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Control of Chrome Pollution in Tannery Wastewaters with Humic Acids

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Abstract. Tannery industry in Pakistan occupies an important place in the national economy. The magnitude of chrome effluent waste generated by the industry has rapidly multiplied during the past decade. This has caused an irreversible damage to the 'flora and fauna', which demands immediate remedial action. An effort has been made to develop indigenous means to combat chromium pollution with humic acids. Humic acids (HA) are polymeric, brown complex of compounds occurring in the aquatic, terrestrial and sedimentary environments. Soft brown coals and leonardite are major sources of humic acids, which contain up to 80% extractable humic acids. These economical, coal-derived humic acids are useful for soil and water remediation. The process reported in the present study for this purpose is simple, economical and avoids the problems associated with the disposal of bulky chromium waste produced using coagulation and other techniques.

Keywords: chrome effluents, tannery wastes, humic acids, lignitic coal, wastewaters treatment

Introduction

The rapid industrial growth in Pakistan has greatly enhanced concerns for the development of remedial measures to combat the resultant generation of industrial wastes and the water pollution problem. The leather industry occupies an important position in Pakistan's economy, ranked third in the export earnings, registering an annual growth of 24.3% during the past years (Iqbal, 1995). Because of the lack of tannery wastewater treatment facilities, the industry has caused an alarmingly irreversible degradation of the environment. There are 415 tannery units in Pakistan, out of which 50% are located in Karachi. These tannery units have an estimated installed capacity of about 47.58 million square metre of chrome leather production (Meynell and Tharwani, 1992). The tannery effluents are divided into beam-house effluents and the tanning operation effluents. During the tanning process, chrome liquor is the major pollution-causing effluent, usually containing 100-540 mg chromium per litre. This is being mixed with the beam-house effluents and discharged untreated by the tannery industries in the nearby streams and rivers or even on open land. It has been shown by various studies that along the way, chromium settles down in the sediments which finds its way via the Malir river to the Arabian sea (Beg *et al.*, 1990; Driver, 1987). Chromium-bearing tannery waste has also affected the quality of groundwater, as shown by the study where the samples of every well of the tannery area contained upto 0.39 mg per litre of chromium (Othmer, 1982). With the rapid growth of tannery industry, the level of chromium in the effluents is rising sharply and posting a constant threat to the environment, affecting aquatic life and polluting groundwater. Chromium compounds are toxic and can cause harmful and irreversible damage to health by single, repeated, or prolonged absorption (Sato *et al.*, 1979).

The tanning process itself utilizes only one-tenth of the huge amount of water consumed in leather processing. This water is acidic, highly coloured and contains alarming levels of chromium. Treatment of this water before dumping can prevent major health hazards created by the leather industry in Pakistan. The adaptation of advanced treatment technologies is not cost-effective. Therefore, there is an urgent need for the evelopment of indigenous treatment technologies, accessible to both large and small scale industries at affordable costs.

Humic acids, a lignitic coal-derived polymeric, brown complex of compounds occur in aquatic, terrestrial and sedimentary environments (Hanninen and Niemela, 1991). Due to their known ion exchange properties, the complex is widely used in metallurgical wastewater treatments (Baruah *et al.*, 1981; Ibarra *et al.*, 1979). Humic acids are essential and remarkable products of soil chemistry (Davies *et al.*, 2001). Humic acids form complexes with metals and the metal relationship capcity of humic acids is dependent on the pH and the concentration of humic acids used. The resulting metal plus the humic acids complex is non-toxic and can be utilized in agriculture and industry (Khan *et al.*, 1996). Humic acids have higher metal-binding capacities than most commercial ion exchangers and they selectively bind, store and release metals, so that they can be substituted for other more expensive, organic and inorganic adsorbents (Janos, 2005).

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A technoeconimically feasible process for the production of humic acids from lignitic Lakhra coal has been developed at the FRC-PCSIR Laboratories, Karachi, Pakistan. Keeping in view the irreversible damage caused by the chrome effluents, the necessity of controlling the point-source of pollution and the known attribution of humic acids, a study was considered appropriate to use humic acids for the treatment of metal-contaminated wastewaters. The present study was, therefore, undertaken with the objective to develop a procedure for the treatment of chromium pollution in tannery wastewaters, and the possibility of utilizing lignitic derived humic acids in the abatement of chromium pollution.

Materials and Methods

The humic acids complex was prepared from lignitic Lakhra coal. The coal was ground to 60 mesh and dissolved in mild alkali. The resulting water soluble humate was utilized in the present study. The elemental and proximate composition of the Lakhra coal and humic acids are given in Table 1.

A survey was done of seventeen tanneries from the Sindh Industrail Trading Estate (SITE) and the Korangi Industrial Area, Karachi, Pakistan. The survey showed 1200 to 10,000 litres of chrome effluent discharge per day from the tanneries located at these sites. There were very few tanneries where pretreatment facilities were available. Samples of the chrome effluents were collected immediately after the tanning process from five tanneries, having the minimum (375 ppm) to maximum (2200 ppm) chrome effluent dischange per day. The samples were collected in plastic bottles of 1 litre capacity.

Results and Discussion

Chrome retention by humic acids, as a function of pH, was determined (Table 2). To a series of 20 ml humic acids solution containing 0.01, 0.02, 0.03 g of humic acids, respectively, chromium chloride solution (20 ml) containing 520 ppm of chromium was added. pH values of the solutions were adjusted to 7.5, 8.0 and 8.5 by adding mild alkali to make up a final volume of 50 ml. The recation was noticed to take place, as the pH increased towards alkalinity, by the formation of grey coloured metal-humic acids complex, which settled down as fine precipitate while the dark-green colouration of the chrome water disapperaed. Clear water was obtained at the solution pH of 8.5. The amount of chromium in water was determined by atomic absorpation spectrometer (Perkin Elmer, model 3030B).

Table 1. Proximate and ultimate analyses of Lakhra coal and humic acids prepared from this coal (%)

Sample category	Ash	Volatile matter	Fixed carbon	C	H	N
Lakhra coal	17.23	44.50	34.19	63.31	5.09	1.87
Humic acids	4.84	44.54	38.4	57.30	4.43	6.86

Tabel 2. General metal retention ability of humic acids as a function of pH

Amount of chromium in solution (ppm)	Amount of humic acids added (g/100 ml)	pH of the solution	Amount of chromium after treatment (ppm)
520	0.01	7.5	170
		8.0	70
		8.5	12.5
	0.02	7.5	160
		8.0	5.0
		8.5	2.5
	0.03	7.5	90
		8.0	3.5
		8.5	0.45

In the second part of the study, 40 ml aliquotes of the chrome effluent samples collected from different five tannaries were taken in breakers, pH was adjusted from 8.5 to 9. To this chrome effluent was slowly added 1% humic acids solution. The amount of chromium removed was measured by atomic absorption spectroscopy, after the successive addition of humic acids solution, untill chromium removal was complete. At the end of reaction, a pH drop of 0.5 was noted.

Physical parameters of the chrome effluents, such as pH and colour, are shown in Table 3. The chrome effluents collected were highly acidic, having pH of 3.5-3.7. The lower pH was due to the conversion of sulphides to harmful H_2S gas. The effluents were dark-greenish to blue in colour. The colour of the effluents was also an important negative indicator of environmental pollution. This affected the water ecosystem through hindering light accessibility to living organisms present in the water bodies. The inadequate light affected growth of aquatic biots adversely. Thus, the indiscriminate chrome effluent discharge by tanneries of the Korangi Industrial Area is highly affecting the water quality of Malir river and then the Arabian Sea. An increasing trend in the chromium concentration discharged by the Korangi Industrial Area industries in the sediments leading to Malir river has been noted during various studies conducted earlier. Studies carried out by PCSIR laboratories have shown the amount of chromium level to be 0.25 to 0.5 ppm during 1982, and 2-14 ppm during 1985. The IUCN study performed in 1987 showed the chormium concentration

Table 3. Chrome pollution reduction using humic acids in the treatment of chrome effluents generated by the tanneries located in industrial areas of Karachi, Pakistan

Tannery identity	pH of the tannery effluent at discharge (untreated)	Amount of chromium in the untreated tannery effluent (ppm)	Amount of humic acids added for treatment (g/100 ml)	pH of the solution adjusted to	Amount of chrome after treatment with humic acids (ppm)
Karachi Tannery	3.5	375	0.01	8.5	12.5
			0.02	8.5	1.9
			0.023	8.5	0.57
			0.025	8.5	0.50
Shafi Tannery	3.5	514	0.002	8.5	197.7
			0.005	8.5	131.8
			0.010	8.5	19.0
			0.015	8.5	1.08
			0.025	8.5	0.83
Zahoor Tannery	3.7	510	0.005	8.5	600.0
			0.01	8.5	4. 28
			0.015	8.5	3.10
			0.02	8.5	1.02
			0.25	8.5	0.066
International Chrome Tannery	3.5	520	0.01	8.5	320.0
			0.02	8.5	10.5
			0.025	8.5	0.99
			0.028	8.5	0.22
Matka Tannery	3.7	2200	0.01	9.0	600.0
			0.02	9.0	175.0
			0.04	9.0	35.0
			0.06	9.0	6.4

levels of some areas to be 57 ppm (Driver, 1987). This latter study concluded that 225 tons of chromium was discharged per annum into the surrounding environment by the tanneries sector. Another study, conducted in 1993 in the same area, showed a dramatic increase in chromium level to 540 ppm, indicating over nine-fold increase in chromium concentration in the tannery wastewaters. The increase is ascribed to the rapid growth in volume of tanneries in Pakistan. Another study at the industrial city of Faisalabad, Pakistan, showed high levels of chrome effluent, containing 540 ppm of chromium being discharged, untreated, in the surrounding ecosystem causing serious groundwater pollution. Chromium is known to be toxic, causing perforations and bronchiogenic carcinoma on continuous exposure. The chromium retention activity of humic acids has been adequately shown during the present study (Table 3). This ability is pH dependent. As the metal-humic acids complex is formed, a pH drop is also noticed which is due to the increment of protons of functional groups displaced by metal ions. These initial studies have thus shown that humic acids, derived from Pakistani lignitic coals, offer an option for the abatement of pollution caused by chrome liquor.

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