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Efficiency of Mono and Mixed Columns of Vermiculite for Treating Raw Tannery Effluent

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Abstract: Raw tannery effluent was leached through mono and mixed columns (different grades) of vermiculite to evaluate their removal efficiency for chromium and other pollutant. It was found that among mono-columns, the chromium removal was the highest in RVG_2 (T_1) where it was 63.6% at the first pore volume but incase of mixed columns of RVG_2+RVG_3 still a higher quantum of chromium removal (74.6%) in the first pore volume was evidenced. In case of removal of cations the vermiculite columns retained most of the cations viz., Ca, Mg, Na and K as evidenced by the substantial decrease in the concentration of these ions in the leachate of the first pore volume. The retention of total chromium, anions and cations by the mono and mixed columns of vermiculite followed a general trend of maximum adsorption during the first pore volume followed by a linear decreasing trend upto third pore volume and in the fourth pore volume the adsorption decreased drastically as a result, the leachate of fourth pore volume was almost equal to that of the original effluent with reference to the pollution load.

Key words: Raw vermiculite grades, exfoliated vermiculite grades, tannery effluent, chromium, pore volumes, mono-columns, mixed-columns

INTRODUCTION

The discharge of wastes, particularly the industrial wastes into the water bodies has been a matter of great concern in the industrialized countries of the world since long. With the rapid growth of industries in India, pollution has increased tremendously.

Tanning industry is one of the important industries in India, which earns considerable foreign exchange through the leather export. There are about 5000 tanneries in India. The quantity of effluent released from the tanneries is about 50 to 60 L kg^{-1} of leather tanned. The tannery wastes are ranked as high pollutants among the industrial wastes. Tannery effluent is rich in salt content especially the chromium. Chromium in its hexavalent form is one of the undesirable heavy metals because it affects human physiology, accumulates in the food chain and causes several ailments (Park and Jung, 2001).

The trivalent form is relatively innocuous, but hexavalent chromium is toxic, carcinogenic and mutagenic in nature, highly mobile in soil and aquatic system and also is a strong oxidant capable of being adsorbed by the skin (Singh and Singh, 2002). So the removal of Cr (VI) besides colour, sodium, calcium, magnesium salts from tannery effluents is important before discharging them into aquatic environments or on to land.

A wide range of physical and chemical processes are available for the removal of Cr (VI) and salts from tannery effluents include chemical precipitation, reverse osmosis, evaporation, ion exchange and adsorption. Adsorption on Activated Carbon (ARC) has been adopted as tertiary treatment in various types of industries because of its excellent adsorption capability (Bailey *et al*., 1999). However, it's use is limited by its high cost (El-Geundi, 1997). In this context, vermiculite mineral with its high cation exchange capacity and reactive surface area was scientifically evaluated for its potential to substitute the activated carbon which could be cost effective and economically feasible treatment method. Column studies were carried out to assess the suitability of raw and exfoliated vermiculite grades obtained from Tamil Nadu Minerals Ltd., Chennai for the removal of Cr (VI) and specific pollutants from tannery effluent.

MATERIALS AND METHODS

The untreated chrome tan liquor collected from a tannery at Erode, Tamil Nadu was analysed for its physical and chemical properties following the standard procedures.

Raw vermiculite comprising of aluminium, iron, magnesium, silicate mineral mixtures, which is excavated

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as a mineral comprising of thin layers was obtained from M/s. TAMIN, Chennai. Exfoliated vermiculite is obtained by heating the raw vermiculite to temperatures upto 1000°C. These vermiculite are graded accordingly to specific sizes.

Mono and mixed vermiculite columns: Mono and mixed column experiments using selected raw (RVG) and Exfoliated Vermiculite Grades (EVG) were carried out using PVC pipes of 5 cm diameter and 50 cm long (height). The bottom of the pipe was fitted with a filter paper (Whatman No. 1) and a wire mesh (0.1 mm), which were tightly wrapped to hold the weight of different grades of vermiculite. At the bottom, the treated effluent (leachate) was collected through a funnel.

Four selected grades of vermiculites (RVG 2, 3, 4 and EVG 5) were gently packed in the PVC pipes of required height in the column which exhibited varied bulk densities ranging from 0.95 to 1.48 g cc^{-1} with four replications. Four treatments with mixed grades of vermiculite (RVG_2 mixed with equal quantities of RVG_3 (T_1). RVG_4 (T_2), EVG (T_3) and RVG_5 (T_4)) were also gently packed to required column height which exhibited varied bulk densities ranging from 1.61 to 1.98 g cc^{-1}.

Calculation of pore volume: To calculate one pore volume, the weight of the columns packed with mono and mixed grades of vermiculites saturated with tannery effluent was substracted from its original weight. The columns were leached based on pore volumes and leachates collected from four pore volumes were analyzed for pH, EC, TS, chromium (VI), sodium, sulphate, calcium and magnesium following standard methods.

RESULTS AND DISCUSSION

The analytical results of the chrome tan liquor are furnished in Table 1. The effluent was neutral in reactions with high EC (20.3 dS m^{-1}), TS (12871 mg L^{-1}), colour (3.15 OD unit), total chromium (206 mg L^{-1}), sodium (2816 mg L^{-1}), sulphate (1496 mg L^{-1}), calcium (216 mg L^{-1}) and magnesium (123 mg L^{-1}). The composition of chrome tan liquor mainly depended on the chemicals present in hides, products formed during the decomposition and chemicals used in the tanning of the hides.

Table 1: Physico-chemical characteristics of raw tannery effluent

Characteristics	Chrome tan effluent
pH	7.81
EC(dS m^{-1})	20.30
Total Solids (mg L^{-1})	12871.00
Colour	3.15
Total chromium (mg L^{-1})	206.00
Sodium (mg L^{-1})	2816.00
Sulphate (mg L^{-1})	1496.00
Calcium (mg L^{-1})	216.00
Magnesium (mg L^{-1})	123.00

Table 2: Physical and chemical properties of different grades of raw and exfoliated vermiculites

Particulars	Unit	RVG 2	RVG 3	RVG 4	RVG 5	EVG5
Bulk density	g cc^{-1}	1.00	0.73	1.38	1.38	0.49
Particle density	g cc^{-1}	2.50	2.00	1.82	1.61	0.68
Total surface area	g m^{-2}	42.00	26.20	19.20	25.40	38.90
pH		9.06	9.22	9.44	9.15	8.61
EC	(dS m^{-1})	0.03	0.07	0.04	0.02	0.10
Cation exchange capacity	Cmol $(p)^{+}$ kg^{-1}	112.00	104.00	98.80	92.40	84.50

(Mean of three replications); RVG-Raw vermiculite grade; EVG-Exfoliated vermiculite grade

Table 2 records the analytical results of the both the raw and exfoliated vermiculite grades. These adsorbent materials were alkaline in nature which could be due to the presence of associated carbonate rock impurities, the reaction of which is normally alkaline. The bulk density, total surface area, particle density and CEC were the highest in RVG_2.

The trend of retention of soluble salts and removal of colour by mono (0.73 v/v) and mixed columns (1.52 v/v) (Table 3 and 4) was a maximum adsorption during the first pore volume, followed by a linear decreasing trend upto the third pore volumes. In the fourth pore volume, the adsorption was the least. There was only a meager difference with reference to pollutant load between the leachate of fourth pore volume compared to that of the original values, indicating that the vermiculite at this stage has attained the point of saturation of all its exchange sites.

Among mono columns, reduction of total solids was maximum in RVG_2 (T_1) which was found to be 51.1% in the first pore volume, 48.1, 35.3, 5.34% in the 2nd, 3rd and 4th pore volumes. But incase of mixed columns, 50% RVG_2 + 50% RVG_3 columns (T_1) was found to reduce total solids by 52.8, 51.5, 37.8 and 8.13% in the 1st, 2nd, 3rd and 4th pore volumes. The differences in the per cent removal of total solids among mono and mixed column could be ascribed to the increased bulk density of the latter system than the former, besides the enhanced CEC.

The percentage reduction of total solids which decreased with the advancement of pore volumes indicated that the predominant sorption mechanism initially was probably physical sorption associated with the Van Der Waals force which consequently would have been reversed due to weak adsorption as the pore volume advanced. A similar result was observed by Sasi Kala Rani (2003) who reported that vermiculite layer showed

Table 3: Characteristics of vermiculite mixed-columns leachates of raw tannery effluent

	pH					Ec (dS m^{-1})				
Treatments	PV_1	PV_2	PV_3	PV_4	Mean	PV_1	PV_2	PV_3	PV_4	Mean
zT_1	6.23	6.87	7.42	8.05		9.43	9.95	12.7	18.7	
	(20.2)	(12.0)	(4.99)	(-3.07)	7.14	(53.5)	(51.0)	(37.4)	(7.88)	12.7
T_2	6.94	7.12	7.53	8.14		9.95	13.1	15.6	19.2	
	(11.1)	(8.83)	(3.59)	(-4.23)	7.43	(50.9)	(35.5)	(23.2)	(5.42)	14.5
T_3	7.02	7.22	7.26	8.21		10.2	14.5	16.2	19.8	
	(10.1)	(7.55)	(7.04)	(5.12)	7.43	(49.8)	(28.6)	(20.2)	(2.46)	15.2
T_4	7.330	7.38	8.22	8.66		11.2	13.0	16.1	20.3	
	(6.15)	(5.51)	(-3.97)	(-10.9)	7.89	(44.8)	(36.0)	(20.7)	(0.00)	15.1
Mean	6.88	7.15	7.61	8.25	7.47	10.2	12.7	15.2	19.5	14.4
	TS (mg L^{-1})					Colat at 358.0 nm (OD unit)				
Treatments	PV_1	PV_2	PV_3	PV_4	Mean	PV_1	PV_2	PV_3	PV_4	Mean
T_1	6074	6238	8011	11825	8037	0.62	1.07	1.42	2.33	1.36
	(52.8)	(51.5)	(37.8)	(8.13)	9204	(80.3)	(66.0)	(54.9)	(26.0)	1.4
T_2	6252	8317	10034	12215	9671	0.77	1.12	1.3	2.41	1.43
	(51.4)	(35.4)	(22.0)	(5.10)	9528	(75.6)	(64.4)	(58.7)	(23.5)	1.52
T_3	6434	9217	10395	12638	9110	0.82	1.03	1.51	2.38	1.43
	(50.0)	(28.4)	(19.2)	(1.81)		(73.9)	(67.3)	(52.1)	(24.4)	
T_4	7024	8123	12744	9528		0.92	1.21	1.62	2.34	
	(45.4)	(36.9)	(20.6)	(0.99)		(70.8)	(61.6)	(48.60)	(25.7)	
Mean	6446	7974	9665	12335		0.78	1.1	1.46	2.37	
	SEd	CD (0.05)	SEd	CD(0.05)	SEd	CD (0.05)		SEd		CD(0.05)
T	0.03	0.06	0.027	0.053	1.23	2.47		0.012		0.025
V	0.03	0.6	0.027	0.053	1.23	2.47		0.012		0.025
TV	0.6	0.121	0.053	0.107	2.46	4.94		0.025		0.05

T_1- 50% Raw vermiculite grade 2 + 50% Raw vermiculite grade 3 T_2- 50% Raw vermiculite grade 2 + 50% Raw vermiculite grade 4
T_3- 50% Raw vermiculite grade 2 + 50% Exfoliated vermiculite grade 5 T_4- 50% Raw vermiculite grade 2 + 50% Raw vermiculite grade 5

Table 3: Characteristics of vermiculite mixed-columns leachates of raw tannery effluent

	Total Chromium (mg L^{-1})					Sodium (mg L^{-1})				
Treatments	PV_1	PV_2	PV_3	PV_4	Mean	PV_1	PV_2	PV_3	PV_4	Mean
T_1	52.3	62	83.5	107		1214	1314	1972	2213	
	(74.6)	(69.9)	(59.5)	(48.1)	76.2	(56.9	(53.3)	(30.0	(21.4)	1678
T_2	57.5	66.0	92.0	128		1233	1374	1933	2240	
	(72.1)	(68.0)	(55.3)	(37.9)	85.8	(56.6	(51.2)	(29.2	(20.5)	1707
T_3	67.5	74.5	94.5	117		1262	1355	1983	2245	
	(67.2)	(63.8)	(54.1)	(43.2)	88.3	(55.1	(51.9)	(29.6	(20.3)	1711
T_4	73.5	77.0	95.0	125		1277	1361	2003	2317	
	(64.3)	(62.6)	(53.9)	(39.2)	92.6	(54.7)	(51.7)	(28.9)	(17.7)	1739
Mean	62.7	69.9	91.3	119	85.7	1244	1351	1988	2254	1709

Table 3: Characteristics of vermiculite mixed-columns leachates of raw tannery effluent

	Sulphate (mg L^{-1})					Calcium (mg L^{-1})					Magenasium (mg L^{-1})				
Treatments	PV_1	PV_2	PV_3	PV_4	Mean	PV_1	PV_2	PV_3	PV_4	Mean	PV_1	PV_2	PV_3	PV_4	Mean
T_1	1231	1255	1304	1438	1307	114	133	156	184	147	66.3	70.5	81.5	104	80.5
	(17.7)	(16.1)	(12.8	(3.90)	1317	(33.3)	(38.4)	(27.8)	(14.5)	159	(46.1)	(52.5)	(33.7)	(15.4)	81.3
T_2	1237	1262	1314	1455	1319	125	145	173	193	167	73.0	76.5)	84.3	107	91.1
	(17.3)	(15.6)	(12.1	(2.70)	1323	(42.1)	(32.9)	(19.9)	(10.6)	182	(40.7)	(37.8	(31.5)	(13.0)	91.2
T_3	1241	1267	1314	1453	1316	157	157	175	201	164	783	81.5)	91.5	113	87
	(17.0)	(15.3)	(12.2)	(2.90)		(38.4)	(27.3)	(19.0)	(6.90)		(36.3)	(33.7	(25.6)	(8.10)	
T_4	1243	1273	1321	1455		176	176	194	211		75.5	83.5	91.5	114	
	(16.9)	(14.9)	(11.7)	(2.71)		(31.0)	(18.5)	(10.2)	(2.30)		(38.4)	(32.1)	(25.6)	(7.30)	
Mean	1238	1264	1313	1450		143	153	175	197		73.3	78	81.2	110	

Values in parenthesis are percentage reduction from its original value

	SEd	CD (0.05)	SEd	CD (0.05)	SEd	CD (0.05)	SEd	CD (0.05)	SEd	CD (0.05)
T	1.044	2.099	1.039	2.09	1.01	2.02	1.35	2.72	0.75	1.51
V	1.044	2.099	1.039	2.09	1.01	2.02	1.35	2.72	0.75	1.51
TV	2.088	4.198	2.08	4.18		NS	NS		NS	

T_1- 50% Raw vermiculite grade 2 + 50% Raw vermiculite grade 3 T_2- 50% Raw vermiculite grade 2 + 50% Raw vermiculite grade 4
T_3- 50% Raw vermiculite grade 2 + 50% Exfoliated vermiculite grade 5 T_4- 50% Raw vermiculite grade 2 + 50% Raw vermiculite grade 5

Table 4: Characteristics of vermiculite mono-columns leachates of raw tannery effluent

	pH					EC (d Sm^{-1})				
Treatments	PV_1	PV_2	PV_3	PV_4	Mean	PV_1	PV_2	PV_3	PV_4	Mean
T_1	6.43	6.94	7.24	7.52		9.95	10.5	13.2	19.4	
	(17.7)	(11.1)	(7.30)	(3.71)	7.03	(50.9)	(48.3)	(35.0)	(4.43)	13.3
T_2	6.52	6.98	7.28	7.56		10.1	12.1	14.2	20.3	
	(16.5)	(10.6)	(6.79)	(3.20)	7.09	(50.2)	(40.4)	(30.0)	(0.00)	14.2
T_3	6.58	6.72	7.34	7.59		10.9	13.1	15.2	19.6	
	(15.7)	(13.9)	(6.02)	(282)	7.06	(46.3)	(35.5)	(25.1)	(3.45)	14.7
T_4	7.00	7.12	7.44	7.81		11.7	12.9	15.9	19.3	
	(10.4)	(8.83)	(4.74)	(0.00)	7.34	(42.4)	(36.5)	(21.7)	(4.93)	15.0
Mean	6.63	6.94	7.33	7.62	7.13	10.7	12.2	14.6	19.7	24.3

	TS (mg L^{-1})					Colat at 358.0 nm (OD unit)				
Treatments	PV_1	PV_2	PV_3	PV_4	Mean	PV_1	PV_2	PV_3	PV_4	Mean
T_1	6218	6678	8326	12184		0.85	1.13	1.82	2.28	
T_2	(51.07)	(48.1)	(35.3)	(5.34)	8351	(73.0)	(64.1)	(42.2)	(27.60	1.52
T_3	6320	7626	9053	12792		0.93	1.43	1.93	2.37	
T_4	(50.9)	(40.8)	(29.7)	(0.61)	8948	(70.5)	(54.6)	(38.7)	(24.8)	2.66
Mean	7029	8418	9563	12432		0.96	1.48	1.99	2.4	
	(45.4)	(34.6)	(25.7)	(3.41)	9360	(69.5)	(53.0)	(36.8)	(23.8)	1.70
	7329	8262	10166	12277		1.02	1.5	2.09	2.27	
	(43.1)	(35.8)	(21.0)	(4.62)	9509	(67.6)	(52.4)	(33.7)	(27.9)	1.72
	6724	7746	9277	12421	9042	0.94	1.39	1.96	2.32	2.62

Values in parenthesis are percentage reduction from its original value

	SEd	CD (0.05)	SEd	CD (0.05)	SEd	CD (0.05)	SEd	CD (0.05)
T	0.021	0.043	0.063	0.127	1.406	2.828	0.015	0.030
V	0.021	0.043	0.063	0.127	1.406	2.828	0.015	0.030
TV	0.043	0.086	0.226	0.254	2.813	5.656	0.030	0.060

T_1-Raw vermiculite grade 2 T_2-Raw vermiculite grade 3 T_3-Raw vermiculite grade 4 T_4-Exfoliated vermiculite grade 5

Table 4: Characteristics of vermiculite mono-columns leachates of raw tannery effluent

	Total chromium (mg L^{-1})					Sodium (mg L^{-1})				
Treatments	PV_1	PV_2	PV_3	PV_4	Mean	PV_1	PV_2	PV_3	PV_4	Mean
T_1	75	83.5	93.8	125	94.1	1343	1373	1975	2317	1752
	(63.6)	(59.5)	(54.4)	(39.3)	98.4	(52.3)	(51.2)	(29.9)	(17.7)	1774
T_2	79.8	84.5	96.8	133	97.1	1345	1385	1985	2382	1788
	(61.3)	(58.9)	(53.0)	(35.4)	102	(52.2)	(50.8)	(29.6)	(15.4)	1771
T_3	82.8	85	95.0)	126	98.2	1353	1390	1992	2417	1771
	(59.8)	(58.7)	(53.9)	(38.8)		(52.0)	(50.6)	(29.3)	(142)	
T_4	87.3	93.0)	97.3	134		1361	1402	2004	2315	
	(57.6)	(64.9)	(52.8)	(34.9)		(51.7)	(54.2)	(28.8)	(17.8)	
Mean	81.2	86.5	95.7	129		1350	1388	1989	2358	

	Sulphate (mg L^{-1})					Calcium (mg L^{-1})					Magenasium (mg L^{-1})				
Treatments	PV_1	PV_2	PV_3	PV_4	Mean	PV_1	PV_2	PV_3	PV_4	Mean	PV_1	PV_2	PV_3	PV_4	Mean
T_1	1273	1290	1395	1441		147	165	187	203	176	85.3	91.3	107	121	101
	(14.9)	(13.7)	(6.75)	(3.68)	1350	(31.9)	(23.6)	(13.4)	(6.01)	177	(30.6)	(25.8)	(130)	(1.62)	105
T_2	1277	1285	1399	1454		156	158	190	203	184	87.8	93.5	113	125	109
	(14.6)	(14.1)	(6.48)	(2.80)	1354	(27.0)	(26.9)	(12.0)	(6.01)	182	(28.6)	(23.9)	(8.13)	(1.6)	105
T_3	1283	1294	1405	1461		165	176	193	203	180	91.3	98.5	115	129	105
	(14.2)	(13.5)	(6.08)	(2.34)	1361	(23.6)	(18.5)	(10.6)	(6.01)		(25.8)	(19.9)	(6.50)	(4.80)	
T_4	1287	1259	1423	1457		155	172	191	212		90.5	96.3	115	119	
	(13.9)	(15.8	(4.88)	(2.60)	1356	(28.2)	(20.4)	(11.6)	(1.85)		(26.4)	(21.7)	(6.5)	(3.25)	
Mean	1280	1282	1405	1453	1355	156	168	190	205		88.7	94.9	113	123	

Values in parenthesis are percentage reduction from its original value

	SEd	CD (0.05)	SEd	CD (0.05)	SEd	CD (0.05)	SEd	CD (0.05)	SEd	CD (0.05)
T	0.94	1.90	1.12	2.26	1.12	2.32	1.05	2.11	0.99	2.01
V	0.94	1.90	1.12	2.26	1.12	2.32	1.05	2.11	0.99	2.01
TV	1.89	3.80	2.25	4.52	2.30	4.63	2.10	4.23	1.99	4.02

.T_1-Raw vermiculite grade 2 T_2-Raw vermiculite grade 3 T_3-Raw vermiculite grade 4 T_4-Exfoliated vermiculite grade 5 greater percent of removal in the first three pore volumes and the adsorption decreased thereafter with reference to soluble barium and salts.

The same trend was also noticed in case of colour removal where RVG_2 (T_1) recorded 73% removal in the first pore volume in mono-column and in mixed column of 50% RVG_2 + 50% RVG_3 colour removal of as high as 80.3% was observed. This might be due to the retention of total solids on the inter-lattice surfaces of vermiculite which resulted in the colour reduction. Similar observation was also reported by Sumathi (1999 and 2003).

In mono-columns, the chromium removal was the highest in RVG_2 (T_1) where it was 63.6% in the first pore volume but incase of mixed-columns of 50% RVG_2 + 50% RVG_3, still a higher quantum removal of chromium 74.6% in the first pore volume was evident. Incase of removal of cations, the vermiculite mineral in the columns retained most of the cations viz., Ca, Mg, Na and K which was evident from the substantial decrease in the concentration of these ions in the leachate of the first pore volume. The increased adsorption of chromium and cations at varying pore volumes could be attributed to the high cation exchange capacity of RVG_2 (112 Cmol $(p)^+$ kg^{-1}) and mixed column (RVG_3-104 Cmol $(p)^+$ kg^{-1}). These adsorption sites could have adsorbed large amounts of Cr and strongly retained in the exchange sites. Similar observations have been reported by Sumathi (1999) and Sasi Kala Rani (2003).

CONCLUSIONS

The efficacy of chromium removal was maximum of 74.6% in the 1st pore volume of mixed vermiculite column (RVG_2 + RVG_3), whereas among the mono columns, it was the highest in RVG_2, were it was 63.6% in the 1st pore volume. The general trend with reference to the retention and removal efficiency of various cations, anions and chromium by mono and mixed vermiculite columns was of maximum removal during the first pore volume followed by a linear decreasing trend upto third pore volumes and in the fourth pore volume the adsorption decreased drastically as a result, the leachate of fourth pore volume was all most equal to that of the original effluent with reference to the pollutant load. Hence it is inferred that RVG_2 + RVG_3 mixed vermiculite column could be utilized as a substitute for activated carbon in tertiary treatment of tannery effluent.

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