subjecting to some pre-treatment. The post anaerobically treated spent wash contains organic intermediates and inorganic salts in significant quantities which are the essential nutrients for plants.[14-15]

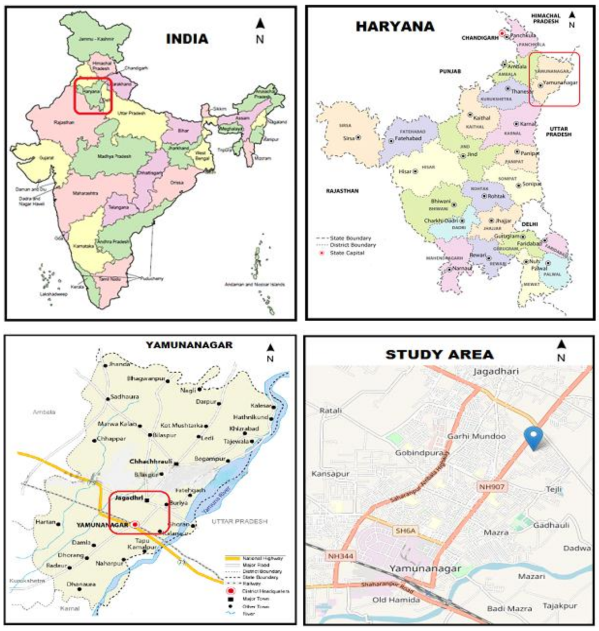
BOD reduction in anaerobic pond from 1600 mgL^{-1} to 550 mgL^{-1} in 7 days, at a loading rate of 0.23 $kgha^{-1}day^{-1}$, this were followed by an oxidation pond, loaded at 316 $kgha^{-1}day^{-1}$, which produced an effluent with a BOD ranging from 34 mgL^{-1} to 180 mgL^{-1} for a retention time of 13 days. Activated sludge process has not been preferred for sugar mill effluent treatment because of the seasonal nature of the industry. Trickling filtration method is also used by few researchers to treat sugar mill effluent and BOD reduction was 70% to 90%.[16]

Use of rotating biological contractor for treating sugar mill effluent with more than 80% COD removal. The maximum COD removal efficiently was found to be 70% with bio-gas yield of 0.65 m^3kg^{-1} COD. Nitrogen content is the digested sludge was found to be 2.32% hence it can be used as fertilizer.[17]

Carboxylated chitosan ion exchanger has been synthesized by K. L. Lu et.al, and used for adsorption of lead and copper in the aqueous solution. Cation exchangers can be produced, apart from synthetic materials, from widely different cellulose based substances like rice husk, paper, lignin, wood etc. by sulphonation.[18]

STUDY AREA

Yamunanagar city and nearby area has been selected for the present study which is comes under the most polluted cities of Haryana. Yamunanagar has the river Yamuna (its namesake) running through the district, which forms the eastern boundary with the neighboring Saharanpur district. The northern boundary is also an interstate boundary with the state of Himachal Pradesh to the north. Well known for 3250 small, medium and large scale industries. It has emerged as an important industrial destination in the state. Due to expanding industries, the city kept on extending geographically. The Yamunanagar District lies between 29 09' 50" and 29 50' North Latitude and 76 31' 15" and 77 12' 45" east longitude.



MATERIAL & METHODS

Preparation of Cation Exchanger

Wheat straw was washed with ethyl alcohol (CH_3CH_2OH) to remove any alcohol soluble gradient. Cation exchanger from agriculture waste i.e. wheat straw had been prepared by sulphonation with conc.H_2SO_4 and decomposition and introduction of sulphonic group had been confirmed by various analytical studies. The resin was washed with distilled water (H_2O) and then dried in the open air and dried product was graded and screened with the help of mesh sieve of different porosity. The cation exchanger formed was then subjected to various studies viz. ash content, moisture content, carbon, sulphur, density and exchange capacity. The various factors affecting the exchange of S.W.S like effect of particle size, effect of flow on exchange and effect of column size on exchange had been undertaken. Cation exchanger from wheat straw had prepared in large quantity for the treatment of sugar mill effluent.

Treatment of Sugarmill Effluent with Newly Formed Cation Exchanger from Wheat Straw

Sugarmill effluent was collected from the Sugarmill. Various physico-chemical parameters i.e. pH, methyl orange alkalinity, acidity, free CO_2, chloride content, DO, BOD, COD, EC, hardness & total solids, DS, SS, Calcium, Magnesium, Chromium, Copper, Manganese and Zinc 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^+ (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. Metals from Plant Samples were extracted using DTPA extraction method. The plant samples were washed with HCl before drying in oven at 65 ± 5 ºC. The various plant samples were dried and weighed. Dry samples were mechanically ground using a sand grass mortar and pestle for digestion. Cr, Cu, Fe, Mn and Zn were analyzed and using Atomic Absorption Spectrophotometer.

RESULTS

Physico-Chemical Studies of Sugar Mill Effluent and its Treatment with S.W.S.

The colour of the effluent from sugar mill was blackish grey with unpleasant alcoholic odour of burnt sugar, rich in highly putrescible organics in contrast to clear and odourless nature of well water. The effluent of sugar mill contain considerable amount of suspended and total dissolved solids and in the present study it varied from 1467 mgL^{-1} to 1652 mgL^{-1} in case of dissolved solids and 689 mgL^{-1} to 786 mgL^{-1} in case of suspended solids in different seasons. It is an important parameter for evaluating the suitability of effluent for irrigation purposes since these solids might clog both the solid pore and components of water distribution system [246]. The pH of the effluent was acidic to neutral 6.5-7.2 whereas well water had a pH nearby area is 7.62-7.9. EC of the effluent ranges from 0.82 dSm^{-1} in winter to 0.98 dSm^{-1} in monsoon season against EC 0.27-0.32 dSm^{-1} for well water. The similar observations were also reported for sugar mill located in Maharashtra [247]. The high value of turbidity in effluent led to very high BOD in different season which ranged from 686-744 mgL^{-1}. Similarly, chemical oxygen demand COD of the effluent was very high in different seasons 11520-16520 mgL^{-1}, whereas, it will very low 214-276 mgL^{-1} for well water (Table 1-2). Very high value of BOD and COD for the effluent of sugar industry was also noticed [248]. Chloride content was also high 69-89 mgL^{-1} as compared to well water. The cationic concentration of Ca^{2+}, Mg^{2+} was relatively high in the effluent than well water. The cation was higher in summer followed by winter and monsoon season. The similar observation was also reported [249-250]. After tertiary treatment with indigenously prepared cation exchanger S.W.S. the pollution load was reduced. Alkalinity reduced up to 56.6%, chloride content 46.06%, BOD 48.38%, total hardness 42.11%, total solids 42.20%, Cr^{6+} 35.61%, Cu^{2+} 39.80%, Zn^{2+} 40.16% and Mn^{2+} 39.58%. The pollutant in the sample were reduced to such an extent that it can be successfully used after dilution for irrigation purposes or may be drained into water bodies without causing any harmful effects on soil or in water showing in (Table 3).

Analysis of Heavy Metals in the Plants Grown in the Pilot Plot

SWS Treated industrial effluent was being used for irrigation of various plants because these effluents contain some nutrients that enhance the growth of crop but these effluents also have some toxic materials. Irrigation of treated sugar mill effluent with S.W.S. after varying dilution had shown very encouraging results on the growth of marigold plants. Concentration of metal in parts of plants ranged from Fe from 26.234 - 38.410 $mgkg^{-1}$, Mn 7.342-9.646 $mgkg^{-1}$, Cu: 0.712–1.289 $mgkg^{-1}$, Cr: 0.138 – 0.245 $mgkg^{-1}$, Zn 3.434-5.628 $mgkg^{-1}$ dry basis while in ground water treated soils it ranged from 2.475-5.789 mgkg-1, 1.867-6.384 mgkg-1, 0.7576-1.9870 mgkg-1, 0.0624-0.1864 mgkg-1, 0.5642-1.2960 mgkg-1 and 1.48-3.78 mgkg-1 dry basis. These data denotes that the concentration of all these heavy metals in the plants parts were within the permissible limit similar results were also reported by other workers.[19]

Table 1: Physico-Chemical Studies of Effluent of Sugar Mill

S. No.	Parameters	Summer	Monsoon	Winter	Mean
1.	pH	6.8	7.2	6.5	6.83
2.	Methyl orange alkalinity	120	98	112	110
3.	Acidity phenolphthalein	150	130	142	140
4.	Free CO_2	52	66	50	56
5.	Chloride Content	89	69	76	78
6.	DO	2.3	3.4	2.8	2.83
7.	BOD	744	686	728	719
8	COD	11520	12800	16520	52013
9.	Conductivity(mS/cm)	0.85	0.98	0.82	0.88
10.	Total Hardness	26,800	22420	24360	24526
11.	Permanent Hardness	19,780	17200	18420	18466
12.	Temporary Hardness	7,020	5220	5940	6060
13.	Total Solids	2156	2438	2232	2275
14.	Dissolved Solids	1467	1652	1508	1542
15.	Suspended Solids	689	786	724	733
16.	Calcium	698	582	688	553
17.	Magnesium	296	234	276	268
18.	Cr^{6+}	146	125	148	139
19.	Cu^{2+}	80.4	72.6	82.6	78.53
20.	Mn^{2+}	4.78	3.84	4.62	4.41
21.	Zn^{2+}	4.8	3.96	4.22	4.32

* All the values are in ppm except pH and conductivity

Table 2: Physico-Chemical Studies of Tube Well Water in Old Hamida near Sugarmill in Yamunanagar City

S. No.	Parameters	Summer	Monsoon	Winter	Mean
1.	pH	7.90	7.62	7.60	7.70
2.	Temperature °C	23.80	18.60	18.30	20.23
3.	Conductivity(mS/cm)	0.32	0.27	0.29	0.29
4.	Methyl orange alkalinity	198	234	186	206
5.	Free CO_2	20.80	21.80	26.40	23.00
6.	Total solid content	478	584	536	532.66
7.	Total dissolved solid	312	378	342	344
8	Total suspended solid	166	202	194	187.33
9.	Dissolved oxygen	7.50	7.90	7.20	7.53
10.	BOD	34.80	28.60	26.40	29.93
11.	COD	248	276	214	246
12.	Chloride content	58.60	62.00	49.80	56.80
13.	Total hardness	780	696	746	740.66
14.	Permanent hardness	436	384	412	410.66
15.	Temporary hardness	344	312	334	330
16	Calcium	182	168	162	170.66
17	Magnesium	97	86	92	91.66
18	Copper	1.84	1.62	1.78	1.74
19	Iron	1.72	1.58	1.52	1.60
20	Manganese	0.74	0.69	0.68	0.70

*All the values in the table are in ppm except pH, temperature and conductivity.

Table 3: Physico-Chemical Studies of Treated Sugar Mill Effluent with H^+ Form of S.W.S.

S. No.	Parameters	Untreated	Treated	% age reduction
1.	pH	6.8	7.5	9..33
2.	Methyl orange alkalinity	120	52	56.66
3.	Acidity phenolphthalein	150	76	49.33
4.	Free CO_2	52	33	36.55
5.	Chloride Content	89	48	46.06
6.	DO	2.3	4.9	53.06
7.	BOD	744	384	48.38
8	COD	11520	9820	14.75
9.	Conductivity(mS/cm)	0.85	0.64	24.70
10.	Total Hardness	26800	15246	42.11
11.	Permanent Hardness	19780	9876	50.07
12.	Temporary Hardness	7020	4336	38.23
13.	Total Solids	2156	1246	42.20
14.	Dissolved Solids	1467	898	38.78
15.	Suspended Solids	689	426	38.17
16.	Calcium	698	448	34.97
17.	Magnesium	296	186	37.16
18	Cr^{6+}	146	94	35.61
19	Cu^{2+}	80.4	48.4	39.80
20	Zn^{2+}	4.78	2.86	40.16
21	Mn^{2+}	4.8	2.9	39.58

* All the values are in ppm except pH and conductivity

Table 4: Heavy Metals Analysis of Soil Samples for Growing Marigold Plants in Pots by Irrigation with Treated Effluent of Sugar mill with SWS after Varying Dilution

S. No.	Effluent (%)	Pre flowering ($mgkg^{-1}$)					Post flowering ($mgkg^{-1}$)				
		Cr	Cu	Fe	Mn	Zn	Cr	Cu	Fe	Mn	Zn
1	100	0.164	1.289	28.242	7.496	3.758	0.172	1.214	22.480	6.395	3.515
2	100	0.162	1.033	26.234	7.342	3.434	0.152	1.134	22.554	6.002	3.015
3	60	0.184	1.029	28.460	7.984	4.530	0.178	1.109	25.620	6.984	4.450
4	60	0.165	1.000	26.340	7.343	4.344	0.138	1.012	24.430	6.322	4.540
5	40	0.216	0.987	36.420	9.211	4.864	0.180	0.997	28.414	7.445	4.960
6	40	0.211	0.904	35.550	9.234	4.344	0.145	0.923	28.045	7.034	4.060
7	20	0.248	0.864	36.862	9.646	5.409	0.186	0.980	32.820	7.926	5.452
8	20	0.232	0.803	36.453	9.453	5.435	0.156	0.943	32.430	7.236	5.442
9	10	0.184	0.841	38.410	8.294	5.628	0.214	0.884	34.980	8.117	5.498
10	10	0.133	0.801	38.242	8.344	4.984	0.245	0.844.	34.640	8.038	5.186
11	0	0.201	0.712	29.764	7.356	4.728	0.226	0.841	32.118	6.894	4.864
12	0	0.211	0.722	27.753	7.343	4.434	0.233	0.823	32.234	6.324	4.434

Table 5: Heavy Metal Analysis of Marigold Plant Irrigated with Treated Sugar Mill Effluent with SWS after Varying Dilution in a Pilot Plot (mgkg^{-1} Dry weight)

S.No.	Effluent (%)	Cr	Cu	Fe	Mn	Pb	Zn
1	100	0.045	0.278	5.460	2.348	4.68	1.208
2	100	0.035	0.252	5.026	2.233	4.46	1.033
3	60	0.048	0.214	5.124	2.120	5.24	1.116
4	60	0.040	0.189	5.100	2.003	5.22	1.124
5	40	0.052	0.186	5.260	2.064	3.28	0.978
6	40	0.041	0.172	5.037	1.991	3.17	0.938
7	20	0.057	0.174	4.384	1.848	3.67	0.862
8	20	0.051	0.162	4.214	1.848	3.67	0.825
9	10	0.043	0.143	4.468	1.432	2.68	0.638
10	10	0.040	0.136	3.894	1.046	2.26	0.610
11	0	0.051	0.148	3.763	1.128	3.29	0.678
12	0	0.047	0.135	3.261	1.073	3.02	0.656

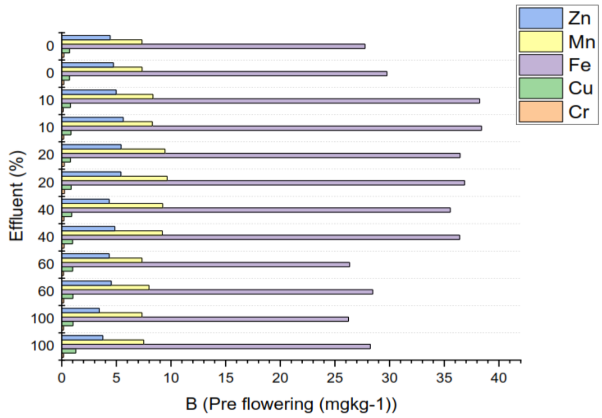


Figure 1: Pre Flowering Heavy Metals Analysis of Soil Samples for Growing Marigold Plants in Pots by Irrigation with Treated Effluent of Sugar mill with SWS after Varying Dilution

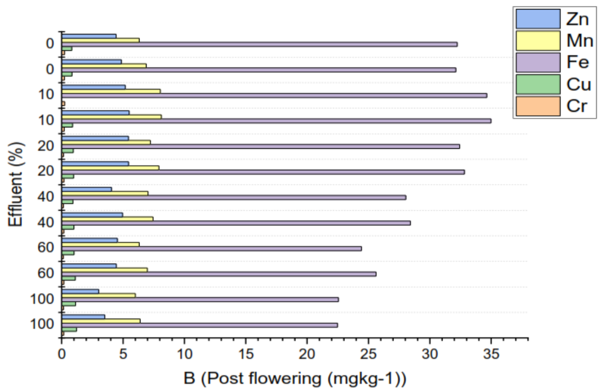


Figure 2: Post Flowering Heavy Metals Analysis of Soil Samples for Growing Marigold Plants in Pots by Irrigation with Treated Effluent of Sugar mill with SWS after Varying Dilution

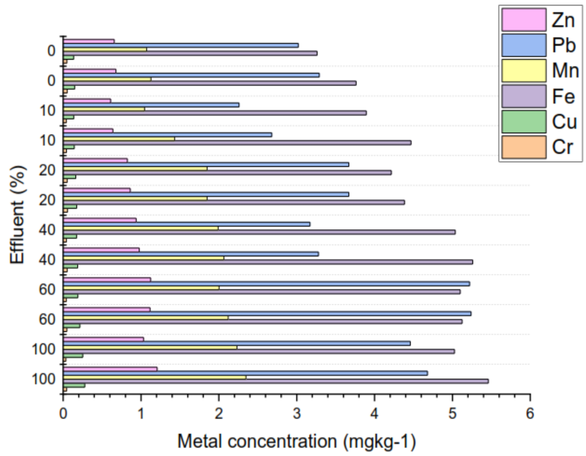


Figure 3: Heavy Metal Analysis of Marigold Plant Irrigated with Treated Sugar Mill Effluent with SWS after Varying Dilution in a Pilot Plot (mgkg^{-1} Dry weight)

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