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EFFECT OF NATURAL ZEOLITE MATERIAL ON HEXAVALENT CHROMIUM ADSORPTION

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ABSTRACT

Huge amounts of chromium (Cr) compounds are being releasing into the environment as a result of anthropogenic activities. Speciation of chromium compounds is important in understanding the toxicity because of contrasting characters of hexavalent (Cr (VI) and trivalent Cr (III) chromium). An improved method for the removal of chromium is carried by natural materials. Certain natural Zeolite, especially the Clinoptilolite variety, has been demonstrated to be effective in removing heavy metals from water. The principles involved in removal of several toxic metals are Ion exchange, removing the metal and releasing another non toxic ion such as potassium or sodium, from the crystal. Zeolites, like many other synthetic ion exchangers (silica gel, wheat bran, tamarind seed, etc.) are adsorbed the metals from wastewater. Hexavalent chromium was adsorbed by Zeolite upto 92% from the solution. The results showed that, the Zeolite material was found to adsorb hexavalent chromium very effectively and can be recommended for water and wastewater treatment.

INTRODUCTION

The leather industry is one of the major export industries in India, earning about 7000 crore rupees annually. It is estimated that about 70% of the total exports of leather and leather products are from Tamil Nadu. However, it is also one among the major sources of pollution in the state of Tamil Nadu. The effluent and sludge discharged from these tanneries into rivers and onto land has led to extensive degradation of productive land. The tannery wastes (effluents and sludge) contain high concentrations of salts (sodium, chloride and sulfates, etc.) and chromium (Cr). The indiscriminate disposal of these wastes resulted severe pollution of soil and water in Vellore where most of the tanneries are located. Pollution of soil and water drastically reduced the crop yields (25 to 40%) over the years and total cropped area decreased significantly. Within 20 years, the total cropped area has fallen to about 10.5% in Vellore district.

The sources of contamination are electroplating,

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metal ?nishing industries (hexavalent chromium) and tanneries (trivalent chromium). Chromium occurs most frequently as Cr (VI) or Cr(III) in aqueous solutions (Dakiky *et al*., 2002). Both valences of chromium are potentially harmful but hexavalent chromium poses a greater risk due to its carcinogenic properties (Dakiky *et al.,* 2002). Hexavalent chromium, which is primarily present in the form of chromate (CrO_4^{2-}) and dichromate ($Cr2O_7^{2-}$), poses signi?cantly higher levels of toxicity than the other valency states (Sharma and Forster, 1995).

Conventional methods for removing Cr (VI) ions from industrial wastewater include reduction (Kim *et al.*, 2002), reduction followed by chemical precipitation (Ozer *et al.,* 1997), adsorption on the activated carbon (Lotfi and Adhoum, 2002), solvent extraction (Mauri *et al*., 2001) cementation, freeze separation, reverse osmosis (Padilla and Tavani, 1999), ion-exchange (Rengaraj *et al*., 2003) and electrolytic methods (Namasivayam and Yamuna, 1995). These methods have found limited application because they often involve high capital and operational costs. Adsorption is an effective and versatile method for removing chromium. Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive sorbents. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration. Most of the low cost sorbents have the limitation of low sorptive capacity and thereby, for the same degree of treatment, it generates more solid waste (pollutant laden sorbent after treatment), which poses disposal problems. Therefore, there is need to explore low cost sorbent having high contaminant sorption capacity.

Zeolites are naturally occurring hydrated aluminosilicate minerals. They belong to the class of minerals known as tectosilicates. Most common natural Zeolites are formed by alteration of glass-rich volcanic rocks (tuff) with fresh water in playa lakes or by seawater (Badillo-Almaraz *et al*., 2003). The structure of Zeolites consists of three-dimensional frameworks of SiO_4 and AlO_4 tetrahedra. The aluminum ion is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms, and the isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge in the lattice. The net negative charge is balanced by the exchangeable cation (sodium, potassium, or calcium). These cations are exchangeable with certain cations in solutions such as lead, cadmium, zinc, and manganese (Barer, 1987 and Breck, 1964).

The fact that Zeolite exchangeable ions are relatively innocuous (sodium, calcium, and potassium ions) makes them particularly suitable for removing undesirable heavy metal ions from industrial effluent waters. One of the earliest applications of a natural Zeolite was in removal and purification of cesium and strontium radioisotopes (Hafez *et al*., 1978).

MATERIALS AND METHODS

Process of leather tanning

Tannery waste water was collected from Co-operative tanning Industry, Bhavani, Erode district. The monthly production of leather from this industry is about 52 tones. The processes involved to obtain finished leather are furnished.

After processing, the wastewater produced from the industry is subjected to various treatments. As the first step, the wastewaters are released into the Dual media filter where in the impurities are removed. From here, the effluent passes through Ultra filter, Reverse Osmosis I and Reverse Osmosis II. After the completion of RO II, the effluent is completely treated which is recycled for processing once again.

The actual tanning process (Chrome tanning) generates waste water which is allowed to evaporate in open lagoons, where in magnesium oxide is added to remove the color from the waste water. The settleable materials, especially the salts are called the sludge, while the clear water on the surface are being pumped out and reused for the tanning process (Figure 1).

Chromium adsorption study

A laboratory experiment was conducted for chromium adsorption using Zeolites as at various concentrations with two different salts. To start with the adsorption of Chromium at a range of equilibrium period was examined (24 hrs) at a single input concentration of 0, 20, 40, 60, 80 and 100 mg L^{-1}. One gram of Zeolite was added in polypropylene centrifuge tubes (50mL). To the tubes containing air and dry Zeolite, Chromium standard ($K_2Cr_2O_7$, Cr_2 $(SO_4)_3$. $6H_2O$) solution (i.e. 0, 20, 40, 60, 80 and 100 mg L^{-1}) of 1mL was added followed by addition of 24 mL of distilled water. Then the

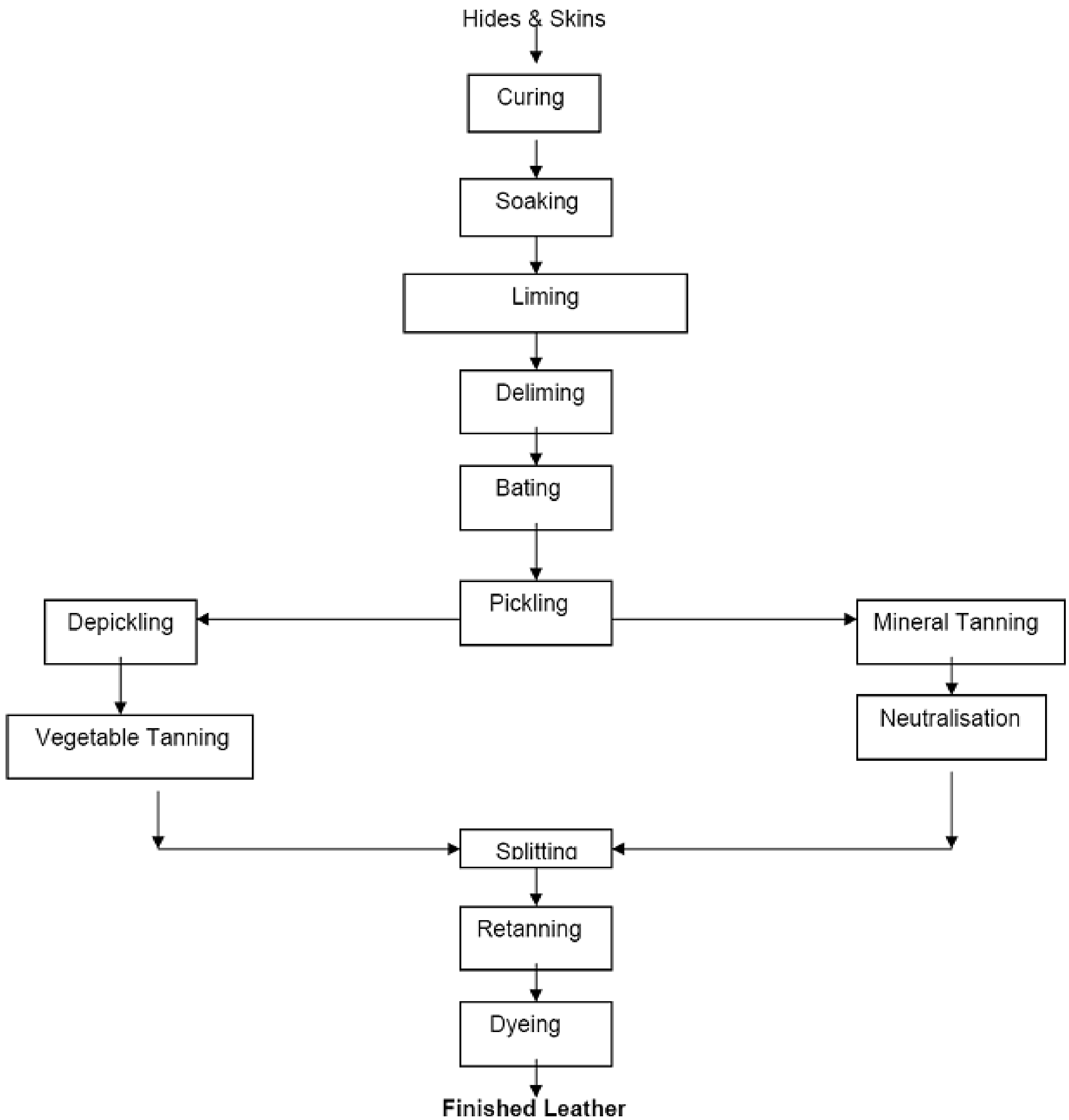

Fig. 1 Schematic representation of tanning (Nandy *et al*., 1993)

tubes containing the Zeolite and Cr solution were kept subjected to centrifuge at a range of 24 hrs period. Then the heavy metals (Cr) concentration in the filtrate was measured by Diphenyl Carbazide method (USEPA, 1979). The treatments comprised of three different sources of Cr namely Potassium dichromate ($K_2Cr_2O_7$), Chromium Sulphate ($Cr_2(SO_4)_3 \cdot 6H_2O$ and Chrome wastewater in incremental concentrations of Cr ranging from 0 ppm to 100 ppm. This was done to find out the sorption equilibrium. The amount of heavy metals adsorbed per unit mass of Zeolite was determined by computing the difference in the initial and equilibrium solution concentrations.

RESULTS AND DISCUSSION

The chromium hexavalent ion was adsorbed by Zeolites at different higher level of concentrations. Table 1 represents initial characteristics of wastewater and Zeolite. The adsorption concentration was given in Table 2. Potassium dichromate and Chromium sulphate salts that contain hexavalent chromium and these solutions were taken for adsorption studies. The effect of Zeolite on the rate of Cr (VI) sorption was investigated at different level concentration as indicated in Fig. 2 and 3. These graphs were explained with when the concentration of hexavalent chromium increases the adsorption of Cr (VI) by Zeolite was increased. Chromium (VI) was adsorbed very effectively by Zeolite in 100 µg/g and the same adsorption studies was observed in chromium sulphate solution at 100 µg/g concentration (Fig. 2 and 3). The cation exchange capacity of Zeolite was high and it's having honey comb structure. The inner side of Zeolite particles are having positive charged so adsorption of chromium (VI) is high. Hence, the surface area of Zeolite was very broad and can easily adsorb the elements from the solution. Hu *et al*. (2003) reported Cr (VI) sorptive capacity in the range of 30 to 40 mg g^{-1} for three different commercial activated carbon at equilibrium Cr (VI) concentration of 3 - 10 mg L^{-1} at pH 3. Granulated activated carbon and fibrous activated carbon have approximately 10 mg g^{-1} of Cr (VI) at equilibrium Cr (VI)

Table 1. Initial characterization of tannery wastewater and Zeolite

Parameters	Untreated wastewater	Treated wastewater	Salt water	Chrome water	Lime sludge	Chrome sludge	Zeolite
pH	11.24	7.01	8.64	4.33	8.36	5.01	9.22
EC	20.4	6.7	29.7	30.6	9.75	2.34	0.30
CEC m.eq / 100g	-	-	-	-	-	-	49.9
N (mg L^{-1})	11.2	14	11.2	14	19.6	30.8	
P (mg L^{-1})	29	52	359.5	589	23	531	
K (mg L^{-1})	70	20	120	60	110	80	
Na (mg L^{-1})	37200	12700	68000	48700	5300	1200	
Ca (mg L^{-1})	256	280	360	32	224.2	158.2	
Mg (mg L^{-1})	268.8	288	528	153.6	376	422.5	
Cl (mg L^{-1})	53250	35500	88750	62125	7100	8875	
SO4 (mg L^{-1})	409.2	66.075	29.3	1291.9	89.43	482.75	
CO3 (meq.L^{-1})	1200	2600	1520	520	-	-	
HCO3 (meq. L^{-1})	620	1000	120	280	-	-	
BOD (mg L^{-1})	1390	-	750	480	-	-	
COD (mg L^{-1})	2240	-	1500	2080	-	-	
Total Chromium (mgL^{-1})	-	2.0	-	275	225	2345	-

Table 2. pH and EC changes after incubation and Adsorption of Chromium hexavalent on Natural Zeolite

Treatments (µg/g)	pH	EC	Cr(VI) in Solution (µg/mL)	Cr (VI) adsorbed by Zeolite (µg/g)
Potassium dichromate				
0	9.27	0.13	0	0
20	9.30	0.17	15.575	3.725
40	9.21	0.18	10.22	29.78
60	9.27	0.17	18.67	41.33
80	9.22	0.17	42.32	37.68
100	8.67	0.13	19.78	80.22
Chromium sulphate				
0	9.27	0.13	0	0
20	9.33	0.17	5.45	14.55
40	9.05	0.22	6.41	33.59
60	9.10	0.23	7.93	52.07
80	9.13	0.18	6.97	73.03
100	8.92	0.21	7.83	92.18
Chrome waste water	6.88	42.6	0	0

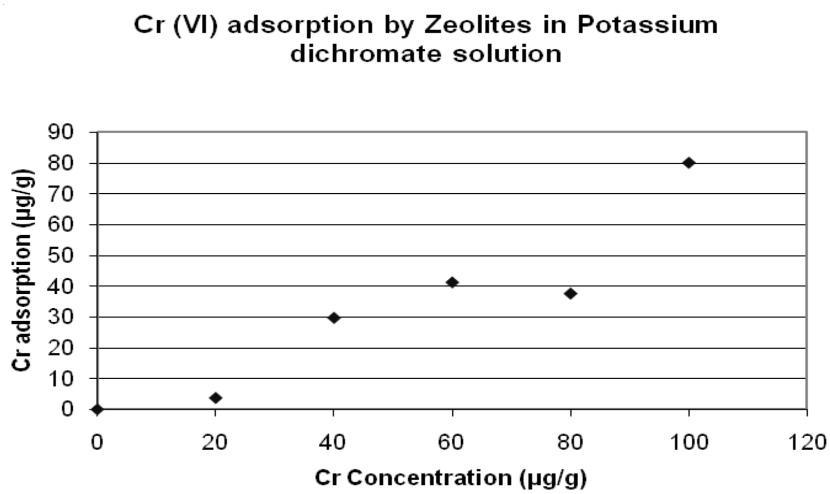

Fig. 2 Cr(VI) adsorption by Zeolites in Potassium dichromate solution

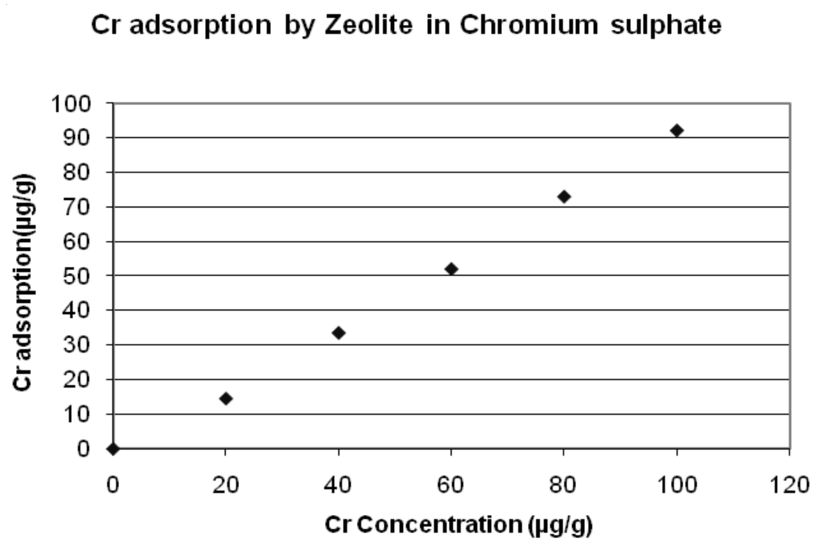

Fig. 3 Cr(VI) adsorption by Zeolites in Chromium sulphate solution

concentration of 35 mg L^{-1} (Agarwal *et al*., 1999). Lotfi and Adhoum (2002) have reported a Cr (VI) removal capacity of 6.84 mg/g for modified activated carbon (sodium diethyl dithiocarbamate immobilized at the surface), which was almost two times that of plain activated carbon. The maximum adsorption capacities of Cr (VI) removal reported by Bailey *et al*. (1999) are 16.05 mg g^{-1} for sawdust, and 0.65 mg g^{-1} for Zeolite. This indicates that natural Zeolite material can be effectively removed hexavalent chromium from the solution.

CONCLUSION

From this adsorption study, the chromium was adsorbed by Zeolite very efficiently. The chromium hexavalent was adsorbed higher amount in chromium sulphate compare to potassium dichromate standard solution. It was observed that the removal percentage increased at the lower initial chromium concentration and higher adsorbent doses. The Cr (VI) adsorption by Zeolite is 92.18 µg/g from 100 µg/g of chromium sulphate solution. Hexavalent chromium was adsorbed by Zeolite upto 92% from the solution. The use of natural Zeolite material as an adsorbent seems to be an economical and worthwhile alternative over conventional methods. Hence, we can conclude that the natural Zeolite material is suited for hexavalent chromium adsorption.

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