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Study of Tannery Wastewater Treatability by Precipitation Process

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Abstract. A study was conducted for the removal and recovery of chromium from tannery wastewater, using NaOH, MgO, $Ca(OH)_2$ and $Al_2(SO_4)_3.18H_2O$ as precipitating agents and comparing their effect on pH, total dissolved solids (TDS), total suspended solids (TSS), sludge volume and chromium removal. MgO and $Ca(OH)_2$ produced least amount of sludge and dewatering of sludge was also easy as compared to $Al_2(SO_4)_3.18H_2O$ and NaOH. The chromium removal of MgO and $Ca(OH)_2$ was 95% and 96%, respectively.

Keywords: precipitating agents, chromium removal, tannery wastewater, sludge volume

Introduction

Pakistan leather industry is one of the major foreign exchange earners of the country. About 90% of leather products are exported in finished form. However, the operation of tanneries is causing severe environmental degradation due to the disposal of untreated effluent on land and in water bodies. High chromium concentration is harmful for environment and human health (Zayed and Terry, 2003).

In tanning process, chromium compounds are commonly used for processing of hides, 60-70% of which react with the skin and the remaining amount is discharged as effluent (Mant *et al*., 2005; Sreeram and Ramasami, 2003).

The remaining chromium (about 30-40%) in the solid and liquid waste contributes to the environmental pollution. Considering the high cost of chromium metal, it would be preferable to recover it from the wastewater (Kocaoba and Akcin, 2002; Ludvik, 2000; Fabiani *et al*., 1997).

Various methods have been used for removing toxic metal ions from aqueous solutions including chemical precipitation, ion exchange, reverse osmosis, evaporation, solvent extraction, electroprecipitation, coagulation and adsorption (Dhungana and Yadav, 2009; Rashed, 2008; Kongjao *et al*., 2007; Esmaeili *et al*., 2005; Kocaoba and Akcin, 2002). Among these, chemical precipitation is the most commonly used method. Many factors affect the process of chemical precipitation including the type of precipitation agent, pH, nature, velocity of precipitation, sludge volume, time of mixing and complexing agents (Patterson, 1985). Precipitation can be followed by coagulation and flocculation, in order to enhance sedimentation. The process is very effective for the removal of precipitated solids and is used to treat the industrial effluent before discharging them into receiving water (Noyes, 1994). The precipitation process is not always perfect and chemical characteristics of the treated wastewater may not meet the standards. Consequently, a further treatment is often necessary.

Kasur town is located 55 Km southeast of Lahore in the province of Punjab, Pakistan. The city is well known for its tanning industry with more than 250 tanneries discharging large volumes of untreated tannery waste in the form of wastewater, sludge and solid waste. There is an urgent need for the treatment of tannery effluents prior to their disposal. The main purpose of this research was to compare pH, chromium concentration, sludge volume, colour, TDS and TSS using $Al_2(SO_4)_3.18H_2O$, $Ca(OH)_2$, NaOH and MgO in the precipitation process, so as to find the best precipitating agent for chromium removal and recovery.

Materials and Methods

The study was carried out at Pakistan Council of Scientific and Industrial Research (PCSIR) Laboratories Complex, Lahore, in June 2009. Samples were brought from inlet of Kasur treatment plant and

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transported to the laboratory for determination of the most important parameters which included biological oxygen demand (BOD_5), chemical oxygen demand (COD), pH, total suspended solids, total dissolved solids, colour, conductivity and chromium concentration. Each test was performed in triplicate and the average value was reported. Analysis was carried for 12 metals namely Mn, Cd, Pb, Se, Zn, Cr, Cu, Ba, Fe, B, Ag and Hg.

All chemicals used were of analytical reagent grade; Jar test was conducted as described by Esmaeili *et al*. (2005). In the first step, 600 mg/L of each precipitating agent was added to the samples. In the second step, samples were mixed for 30 min at 670 rpm. In the last step, after 6 h settling time, samples were taken from the supernatant. To evaluate the efficiency of precipitating agent of tannery wastewater, the parameters measured were sludge volume, pH, conductivity, total dissolved solids (TDS), total suspended solids (TSS), BOD_5, colour and chromium volume.

In order to determine the sludge volume, samples were poured in calibrated cylinder and after 6 h the height of supernatant and sludge volume was read. pH was measured by digital pH meter (JENO 6173). Standard solution with pH 4, 7 and 10 were used for calibration. Conductivity, TDS, TSS, BOD_5 and COD were measured and calculated according to the standard methods for water and wastewater testing (APHA, 2005).

The colour of samples before and after treatment was measured by tintometer (LOVIBOND PFX 995). The path length of cell used was 100 mm. Before the measurement, samples were filtered to prevent turbidity.

For metal analysis, samples were digested (Iqbal *et al*., 2009) and different standard of chromium, prepared for calibration curve, were used. Atomic absorption spectrophotometer (Perkin Elmer Analyst 300) was used to measure chromium concentration in wastewater before and after the treatment. The analysis of effluent metal was carried out by inductive couple plasma (Perkin Elmer Optimum 5300).

Results and Discussion

Tannery effluents are highly polluted fluids and contain protein, colloids, fats, fragments of flesh, hair, lime, colouring matter, sulphide and chromium left after chemical tanning. It was found that no special treatment process was used for the high polluted wastewater, generated in the tannery area. The chemical characteristics of effluent (Table 1) showed high values of pH, conductivity, TDS, TSS, BOD_5, COD, chromium and colour concentration as compared to national environmental quality standard (GOP, 2000). If this wastewater is discharged without treatment, it may cause severe environmental problems. Most of the metals in the effluent were below NEQS level (Table 2). However, the concentration of chromium and iron were 25.01 ppm and 3.740 ppm, respectively, being higher than the NEQS limits.

Table 1. Characterisation of effluent of tannery treatment plant, District Kasur number of samples=6

Parameters	Range (effluent) (mg/L)	NEQS limits (mg/L)
pH (unsettled effluent)	7.5-10	6-10
Conductivity, (ms/cm)	16.0-18.0	—
Total dissolved solid*, (mg/L)	9214-12000	3500
Total suspended solid*, (mg/L)	400-600	150
Chloride*, (mg/L)	2000-3000	1000
BOD_5*, (mg/L)	800-4000	80
COD*, (mg/L)	1300-6500	150
Chromium*, (mg/L)	25-50	1.0
Colour, Pt-Co/Hazan	500-510	—
Unsettled effluent		—

* = (30 min settling).

Table 2. Results of metal analysis of tannery effluent treatment plant, District Kasur

Metals	Measured value (mg/L)	NEQS limits (mg/L)	Metals	Measured value (mg/L)	NEQS limits (mg/L)
Mn	0.0172	1.5	Cu	0.078	1.0
Cd	N.D	0.1	Ba	0.231	1.5
Pb	0.041	0.5	Fe	3.740	2.0
Se	0.012	0.5	B	0.698	6.0
Zn	0.030	5.0	Ag	0.001	1.0
Cr	25.01	1.0	Hg	ND	0.01

ND = not detected.

Effect of precipitating agents on pH. pH of solution is an important factor in precipitation process. pH was greatly affected when different precipitating agents were added (Fig. 1). pH increased to 12.76 after 50 min of adding NaOH. However, the values of pH in case of MgO, $Ca(OH)_2$ and $Al_2(SO_4)_3.18H_2O$ were 9.99, 12.18 and 7.45, respectively. The literature shows that the optimum pH for chromium removal in case of MgO is 7-8 (Pansward *et al*., 1995).

Effect of precipitating agents on chromium concentration. Same amount of each precipitating agents was added for comparison of maximum chromium removal and minimum sludge production. The percentage removal of chromium in case of NaOH was much less (Fig. 2). Since NaOH increases the pH causing peptizing and chromium is re-dissolved, hence chromium concentration in supernatant increases. However, with MgO, $Ca(OH)_2$ and $Al_2(SO_4)_3.18H_2O$ percentage removal of chromium was 95%, 96% and 94%, respectively (Table 3).

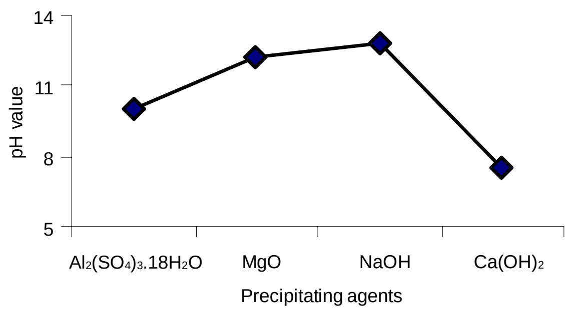

Fig. 1. Variation of pH for the four precipitating agents.

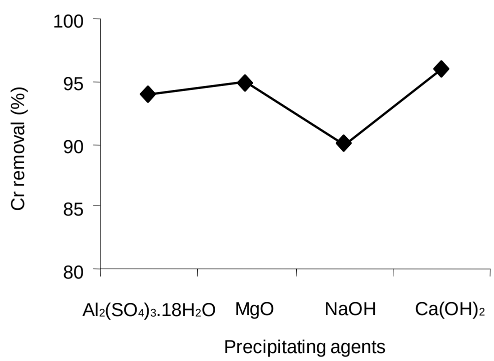

Fig. 2. Percentage removal of chromium (—◆—) for the four precipitating agents.

Effect of precipitating agents on TDS and TSS. Percentage removal of TDS and TSS are shown in Fig. 3. Better results were obtained in case of MgO and $Ca(OH)_2$ as compared to NaOH and $Al_2(SO_4)_3.18H_2O$. The results of BOD_5 for all precipitating agents were very good and below NEQS level.

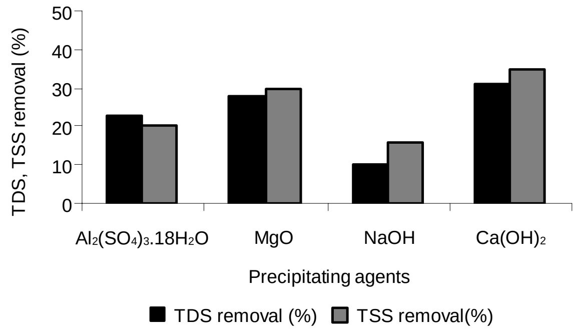

Fig. 3. Effect of precipitating agents on TDS and TSS removal.

Effect of precipitating agents on colour removal. The effect of precipitation on colour removal was good and showed that this process was effective for the colour reduction. Substances producing colour consist either of colloidal metallic hydroxides (e.g., iron hydroxides) or of organic compounds (e.g., dyestuff), which have a much smaller particle size. These substances can be removed by coagulation, which serves to agglomerate very small particles into sizes that can be settled or can be removed by filters or absorption. (Aboulhassan *et al.*, 2008); Fig. 4 shows the percentage removal of colour, 78% colour was removed when $Ca(OH)_2$ was used as precipitating agent and 40% in case of NaOH. Colour removal of MgO and $Al_2(SO_4)_3.I8H_2O$ were 60% and 63%, respectively.

Table 3. Residual values and percentage removal of various parameters after treatment of tannery wastewater with different precipitating agents

Parameters	$Al_2(SO_4)_3.18H_2O$		MgO		NaOH		$Ca(OH)_2$	
	Residual value	Percentage removal	Residual value	Percentage removal	Residual value	Percentage removal	Residual value	Percentage removal
Colour	85	63	209	60	305	40	109	78
TDS (mg/L)	9200	23	8600	28	9900	10	8181.8	31
TSS (mg/L)	490	20	400	30	598	16	400	35
BOD_5 (mg/L)	35	98	28	99	44	90	4	99
Cr (mg/L)	0.986	94	1.015	95	1.376	90	0.935	96

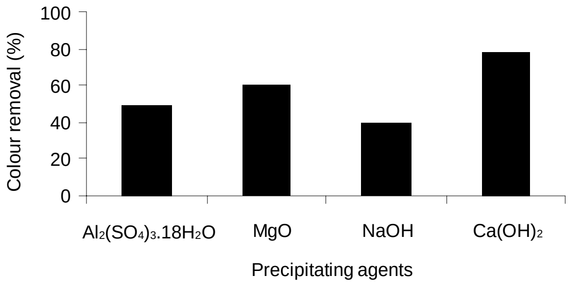

Fig. 4. Effect of precipitating agents on colour removal.

Effect of precipitating agent on sludge volume. $Al_2(SO_4)_3.I8H_2O$ and NaOH produced very large amount of sludge, as compared to MgO and $Ca(OH)_2$ (Fig. 5). The sludge from MgO and $Ca(OH)_2$ was grainy, dense, easily settleable and de-watering could be easily carried out for recovery of chromium. However, sludge obtained from NaOH and $Al_2(SO_4)_3.18H_2O$ was very gelatinous and dewatering of sludge was difficult which created problem in the recovery of chromium and large area was required for sludge storage (Esmaeili *et al*., 2005; Pansward *et al*., 1995). Thus MgO and $Ca(OH)_2$ produced the least amount of sludge and the removal of colour, TDS and TSS was better as compared to NaOH and $Al_2(SO_4)_3.18H_2O$.

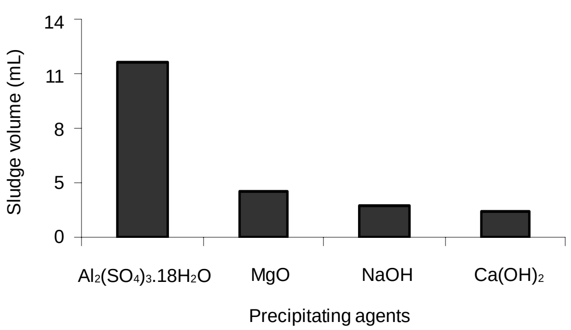

Fig. 5. Effect of precipitating agents on sludge volume.

Conclusion

The results showed that MgO and $Ca(OH)_2$ as precipitating agents produce less amount of sludge and chromium removal from the supernatant yielded good result. For the recovery of chromium dewatering of sludge was also easily done. However, NaOH and $Al_2(SO_4)_3.18H_2O$ produced large volume of sludge and dewatering of the sludge was difficult. The percentage removal of colour was 78%, 40% when $Ca(OH)_2$ and NaOH were used. Colour removal of MgO and $Al_2(SO_4)_3.I8H_2O$ were 60% and 63%, respectively. It is concluded that for the removal and recovery of chromium, MgO and $Ca(OH)_2$ are much more desirable precipitating agents than NaOH and $Al_2(SO_4)_3.18H_2O$.

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