African Journal of Environmental Science and Technology Vol. 5(6), pp. 409-419, June 2011
Available online at http://www.academicjournals.org/AJEST
ISSN 1996-0786 ©2011 Academic Journals

Full Length Research Paper

Efficiency of different coagulants combination for the treatment of tannery effluents: A case study of Bangladesh

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Accepted 30 May, 2011

This study has focused on the physico-chemical parameter of tannery effluents as well as the treatment efficiency of alum, ferric chloride and lime, addressed as different treatments. Sample collection and analysis were performed using standard method. Pollutant removal efficiency was measured in terms of reduction in value of total solid (TS), suspended solid (SS), total dissolved solid (TDS), color, pH, [Cl^-], Alkalinity, biological oxygen demand (BOD_5), chemical oxygen demand (COD), [Cr^{6+}] and salinity. While analyzing the physico-chemical parameters of the tannery effluents, before treating with coagulants, the odor of the effluents was found to be invariably objectionable. After treatment of the tannery effluents, the lowest value for color (246.67 in Hazen unit) was found in the treatment T_5, pH value 7.13 was found in treatment T_7 followed by 7.23 in T_2 and T_6, the lowest TS (3833.33 mg/L) was recorded in the treatment T_5 and SS observed as 0 mg/L in case of both T_5 and T_1 treatments. Cr^{6+} concentration was reduced considerably in treatment T_5 (0.03 mg/L) and T_7 (0.07 mg/L). Reduction in values of TDS, alkalinity, salinity, Cl^-, BOD5 and COD in treated effluents was also notable. The study recommended the combination of alum and ferric chloride (T_5) as well as alum (T_1) for the effective primary treatment of tannery effluents.

Key words: Coagulation, alum, lime, ferric chloride, biological oxygen demand (BOD_5) and chemical oxygen demand (COD).

INTRODUCTION

All sectors of our society like industry, agriculture, mining, energy, transportation, construction and consumers generate wastes. Industrial wastes are usually generated from different industrial processes, as a result the amount and toxicity of waste released from industrial activities varies with the industrial processes. Again, among all the industrial wastes tannery effluents are ranked as the highest pollutants (Shen, 1999). In developing countries, many industrial units are operating in a small and medium scale. These industrial units can generate a considerable pollution load by discharging untreated effluents directly into the environment due to the poor enforcement of law. For example, there are nearly 300 tanneries in Hazaribagh, Dhaka; which are discharging about 18,000 L of liquid waste, 115 tones of solid wastes during off-peak time daily (SEHD, 2002). According to a recent estimate, about 60,000 tones of raw hides and skins are processed in these tanneries every year, which release nearly 95,000 L of untreated effluents into the open environment daily, resulting into a dead river, named Buriganga (Rusal et al., 2006). There is an increasing society concern with regard to the importance of the preservation of our environment and the corresponding legislation which regulates effluents

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discharges. So any contaminating substance which, though having been processed, is not of free disposition, represents a “mortgage” for the industry.

There are considerable dissimilarities in the concentration range of pollutants in tannery wastewaters given by different authors (Ates et al., 1997; Balasubramian et al., 1999; Bartkiewicz, 2000; Dhungana and Yadav, 2009; Krishanamoorthi et al., 2009; Nourisepehr et al., 2005), but all of the authors observed that the tannery industry causes horrendous environmental pollution and high environmental impact of tannery effluents makes its treatment an essential fact, mainly due to its volume, nature and concentration of pollutants such as tanning agents (chromium and tannin), color, organic matter and others (Mohanta et al., 2010). So, the treatment of tannery effluents is a matter of great concern in the country having leather tanning industry. As a result, a number of research work carried out around the world regarding the treatment of tannery effluents using different technology. For example, Dhungana and Yadav (2009), worked on adsorption of hexavalent chromium from tannery effluents using formaldehyde treated sawdust and charcoal of sugarcane begasses. Again some of the authors, studied on the treatment tannery waste water using filtration, ultra-filtration and reverse osmosis process with a view to reuse it again (Krishanamoorthi et al., 2009). Several studies have been carried out for the treatment of industrial effluents through coagulation and flocculation process (Shouli et al., 1992; Stephenson and Duff, 1996).

A few studies focused on bio-remediation of tannery effluents (Haydar et al., 2007; Nourisepehr et al., 2005). But in Bangladesh, most of the work regarding tannery effluents is related to their characterization and impact assessment (Das et al., 2006; Mohanta et al., 2010; SEHD, 2002). Nobody worked on treatment of tannery effluents in Bangladesh. Coagulation or chemical precipitation has been known for treatment of waste water, since the previous century in England, where lime was used as coagulant alone or in combination with calcium chloride or magnesium (Genovese and Gonzale, 1998). So, for the first time in this study, an attempt has been taken to analyze the efficiency of different coagulants to treat the tannery waste water of Bangladesh. There are also other advanced treatment processes available around the world, yet in this study considering the socio-economic aspect of Bangladesh low cost coagulant has been chosen for the treatment of tannery effluents.

METHODOLOGY

Study area

The study was conducted in Madina tannery, the largest tannery in Chittagong, which is situated at Jalalabad area near Oxygen point (22°23’40.63" N and 91°49’14.36"E; elevation 41 feet). The tannery is comprised of two units. Established in 1983, Madina Tannery is a renowned manufacturer of all sorts of Crust and Finished leather in Bangladesh. Every year, it exports crust and finished leather to the USA, Italy, Portugal, Mexico, France and Australia. A considerable proportion of on-going urban development is marked within 1 km area around Madina Tannery. Chittagong University railway line passes by on the back side of the tannery factory buildings.

After the railway line, there are series of hillocks trending north-south direction. A super refinery industry is situated at the south boundary of the industry. Towards the north direction, there are some crop fields, some isolated residential quarters. The area is drained by an extensive network of seasonal, intermittent and perennial streams and streamlets. Besides these, the whole industrial area is criss-crossed with a number of drains. Rainfall average is 2870 mm (113 in) annually and the rain and other waste water from the premises of the industry are drained out quickly through these stream and drains which directly affect the adjacent agricultural field.

Sampling

For the present investigation, all the samples were collected at the same time from three different places of pre discharge drain to sedimentation tank, sedimentation tank and final outlet of the waste water discharge system of Madina Tannery during the period of January to March, 2009. These three replications were treated with various combinations of coagulants under laboratory condition. Effluents of industrial waste were collected into plastic bottles.

Those plastic bottles were thoroughly cleaned with 8 M nitric acid solution followed by repeated washing with distilled water and dried over night. After collection, physical appearance and temperature of the samples were recorded and 1.5 ml of concentrated nitric acid per liter of sample was added as preservative (Dhungana and Yadav, 2009). In the laboratory 1:5 (volume) H_2SO_4 solution (Ramesh et al., 2007) and NaOH (1, 12 or 25%) (Klimiuk et al., 1999) were used to adjust the pH of the waste water and thus observing the impact of the pH on the coagulation. The different treatments under which the study was performed are as follows:

T_0: Raw tannery effluent
T_1: Tannery effluent treated with alum
T_2: Tannery effluent treated with lime
T_3: Tannery effluent treated with ferric chloride
T_4: Tannery effluent treated with alum + lime
T_5: Tannery effluent treated with alum+ ferric chloride
T_6: Tannery effluent treated with lime + ferric chloride
T_7: Tannery effluent treated with alum + lime + ferric chloride

Preparation of the single and mixed coagulant system

Three coagulants, that is alum, ferric chloride and lime were used in various combinations for the experiment. Each of this coagulant weighed individually (15 g) and dissolved in the 1 L of distill water. After rigorous mixing, different doses (20 to 100 mg/L) of coagulant solution were taken to treat 1 L of tannery effluent. Different combinations of coagulants were alum and ferric chloride; alum and lime; ferric Chloride and lime; alum, ferric chloride and lime. Mixed coagulants were added at the same time and at the same ratio.

Flocculation experiment

The jar test is the most widely used method for evaluating and optimizing the flocculation processes (Najm et al., 1998). This study consists of batch experiments involving rapid mixing, slow mixing and sedimentation. The apparatus allowed six beakers to be agitated simultaneously. Tannery waste water with different

Table 1. Physical characteristics (appearance, odor and color) of tannery effluents of Madina Tannery, Chittagong under laboratory condition at 70 mg/L coagulant dose.

Treatments	Appearance	Odor	Color (Hazen unit)
T_0	Bluish green	Objectionable	1966.67[a*]
T_1	Clear	Unobjectionable	286.67[d]
T_2	Light blue	Objectionable	473.33[c]
T_3	Clear	Objectionable	343.33[d]
T_4	Light blue	Objectionable	353.33[d]
T_5	Clear	Unobjectionable	246.67[d]
T_6	Black	Objectionable	943.33[b]
T_7	Clear	Objectionable	926.67[b]

***-** Means followed by the same letter (s) in the same column do not vary significantly at P<0.05, according to Duncan's Multiple Range Test (DMRT).

combination of coagulants was agitated in a flocculator at 100 rpm for 1 min and then 30 rpm was quickly established for 10 min. After slow mixing, the beakers were carefully removed from the flocculator and any floc formed was allowed to settle for 60 min; the clear liquor ranging from the liquor level to 25 mm below the level was taken out for analysis. The different temperature chosen for jar experiments were in the range of 5 to 35°C.

Analysis and data processing

An analytical balance (Delta range, model PM4600, Mettler Instruments, Greifensee, Switzerland) was used for all the determination of weight throughout the experiments. The pH of the samples was determined using a pH meter (model pHs-25, made in China). All the pollutant parameter except the heavy metal [Cr^{6+}] were analyzed following the procedure as per the Standards Methods for the Examination of Water and Wastewater (APHA-AWWA-WPCF, 1998). The [Cr^{6+}] concentration was determined using a spectrometer (HACH DR, model 2000, Fisher Scientific, Pittsburgh, PA) at a wavelength setting of 540 nm. The data were analyzed using MS Excel and the SPSS- 16.

RESULTS AND DISCUSSION

Characterization of tannery effluents before and after treatment

Physical characteristics

Different physical characteristics of tannery effluents after and before treating with different coagulants combination is shown in Table 1. Differences in appearance were observed in different treatment such as bluish green (T_0), clear (T_1, T_3, T_5 and T_7), light blue (T_2 and T_4) and black (T_0). The results obtained are in agreement with Dhungana and Yadav (2009), who reported colorless, clear, dirty, light green and green appearance for tannery effluents of different tanneries from Bara and Parsa districts of Nepal; and Nourisepehr et al. (2005), who reported the color of tanning house effluent as dark blue, due to chromium cation. Odor was found unobjectionable only in T_1 and T_5 but objectionable in the rest of the treatments. The highest value of color (1966.67 in Hazen unit) was found in treatment T_0 and the lowest (246.67 in Hazen unit) in T_5. Responses from all the seven treatments were significantly (P<0.05) different from that of T_0 (Table 1).

Chemical characteristics

Different chemical properties of the tannery effluents after and before treatments have been presented in Tables 2 and 3. The nearest to neutral pH value were found in treatment T_7 (7.13), T_2 (7.23), T_6 (7.23) and T_4 (7.3), whereas pH of raw effluents (T_1) was 10.43 (Table 2). Nourisepehr et al. (2005), reported pH of the tannery effluents as 3 to 3.5, which was a very acidic condition, whereas Krishanamoorthi et al. (2009), observed pH of tannery effluents as 8 to 9. The lowest TS (3833.33 mg/L) were found in T_5 followed by 4333.33 mg/L in T_1 and the highest in T_0 (12333.33 mg/L). The initial SS of the tannery effluents was 2533.33 mg/L, which are in agreement with studies carried out by Nourisepehr et al. (2005), who reported SS in the tannery effluents in the range of 2500 to 3000 mg/L. No SS was observed in T_1 and T_5 treatments. The lowest TDS (4200 mg/L) was found in T_5 followed by T_1 (6000 mg/L). The lowest alkalinity (TA) was recorded in T_1 (1.2 mg/L) followed by T_2 (2.3 mg/L) and in T_4 (3.01 mg/L) treatments. The lowest salinity (632.5 mg/L) was found in T_7 followed by T_4 (649 mg/L) (Table 2).

The lowest [Cl^-] concentration was found in T_7 (383.33 mg/L) followed by T_4 (393.33 mg/L) and T_3 (406.67 mg/L) in comparison with the raw effluents (T_1) concentration of 483.33 mg/L. The present findings markedly deviate from the study of Nourisepehr et al. (2005), who reported 5000 to 6000 mg/L of [Cl^-] concentration in the raw tannery effluents. There was significant difference between the concentrations of BOD_5 at different treatment. The lowest BOD_5 was recorded in T_6 (420 mg/L) followed by T_7 (665

Table 2. Chemical characteristics (pH, TS, SS, TDS, TA, salinity) of tannery effluents of Madina Tannery, Chittagong under laboratory condition at 70 mg/L coagulant dose.

Treatments	pH	(mg/L)				
		TS	SS	TDS	TA	Salinity
T_0	10.43^{a*}	12333.33^{a}	2533.33^{a}	9866.67^{a}	4.9^{a}	797.5^{a}
T_1	6.83^{b}	4333.33^{d}	0^{d}	6000^{c}	1.24^{f}	698.5^{b}
T_2	7.23^{b}	7566.67^{c}	223.33^{cd}	7233.33^{b}	2.35^{e}	698.5^{b}
T_3	5.73^{c}	7966.67^{c}	510^{bc}	7066.67^{b}	3.6^{c}	671^{b}
T_4	7.3^{b}	7100^{c}	580^{bc}	6200^{c}	3.01^{d}	649^{b}
T_5	5.57^{c}	3833.33^{d}	0^{d}	4200^{c}	3.3^{cd}	704^{b}
T_6	7.23^{b}	10100^{b}	593.33^{bc}	9333.33^{a}	4.8^{b}	687.5^{b}
T_7	7.13^{b}	9250^{b}	870^{b}	7700^{b}	3.25^{cd}	632.5^{b}

***-** Means followed by the same letter (s) in the same column do not vary significantly at P<0.05, according to Duncan's Multiple Range Test (DMRT).

Table 3. Chemical characteristics (Cl^-, BOD_5, COD, Cr^{6+}) of tannery effluents of Madina Tannery, Chittagong under laboratory condition at 70 mg/L coagulant dose.

Treatments	Cl^-	(mg/L)		
		BOD_5	COD	Cr^{6+}
T_0	483.33^{a*}	4760^{a}	6650^{a}	70.33^{a}
T_1	423.33^{b}	2460^{b}	1329.33^{cd}	0.53^{b}
T_2	423.33^{b}	1453.33^{c}	2632^{b}	0.53^{b}
T_3	406.67^{b}	900^{d}	1349.33^{c}	0.62^{b}
T_4	393.33^{b}	713.33^{e}	1200^{e}	0.2^{b}
T_5	426.67^{b}	710^{e}	1242de	0.03^{b}
T_6	416.67^{b}	420^{f}	1230^{e}	0.09^{b}
T_7	383.33^{b}	665^{e}	1150^{e}	0.07^{b}

*- Means followed by the same letter(s) in the same column do not vary significantly at P<0.05,

mg/L) and T_5 (710 mg/L) in comparison with the BOD_5 of raw effluents (4760 mg/L). It has been reported by Nourisepehr et al. (2005), that the range of BOD_5 in tannery waste water is 3000 to 3500 mg/L. COD was observed in its lowest concentration in T_4 (1200 mg/L) in comparison with highest concentration (6650 mg/L) of raw effluents (T_1). [Cr^{6+}] concentration was remarkably reduced in T_5 (0.03 mg/L) followed by T_7 (0.07 mg/L) and T_6 (0.07 mg/L) in comparison with the highest value (70.33 mg/L) of T_0. All of the lowest values of the above mentioned chemical characteristics were significantly varied (P<0.05) with T_0 which represents the highest value for all parameters (Table 3).

The findings of the present study are also in agreement with SEHD (2002), where the BOD_5 and COD of the tannery waste waster in Bangladesh are reported as 14675 and 24400 mg/L at the highest and 2439 and 3400 mg/L at the lowest, respectively. The present findings are in agreement with Das et al. (2006), who also studied different physico-chemical parameters as well as metal concentration of the effluent discharged by the Madina Tannery. Das et al. (2006), reported pH and TDS, SS, [Cl^-], BOD, COD and chromium in the ranges of 3.4 to 12.8, 570 to 85340, 68 to 2384, 69 to 23125, 1148 to 8875, 2068 to 16231 and 26 to 68.53 mg/L respectively. The physico-chemical characteristics of the effluents of the Madina Tannery that was investigated during the present study, are also comparable with some other tanning industries located in Chittagong. Rahman (1997) reported different physico-chemical characteristics of Orient Tannery, Madina Tannery, Rift Leather Complex and Prexis Tannery industries located in Chittagong. Rahman (1997) reported the value of pH and concentration of BOD_5, COD, SS, chloride, and chromium of Orient Tannery as 4.9, 8400, 12500, 23945, 24000 and 43.8 mg/L respectively; in Rift Leather Complex, pH, BOD_5, COD, SS, chloride and chromium as 9, 12000, 13800, 25886, 38000 and 479.1 mg/L respectively; and the value of pH (8.8), BOD_5 (11400 mg/L), COD (17500 mg/L), SS (9003 mg/L), Chloride (62500 mg/L) and Chromium (80.6 mg/L) much higher in Praxis Tannery.

The present study showed better results in terms of

Table 4. Comparison between the present findings and characteristics of the tannery liquid waste in Bangladesh.

Parameter	Characteristics of tannery liquid waste*	Present findings							
		T_0	T_1	T_2	T_3	T_4	T_5	T_6	T_7
Color	2480-4800 (TCU)	1966.67	286.67	473.33	343.33	353.33	246.67	943.33	926.67
pH	8.6-10.5	10.43	6.83	7.23	5.73	7.3	5.57	7.23	7.13
TS (mg/L)	3261-16953	12333.33	4333.33	7566.67	7966.67	7100	3833.33	10100	9250
SS (mg/L)	1320-5253	2533.33	0	223.33	510	580	0	593.33	870
TDS (mg/L)	1805-16150	9866.67	6000	7233.33	7066.67	6200	4200	9333.33	7700
TA (mg/L)	868-1060	4.9	1.24	2.35	3.6	3.01	3.3	4.8	3.25
Cl^- (mg/L)	820-1980	483.33	423.33	423.33	406.67	393.33	426.67	416.67	383.33
BOD_5 (mg/L)	660-1350	4760	2460	1453.33	900	713.33	710	420	665
COD (mg/L)	470-920	6650	1329.33	2632	1349.33	1200	1242	1230	1150
Cr^{6+} (mg/L)	1.2-3.2	70.33	0.53	0.53	0.62	0.2	0.03	0.09	0.07

*Source: Rahman, 1997.

Table 5. Comparison between the findings of the present study and the standards of waste discharge quality of industrial units in Bangladesh.

Parameter	Standards*			Present findings							
	[I]ISW	[II]PSSTP	[III]IL	T_0	T_1	T_2	T_3	T_4	T_5	T_6	T_7
pH	6-9	6-9	--	10.43	6.83	7.23	5.73	7.3	5.57	7.23	7.13
TS (mg/L)	2100	2100	2100	12333.33	4333.33	7566.67	7966.67	7100	3833.33	10100	9250
SS (mg/L)	150	500	200	2533.33	0	223.33	510	580	0	593.33	870
TDS (mg/L)	2100	2100	2100	9866.67	6000	7233.33	7066.67	6200	4200	9333.33	7700
Cl^- (mg/L)	600	600	600	483.33	423.33	423.33	406.67	393.33	426.67	416.67	383.33
BOD_5 (mg/L)	50	250	100	4760	2460	1453.33	900	713.33	710	420	665
COD (mg/L)	200	400	400	6650	1329.33	2632	1349.33	1200	1242	1230	1150
Cr^{6+} (mg/L)	0.1	1	1	70.33	0.53	0.53	0.62	0.2	0.03	0.09	0.07

*Source: (GOB, 1997; ECR, 1997). [I]ISW = Inland Surface Water; [II]PSSTP = Public Swear at Secondary Treatment Plant; [III]IL = Irrigated Land.

reduction in values of color, pH, SS after treatment using coagulants in comparison with the ranges set by Rahman (1997). One of the major findings of the present study was the reduction of Chromium Hexavalent [Cr^{6+}] concentration, because all the treatment reduced [Cr^{6+}] concentration more than 99%, whereas the initial concentration in the raw effluent was 70.33 mg/L (Table 3). Dhungana and Yadav (2009), noticed chromium in tannery waste water in the range of 0.06 to 345 mg/L and Nourisepehr et al. (2005), reported chromium concentration in the tannery effluents was 1000 to 1300 mg/L. During the present study all the different combination of coagulants removed [Cr^{6+}] quite well. Particularly T_5 (0.03 mg/L) followed by T_7 (0.07 mg/L) in comparison with the range set by Rahman (1997) (Table 4). The entire investigated initial (prior-treatment) physico-chemical characteristics of tannery effluents discharged by the Madina Tannery, Chittagong have crossed the limit of different standard like, Waste Discharge Quality Standards for Industrial Units, Bangladesh; Drinking water quality standard of Bangladesh and WHO (Tables 5 and 6). Table 5 shows the comparison between the present findings and the standards of waste discharge quality of industrial units in Bangladesh. During the present study pH, TS, SS, Chloride, BOD_5, COD, SS and chromium in the tannery effluents before treatment were found almost double than that of the standard limit fixed for the Industrial Units, Bangladesh (ECR, 1997; GOB, 1997). The initial pH (10.43) of tannery effluents crossed the range of both inland surface water (6 to 9) and Public Sewer at Secondary Treatment Plant (6 to 9) in Bangladesh. The near neutral pH value was achieved applying different combination of coagulant system (by treatment T_2, T_6, T_7 and T_4) during the present study (Table 5).

The present findings clearly revealed the SS concentration was possible to keep below different standard by treating with different combination of coagulants, even 0 mg/L by applying T_1 and T_5 treatments (Table 5). In the present investigation, it was possible to limit the value of chloride below the standard (600 mg/L) of inland surface water, Public Sewer at Secondary Treatment Plant and irrigated land in Bangladesh. During the present investigation chromium concentration was remarkably

Table 6. Comparison among the present findings and the River Water Quality (Halda River, Chittagong) and Drinking Water Standards (Bangladesh and WHO).

Parameter	Quality/Standards*			Present findings							
	[I]RW	[II]BGD	[III]WHO	T_0	T_1	T_2	T_3	T_4	T_5	T_6	T_7
pH	7.2	6.5-8.5	6.5-8.5	10.43	6.83	7.23	5.73	7.3	5.57	7.23	7.13
TA (mg/L)	70	--	--	4.9	1.24	2.35	3.6	3.01	3.3	4.8	3.25
SS (mg/L)	1000	10	--	2533.33	0	223.33	510	580	0	593.33	870
TDS (mg/L)	--	1000	1000	9866.67	6000	7233.33	7066.67	6200	4200	9333.33	7700
Cl^- (mg/L)	200	600	250	483.33	423.33	423.33	406.67	393.33	426.67	416.67	383.33
BOD_5 (mg/L)	1.2	0.2	--	4760	2460	1453.33	900	713.33	710	420	665
COD (mg/L)	18	4	--	6650	1329.33	2632	1349.33	1200	1242	1230	1150
Cr^{6+} (mg/L)	0.09	0.05	0.05	70.33	0.53	0.53	0.62	0.2	0.03	0.09	0.07

*Source: Chittagong Water and Sewage Authority (CWASA, 2004), Personal communication of CWASA and different unpublished report) and WHO (2004). [I]RW = Considering the maximum value of river water (Halda River, Chittagong). [II]BGD = Drinking water standard for Bangladesh. [III]WHO = Drinking water standard by WHO.

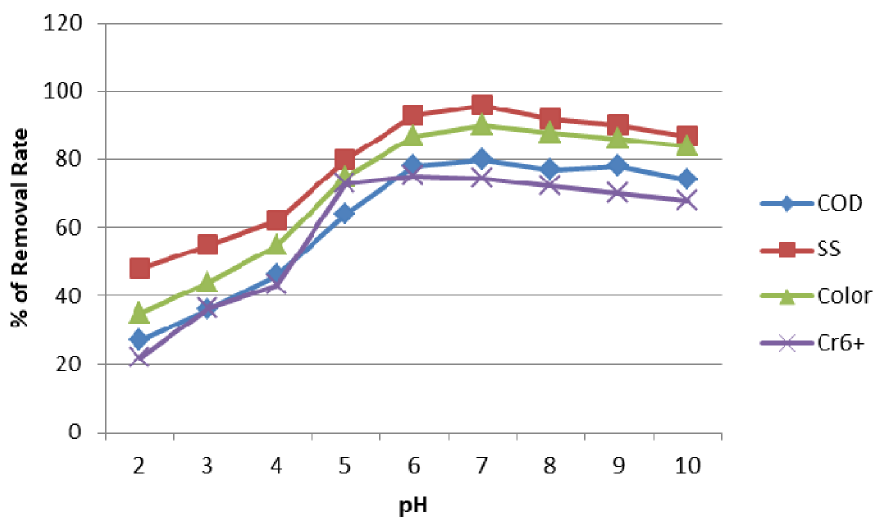

Figure 1. Effect of pH on coagulation.

reduced in comparison with the standard for inland surface water, Public Sewer at Secondary Treatment Plant and irrigated land, respectively in Bangladesh (Table 5).

In Bangladesh, most of the industrial units located in Dhaka, Khulna and Chittagong, which are used to directly discharge the untreated effluents into the nearby rivers. All of these industries pollute the adjacent river and no doubt that tanneries are the notorious one (SEHD, 2002). In Dhaka, the tannery industries of Hazaribagh area discharge their waste water into the Buriganga River through three outlets (Rahman, 1997). From the present investigation, it revealed that treatment T_2 (7.23), T_6, (7.23), T_7 (7.13) and T_4 (7.3) could lowered the pH value of tannery effluents at nearly neutral level (Table 6). For SS, the river (Halda) water quality was 1000 mg/L, whereas the treatment T_1 and T_5 successfully reduced to 0 mg/L. In Halda River water chromium hexavalent (Cr^{6+}) was found to be 0.09 mg/L and the Madina tannery discharged the effluent containing 70.33 mg/L. The present investigation revealed that coagulants are excellent for the treatment of Cr^{6+} because all the treatments remarkably reduced the Cr^{6+} concentration such as treatment T_5 reduced the Cr^{6+} concentration to 0.03 mg/L followed by T7 (0.07 mg/L) (Table 6).

Factors affecting the treatment efficiency

Effect of pH on coagulation

Under normal temperature condition, a dilute solution of sulfuric acid and sodium hydroxide were used to adjust the pH of the waste water and thus the impact of the pH on the coagulation was observed. The outcome of this experiment is shown in Figure 1. From Figure 1 it can be

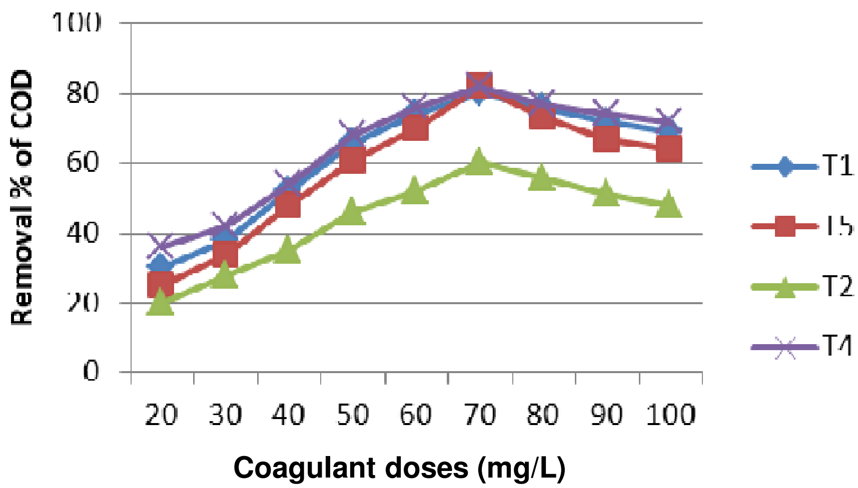

Figure 2. Effect of coagulant doses on the removal of COD.

inferred that, pH value has a significant influence on the coagulation effect of coagulants. Certainly in the range from 5 to 9, pH value has the most effect on the coagulation process and removal of different pollutants. The colloid substances in the tanning waste water usually carry negative electrical charges, whereas different coagulant combination possess a lot of [Al^{3+}] and [Fe^{3+}] ions. In the optimal range of pH value Al (III) and Fe (III) are hydrolyzed into mononuclear and multi nuclear hydroxyl complex ions, which have the capability of electrical neutralization and are able to absorb particles and compress electric double layer for destabilization of the particles (Ratnaweera et al., 1992).

So, pollutant removal is highest at pH 7 and at this level the removal rate was 96.35, 90.62, 80.22 and 74.65% for SS, color, COD and Cr^{6+}, respectively (Figure 1). It was observed that, [Cr^{6+}] removal increased from the pH value of 3 to 6 (Figure 1). The lower adsorption values observed at low pH can be attributed to the competition between protons and [Cr^{6+}] for available binding sites. The adsorption increases at pH range from 3 to 6, since [Cr^{6+}] are cationic and predominant adsorption process must have been electrostatic (Okuda et al., 2001). Rossi and Ward (1993), reported that below pH 2, almost all the binding sites were occupied by proton and the metal binding could not be expected. As the pH value increased, [Cr^{6+}] begun to bind to the functional group and the maximum binding occur at pH 4.3. At lower pH the $CrOH^{2+}$ binding remained at a lower level than that of [Cr^{6+}].

However, it gradually increased with the pH, eventually exceeding the level of Cr^{6+} binding at pH greater than 4.5 (Gregory and Guibail, 1991), which was also observed in the present study, because [Cr^{6+}] removal percentage was highest at pH 5 and it gradually deteriorates as the pH increases. This finding suggested that, in the pH range 2 to 5, the adsorbent surface might have different affinities to chromium present in the solution and their affinities to chromium ions are strongly affected by the pH value of the solution (Vlyssides et al., 2002).

Effect of coagulants doses on coagulation

Under normal temperature and at pH 7, coagulants were used to treat the waste water and Figures 2 and 3 reveal the effect of the coagulants doses on the removal of COD and [Cr^{6+}]. From the figures it can be seen that, T_4, T_5 and T_1 shows better removal of pollutant than that of T_2. As the doses of the coagulant increases, the removal rate of COD and [Cr^{6+}] rises apparently. When the coagulant doses reach 60 mg/L, the removal rate for the pollutant starts to slow down. When the coagulant doses reach 70 mg/L, the removal rate of COD and [Cr^{6+}] was at its peak. After that, the removal rate is gradually decline as the coagulant doses increases. When the coagulant dose is too small, the coagulation is insufficient, resulting in a poor effect of coagulation. When the coagulant dose is too high, the particle in the waste water are enclosed by too much coagulant and as a result their surfaces are saturated resulting into, reduction of chance of the particle to combine with each other and reach another state of stability, in which it is hard for the particles to coagulate (Gregory and Guibail, 1991).

Effect of temperature on coagulation

The relationship between temperature and removal rate of COD is shown in Figure 4. As the temperature increases, the viscosity of waste water decreases and brown movement become fierce gradually, as a result the inorganic coagulant hydrolyzes quickly and the coagulation processes is accelerated (Stephenson and Duff, 1996). Under the experimental conditions, sufficient time is provided for reaction and sedimentation. So the impact

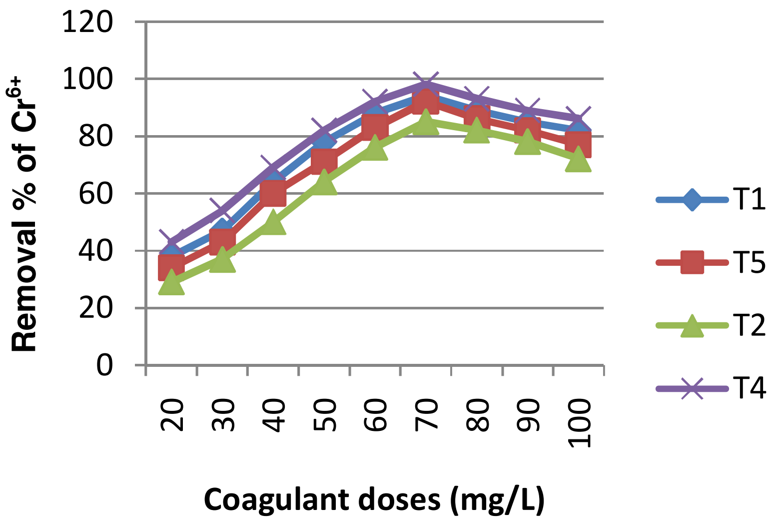

Figure 3. Effect of coagulant doses on the removal of Cr^{6+}.

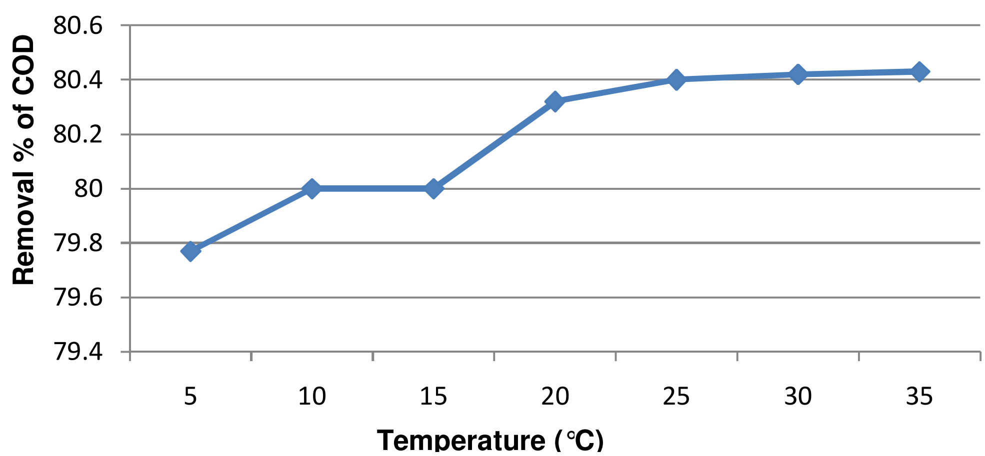

Figure 4. Effect of temperature on the removal of COD.

of temperature on the removal rate of COD is very little (Figure 4).

Comparison of the removal percentage by different coagulants

The highest (87.46%) percent reduction in value of color was recorded in the T_5 treatment (Figure 5). SS was completely reduced (100%) both in the T_1 and T_5 treatments. The next best performance (91.19%) was achieved in T_2 in reducing the SS (Figure 6). While for the percent reduction of chromium hexavalent [Cr^{6+}] was tremendously successful because all the treatments reduced [Cr^{6+}] concentration more than 99% but the highest performance was shown by T5 (99.96%) followed by T_7 (99%) (Figure 7). Similarly, the highest (68.92%) reduction in value of TS was observed after the application of T_5.

The best performance for the percent reduction of biological oxygen demand (BOD_5) was shown by T_6 (91.18%) followed by 85.09% after applying T_5. In case of chemical oxygen demand (COD) the highest percent reduction was possible after applying the treatment T_7 (82.71%) and the treatment T_4, T_5 and T_6 has shown almost the same performance. Almost 57.44% of TDS could be reduced by applying T_5. For alkalinity (TA) the performance was not so good by all the treatments except T_1, in which case the percent reduction was 74.7%. Salinity and chloride [Cl^-] were mostly (20.69%) reduced applying the combination of alum, lime and ferric chloride. Pollutants such as chromium, color, SS, BOD were successfully reduced at 90 to 99%, while COD and TS reduction was achieved at 70 to 80%. However, chloride, salinity, alkalinity were not reduced effectively, since they contain dissolved impurities and for their

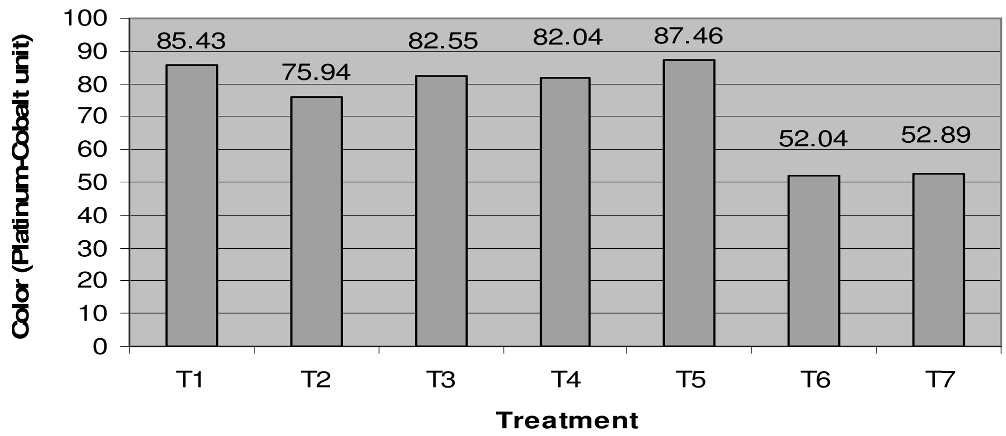

Figure 5. Percent reduction of effluents of Madina Tannery, Chittagong in value of color in all treatments compared to T_0.

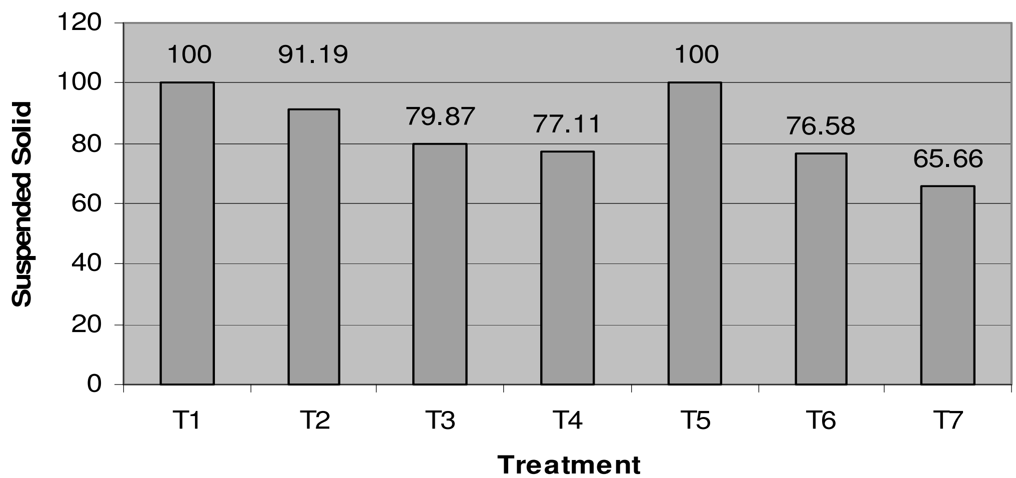

Figure 6. Percent reduction of effluents of Madina Tannery, Chittagong in value of suspended solid (SS) in all treatments compared to T_0.

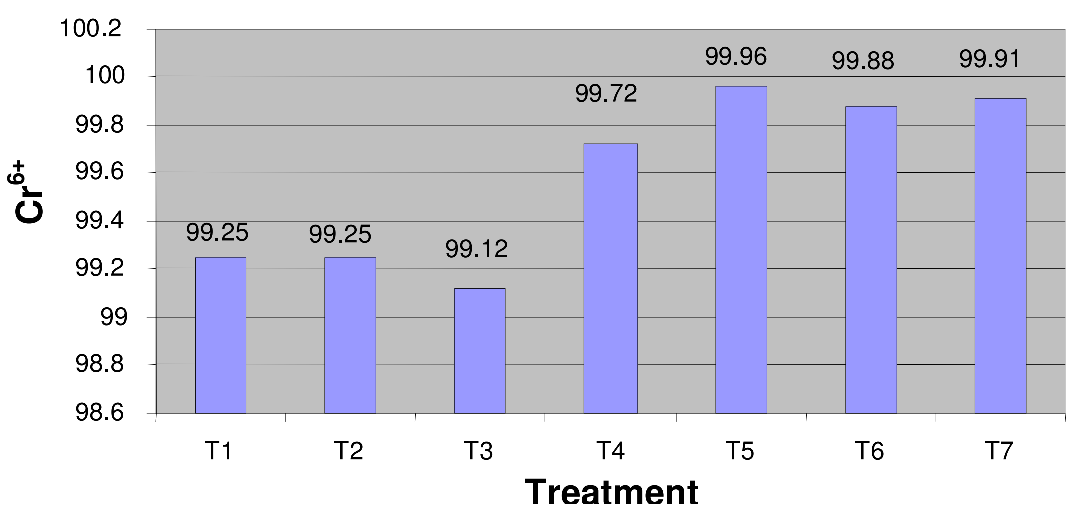

Figure 7. Percent reduction of effluents of Madina Tannery, Chittagong in value of [Cr^{6+}] in all treatments compared to T_0.

treatment it requires more developed technology.

Environmental impacts of tannery effluents

The metal chromium can be extremely toxic to man even at low concentrations (Das et al., 2006; Gauglhofer and Bianchi, 1991). The genotoxicity of chromium has also been indicated (Mohanta et al., 2010; Bianchi and Levis, 1987). Hence, it is necessary for their effective removal from raw water samples during the water treatment. Conventional chrome tanning results in wastewater, containing as high as 1500 to 3000 ppm (parts per million) of chromium. A study done by Marchese et al. (2008) about the rate of accumulation of chromium in four fresh water plant species, clams, crabs, and fishes showed that, all the four fresh water species and animals were found with high concentration of chromium which is an indication of its high accumulation potential. This clearly indicates that this problem become more serious and toxic to human beings which are found at the top of the food web due to its toxicity and bioaccumulation effect.

In Bangladesh, the entire tannery discharges their waste water directly or indirectly into the river without treating. As a result, ever-growing river pollution is of great concern in Bangladesh (Mohanta et al., 2010). This study clearly reveals that by low cost coagulants, chromium can be successfully removed from the waste water of tannery in Bangladesh. The initial pH of the tannery effluents is 10.43, which if discharged into surface water can have serious impacts on the receiving environment. In aquatic ecosystems, the pH of water should fall within the range of 6.5 to 9.0 (Bamber, 1987). A fluctuation in pH within this range is harmless to most fish and other aquatic life. However, as the pH continues to rise above 9.0, it begins to adversely affect most aquatic species, and a pH in the range of 10.0 to 11.5 is lethal to all species of fish (Wurts and Durborow, 1992).

On the other hand, when pH falls within the range of 5.0 to 6.0, rainbow trout, salmonids and molluscs become rare, the rate of organic matter decomposition declines because the fungi and bacteria responsible for degradation are not acid tolerant, and most green algae, diatoms, snails and phytoplankton disappear when the pH drops below 5 (EPA, 2003). Bamber (1990) reported that as the pH of the aquatic environment continues to decrease below 7, the biodiversity of the ecosystem continues to decline, fish population numbers diminish and some aquatic animals such as frogs, toads and salamanders are completely eliminated from the water body. Changes in water chemistry may also occur as a result of a decrease in pH. At low pH, aluminum is released from soils into lakes and streams, and as the pH of the water body decreases, aluminum levels increase leading to weight loss, stunted growth and death of fish (EPA, 2003). Most of the tannery industries in Chittagong, discharge their effluents directly, which reaches the nearby river system (Karnaphuli and Halda) and gradually destroy the river ecosystem. From the present investigation, it was found that the nearest neutral pH value is achievable from treatment T_7 (7.13), T_2 (7.23), T_6 (7.23) and T_4 (7.3).

Conclusion

Having a small industrial base, Bangladesh is in an advantageous position for getting a start in developing clean and sustainable industries. The tannery sector is economically important and that is contribution to the GDP in a poor country like Bangladesh is not negligible. Mismanagement, inferior technologies, lack of facilities for treating industrial wastes, wrong approach towards industrialization aggravating environmental problems in the country day by day. From the present investigation it was clear that coagulants are effective for the treatment of tannery effluents, particularly alum as well as the combination of alum and ferric chloride efficiently control different pollutant well below the different standard (e.g. Waste Discharge Quality of Industrial Units, Bangladesh).

The public demand for color-free waste discharge in receiving waters has made decolorization of a variety of industrial wastes a top priority. Unfortunately, with the complicated color-causing compounds, the decolorization of the effluent is a difficult and challenging task. But from this study, it was revealed that alum and a combination of alum and ferric chloride is effective for the removal of color through coagulation and flocculation process from the tannery effluent. So, these results may lead to a reduction in waste disposal costs for tannery companies.

ACKNOWLEDGEMENTS

Sincere thanks to all the laboratory technicians of the Institute of Forestry and Environmental Science, University of Chittagong and Mohora Water Treatment Plant, Chittagong Water Supply and Sewerage Authority for their continuous support during the analysis phase of this study. We are highly grateful to Professor Dr. K. Maudood Elahi, Chairman, Department of Environmental Science, and Pro-Vice Chancellor, Stamford University Bangladesh, for his constructive comments regarding the research paper.

REFERENCES

APHA-AWWA-WPCF (1998). Standard methods for the examination of water and wastewater, 19th Ed., Washington DC.

Ates E, Orhon D, Tunay O (1997). Characterization of tannery wastewater for pretreatment-selected case studies. Water Sci. Tech., 36: 2-17.

Balasubramian S, Pugalenthi V, Anuradha K, Chakradhar SJ (1999). Characterization of tannery effluents and the correlation between

TDS, BOD and COD. Environ. Sci. Health, 34: 4-16.
Bamber RN (1987). The effects of acidic sea water on young carpet-shell clams *Venerupis decussata.* J. Exp. Marine Biol. Ecol., 108: 241-260.
Bamber RN (1990). The effects of acidic seawater on three species of lamellibranch mollusc. J. Exp. Marine Biol. Ecol., 143: 181-191.
Bartkiewicz B (2000). Industrial wastewater purification. Warszawa, 271-279.
Bianchi V, Levis AG (1987). Recent advances in chromium genotoxicity. Toxicol. Environ. Chem., 15: 1-24.
Das P, Das B, Khan YSA (2006). Environmental Assessment of Tannery Wastes from Chittagong, Bangladesh. Asian J. Water Environ. Pollut., 3(1): 83-90.
Dhungana TP, Yadav PN (2009). Determination of Chromium in Tannery Effluent and Study of Adsorption of Cr (VI) on Sawdust and Charcoal from Sugarcane Bagasses. J. Nepal Chem. Soc., 23: 93-101.
ECR (1997). Ministry of Environment and Forest, Gazette notification 27, Aug.
EPA (2003). Effects of Acid Rain: Lakes and Streams. United States Environmental Protection Agency, Washington, DC. (http://www.epa.gov/acidrain/effects/surfacewater. html. Last accessed on 29 November, 2010).
Gauglhofer J, Bianchi V (1991). Chromium. In: Merian E (ed.) Metals and Their Compounds in the Environment, Occurrence, Analysis and Biological Relevance. VCH, Weinteim, Cambridge. pp. 853-878.
Genovese CV, Gonzalez JF (1998). Solids removal by coagulation from fisheries wastewaters. Water Sci., 24(4): 371-372.
GOB (1997). Report on Bangladesh census of manufacturing industries (CMI), Bangladesh Bureau of Statistics, Dhaka.
Gregory J, Guibail B (1991). Effects of dosing and mixing conditions on polymer flocculation of concentrated suspensions. Chem. Eng. Comm.*,* 108: 3-21.
Haydar S, Aziz JA, Ahmad MS (2007). Biological Treatment of Tannery Wastewater Using Activated Sludge Process. Pak. J. Eng. Appl. Sci., 1: 61-66.
Klimiuk E, Filipkowska U, Korzeniowska A (1999). Effects of pH and Coagulant Dosage on Effectiveness of Coagulation of Reactive Dyes from Model Wastewater by Polyaluminium Chloride (PAC). Polish J. Environ. Stud., 8(2): 73-79.
Krishanamoorthi S, Sivakumar V, Saravanan K, Prabhu S (2009). Treatment and Reuse of Tannery Waste Water by Embedded System. Modern Appl. Sci., 3(1): 129-134.
Marchese M, Gagneten AM, Parma MJ, Pave PJ (2008). Accumulation and elimination of chromium by freshwater species exposed to spiked sediments. Archives of Environ. Contam. Toxicol. Springer, 55(1): 603–609.
Mohanta MK, Salam MA, Saha AK, Hasan A, Roy AK (2010). Effects of Tannery Effluents on Survival and Histopathological Changes in Different Organs of *Channa punctatus.* Asian J. Exp. Biol. Sci., 1(2): 294 – 302.
Najm I, Tate C, Selby D (1998). Optimizing enhanced coagulation with PAC: A case study. J. AWWA., 90(10): 88-95.
Nourisepehr M, Nasseri S, Mazaheri AM, Yaghmaian K (2005). Chromium Bio-removal From Tannery Industries Effluent By *Aspergillus Oryzae*. Iran. J. Environ. Health. Sci. Eng., 2(4): 273-279.
Okuda T, Bacs A, Nishijima W, Okada M (2001). Isolation and characterization of coagulant extracted by salt isolation. Water Res*.,* 35(2): 405 – 410.
Rahman MA (1997). Characteristics of major industrial liquid pollutants in Bangladesh. Masters Project, Department of Civil Engineering, Bangladesh University of Engineering and Technology.
Ramesh BR, Bhadrinarayana NS, Meera Sheriffa Begum KM, Anantharaman N (2007). Treatment of tannery wastewater by electro-coagulation. J. Chem. Technol. Metallurgy, 42(2): 201-206.
Ratnaweera H, Degaard ZH, Fettig J (1992). Coagulation with pre-polymerized aluminium salts and their influence on particle and phosphate removal. Water Sci. Tech., 26: 12-29**.**
Rusal MG, Faisal I, Kamal KMM (2006). Environmental pollution generated from process industries in Bangladesh. J. Environ. Polut., 28(2):44-161.
SEHD (2002). Industrialization and Industrial Pollution, in: Gain, P. (eds,), Bangladesh: Environment Facing the 21^{st} Century. Society for Environment, Human and Development (SEHD), Bangladesh.
Shen TT (1999). Industrial pollution prevention (2nd Ed.). Springer, 40p.
Shouli AS, Bewtra JK, Biswas N (1992). Effectiveness of coagulation and flocculation processes in removal of selected volatile organic contaminants from wastewaters. Int. J. Environ. Stud., 40:2-7.
Stephenson RJ, Duff SJB (1996). Coagulation and precipitation of a mechanical pulping effluent: Removal of carbon, colour and turbidity. Water Res., 30:781.
Vlyssides AG, Karlis PK, Rori N, Zorpas AA (2002). Electrochemical treatment in relation to pH of domestic wastewater using electrodes. J. Hazard. Mater., 95: 215–226.
WHO (2004). Guidelines for drinking water quality. Third Edition, Volume 1. World Health Organization, Geneva. (http://www.lenntech.com/WHO%27s-drinking-water-standards.html Last accessed on 2 April 2010).
Wurts WA, Durborow RM (1992). Interactions of pH, carbon dioxide, alkalinity and hardness in fish ponds. Southern Regional Aquaculture Center (SRAC). SRAC Publication No. 464, Dec.