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Treatment of leather industrial effluents by filtration and coagulation processes

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ABSTRACT

This study focused on effluents characterization and accessing physical and chemical treatment by filtration and coagulation processes. The analysis results of the raw effluents reveal that the effluents were yellowish-brown color, having basic pH, very high values of BOD_5, COD, TDS, TSS, TS and high concentrations of Cr, Na, SO_4^{2-} and other organic and inorganic constituents. After settling and a subsequent filtration of raw tannery effluents through sand-stone, the filtered effluents were treated with various doses of $FeCl_3$. The study observed that coagulant ($FeCl_3$) of 150 mg/L dose near neutral pH showed the best removal efficiencies for major physico-chemical parameters. The analysis results illustrate that most of the physical and chemical parameters were found well below the prescribed permissible limits for effluent discharged. The study suggests that untreated tannery effluents would be treated by a combined process consisting of settling, filtering and coagulating with $FeCl_3$.

1. Introduction

Tanning industry is one of the oldest industries in the world. It is typically characterized as pollutants generated industries which produce wide varieties of high strength toxic chemicals. It is recognized as a

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serious environmental threat due to high chemical levels including salinity, organic load (chemical oxygen load or demand, biological oxygen demand), inorganic matter, dissolved, suspended solids, ammonia, total kjeldahl nitrogen (TKN), specific pollutants (sulfide, chromium, chloride, sodium and other salt residues) and heavy metals etc. [14,15,53,5,35]. Large quantity of water is used in tanning process of which 90% of the water is discharged as effluent. A part of the leather processing, solid and gaseous wastes are also discharged into the environment. During the chrome tanning process, 40% unused chromium salts are usually discharged in the final effluents, causing a serious threat to the environment [55,35,43]. Exposure to chromium, pentachlorophenol and other toxic pollutants increase the risk of dermatitis, ulcer nasal septum perforation and lung cancer [11]. Without any exceptions there is no effluents treatment plant (ETP) in leather tanning industries in the country and moreover, the owners of tannery industries are not much concerned about human health and environmental safety.

The leather industries in Bangladesh are mainly concentrated in Hazaribagh area in the Southwestern part of Dhaka city. More than 200 tannery industries are located in Hazaribagh area, and of them about 90% of tanneries are engaged in chrome tanning process. Daily discharged wastes from all the tanneries in Hazaribagh industrial zone are about 22000 m^3 of liquid waste containing 180 mg/L Cr [49]. Liquid wastes are mostly dumped into the River Buriganga, while part of these wastes is trapped inside Dhaka flood control embankment. Thus, the treatment of tannery effluents is a matter of great concern for the country. A number of research works on tannery effluent treatment using different technologies, such as flotation, electrochemical treatment, sedimentation, coagulation, filtration, ultra-filtration and reverse osmosis process have been reported [41,7,50,32]. Several investigators have used solid supports, including sand, clay, GAC [21,57], glass beds, rock [23] etc. for treating the effluents. Coagulation or chemical precipitation has been known for wastewater treatment since the previous century in England where lime was used as coagulant alone and/or in combination with calcium chloride or magnesium [25].

Most of the research reports on tannery effluents in Bangladesh have focused on characterization and impact assessment [17,40,48]. Only a few of the researches on tannery effluents treatment so far have been reported in Bangladesh. The wastewater treatment process depends on several factors like efficiency, cost-effective and environmental capability [13]. The aim of the study was to evaluate the treatment by filtration and coagulation–flocculation processes. In this study, tannery effluents were characterized and treated using filtration and coagulation processes. The study also investigated the cost effective options for the sustainability of the effluent treatment process.

2. Materials and methods

2.1. Study area

The study area is comprised of tannery area in Hazaribagh Thana situated on the Southwestern part of Dhaka city, Bangladesh. It is located between 23°45′ to 23°44′ north latitudes and 90°21.85′ to 90°22.15′ east longitudes.

Three tannery industries namely of BLC, Karim and BAY Tanneries were selected for collecting the effluent samples. The tanneries are a renowned manufacturer of all sorts of Crust and Finished shoe upper softy type and others leather in Bangladesh. Every year, it exports crust and finished leather to the USA, Italy, Portugal, Mexico, France, Australia and Germany.

2.2. Sample collection

The study was conducted during the year 2008–2009 and the tannery effluents were collected three times in a year from the outlet of the three selected leather industries located in Hagaribagh industrial zone in Dhaka, Bangladesh. 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 the selected tanneries.

These discharged effluents were treated with various physico-chemical processes i.e., settling, filtration and coagulation–flocculation under some specific laboratory conditions. Each time, 20 l of sample was collected, and stored in several polyethylene bottles at 4 ± 1 °C in the Laboratory. Sample collection was based on the techniques outlined by Pearson et al. [44].

2.3. Treatment process

5 L sample was taken in a beaker, 5 mg/L NaOH was added to decrease the solubility of cations in the effluent and allowed to settle for 24 h. In this way total suspended solids (TSS) were settled by flock formation. After settling, the supernatant liquids were passed through sand-stone filter. Filtration process is a primary treatment step to remove organic materials from tannery effluents, including total organic carbon (TOC) and biochemical oxygen demand (BOD_5), and nutrient (ammonia). The efficiency and life span of the process are related to the extent of hydraulic loading and regeneration of the sand-stone and other filters.

Four-layer sand-stone filter beds were designed to achieve optimum removal of organic material, BOD, COD and nutrients. The filtering materials consisted of layers of sand and stones and each individual layer ranged from 10 to 12 cm. The sand layers consisted of two layers, coarse sands (1 mm diameter) at the top and fine sands (≤0.15 mm diameter) at the bottom. The stone layers are also consisted of two layers, larger stone particles (≥5 mm diameter) at the top and smaller ones (≤ 5 mm diameter) at the bottom, these stones were used to reduce clogging in the sand filter. A report suggested that multiple dosing of sand filters provided superior performance in the treatment efficiency and filter run time [33]. The used sand stone beds could be reused and regenerated by cleaning fresh water and boiling at 100–102 °C with saline water ([9]).

The supernatant liquid after settling process was poured into the top of the filter and allowed to pass through different layers and finally percolated water was collected at the bottom of the filter. The filtration process also conducted using saw dust solely and combination with sand stone, but the results were not good enough to consider as a filtration media. Thus the results of these filtration processes were not discussed here.

In chemical treatment, batch experiments were carried out involving coagulation–flocculation and sedimentation techniques. The study considered $FeCl_3$ as coagulant to lower sensitivity to water temperature variation, high removing efficiency for color, organic matter and heavy metals, which are of particular benefit to industrial effluent treatment [52,25]. A definite dose of coagulant (50, 100, 150, 200, 250, 300, 400 and 500 mg/L) was added to the filtered effluents, stirred gently for 15 min and then allowed to settle for 0.5 to 4 days. After settling the supernatants liquid were then analyzed for various physico-chemical parameters everyday during the treatment period.

The optimization of coagulation process depends on the type of coagulant, its dose, pH and time [20,28,34]. Ferric chloride ($FeCl_3$) has been used in wastewater treatment to reduce TSS, TDS, BOD_5, COD, turbidity and mineral content [18,22]. $FeCl_3$ undergoes hydrolyzes in water to produce two monomer species $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_5(OH)]^{2+}$ along with polymer species $[Fe_2(H_2O)_8(OH)_2]^{4+}$ [8]. The overall reactions are normally simplified by the following reaction as stated by Misri and Praswasti Pembangun Dyah Kencana [39].

$$2FeCl_3 + 3Ca(HCO_3)_2 \rightarrow 2Fe(OH)_{3(s)} + 3CaCl_2 + 6CO_2 \quad (1)$$

At first, optimization of coagulant ($FeCl_3$) dose was determined and then optimization of pH was made. The dependency of pH on coagulation process was examined using a wide pH range from 2 to 8. The pH was adjusted with 0.1 M $Ca(OH)_2$ or 0.1 M HCl as required in the beginning of the experiment. Finally the optimization of coagulation period was determined by analyzing the removal efficiencies for each parameter of 0.5–4 days. However, this paper presents only the results of 1-day's treatment as the results obtained after two or more days treatment did show any significant difference from those obtained in 1-day treatment. The entire experiments were conducted at room temperature (30 ± 1 °C). A schematic diagram of the physico-chemical treatment of tannery effluents is shown in Fig. 1.

2.4. Tannery effluent characteristic and treated effluent analysis

The physical parameters including pH, electrical conductivity (EC), total suspended solids (TSS), total dissolved solids (TDS) biological oxygen demand in 5 days at 20 °C (BOD_5), chemical oxygen demand (COD)

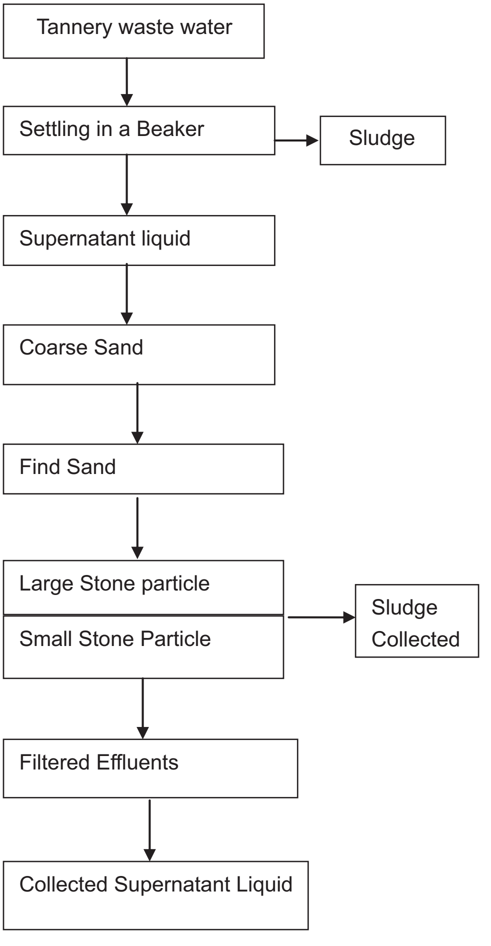

Fig. 1. Schematic diagram of physico-chemical treatment process.

of raw tannery effluent and treated effluent were measured. Other chemical parameters including sulfate (SO_4^{2-}), sodium (Na), calcium (Ca) and heavy metals of untreated and treated effluents were analyzed. Colors (control and treated) were measured in Pt–Co color unit. TSS, TDS and TS were determined gravimetrically [3]. DO, BOD_5, COD, SO_4^{2-}, Cl^-, NO_2^-–N, NO_3^-–N, TN, and NH_4^+–N, were measured as per standard methods of APHA [4]. Na, Ca and concentrations of heavy metals in the effluent were estimated using AAS (Shimadzu GF-AAS Model AA-6800) following digestion of the samples with concentrated nitric acid and perchloric acid mixer in the ratio 6:1 [3]. All chemicals were used of analytical grade reagents and the experiments were performed at least three times to minimize analytical error. The analysis results were compared with the values of Indian Standard Institute ([27]), and Inland Surface Water-Bangladesh Standard (ISW-BDS) for wastewater discharged to evaluate the efficacy of this work. Means and standard deviations of triplicate samples were analyzed for physico-chemical parameters of untreated and treated effluent. A schematic diagram of physico-chemical treatment process is shown in Fig. 1.

3. Results and discussion

The analysis results of untreated (raw) filtered and chemically treated tannery effluents are shown in Tables 1 and 2.

Table 1
The physico-chemical characteristics of tannery effluents (before and after filtration processes) and compare with standard permissible limits.

Parameters	Untreated effluents (raw effluents)	Sand-stone filtered effluents (SSF)	Saw –dust filtered effluents (SDF)	Combined sand-stone and saw-dust filtered effluents (CF)	Standards limits (ISI – 2000/ISW-BDS)
Color units (Pt–Co)	1760 ± 2.35	860 ± 2.39	1470 ± 4.65	1400 ± 3.64	15
pH	7.5 ± 0.11	7.95 ± 0.11	8 ± 0.01	8.10 ± 0.09	6–9
EC (mS/cm)	18.65 ± 0.69	12.68 ± 0.56	20 ± 1.41	27 ± 0.89	0.288
TSS (mg/L)	6800 ± 35.35	4800 ± 28.9	5400 ± 49.18	6000 ± 31.62	100
TDS (mg/L)	14000 ± 50.99	10500 ± 60.60	16000 ± 61.68	20000 ± 70.75	2100
TS (mg/L)	20800 ± 55.01	15300 ± 45.05	21400 ± 50.35	26000 ± 60.37	2200
DO (mg/L)	0.8 ± 0.03	–	–	–	4–6
BOD_5 (mg/L)	920 ± 15.81	810 ± 9.35	1505 ± 11.94	2400 ± 24.49	30/250
COD (mg/L)	3980 ± 29.66	3500 ± 15.81	6800 ± 30.90	14500 ± 100	250/ 400
SO_4^{2-} (mg/L)	4000 ± 14.32	3350 ± 30.82	3510 ± 13.04	3500 ± 15.81	1000

ISI-2000 = Indian Standard Institute–2000, ISW-BDS = Inland Surface Water-Bangladesh Standard [24,19].

Table 2
Physico-chemical characteristics of $FeCl_3$ treated tannery effluents.

Parameters	Coagulant dose $FeCl_3$ (mg/L)						
	50	100	150	200	250	400	500
Color(Pt–Co)	400 ± 1.41	286 ± 0.71	15 ± 1.41	30 ± 1.41	100 ± 1.41	320 ± 3.54	500 ± 1.22
pH	7.5 ± 0.19	7.23 ± 0.1	6.95 ± 0.19	6.5 ± 0.19	5.5 ± 0.07	3.5 ± 0.15	3 ± 0.04
EC (mS/cm)	7 ± 0.19	6.05 ± 0.25	4.68 ± 0.19	5.7 ± 0.25	6.6 ± 0.28	7.5 ± 0.22	9 ± 0.24
TSS (mg/L)	500 ± 2.39	120 ± 3.54	0 ± 0.07	200 ± 3.61	450 ± 3.08	650 ± 1.41	1050 ± 1.41
TDS(mg/L)	5661 ± 7.09	5322 ± 3.03	4075 ± 3.53	5050 ± 3.53	5400 ± 1.41	6071 ± 2.91	8050 ± 1.48
TS (mg/L)	6161 ± 10.58	5442 ± 10.05	4075 ± 8.09	5250 ± 8.60	5990 ± 9.61	6721 ± 3.56	9100 ± 9.85
BOD_5(mg/L)	650 ± 1.48	560 ± 3.81	200 ± 1.41	350 ± 3.61	525 ± 3.08	600 ± 3.81	710 ± 3.54
COD(mg/L)	1230 ± 3.54	930 ± 7.87	300 ± 1.58	560 ± 1.41	730 ± 1.58	1205 ± 3.08	1450 ± 1.41
SO_4^{2-}(mg/L)	1050 ± 3.08	650 ± 1.58	462 ± 1.41	657 ± 1.82	730 ± 1.58	850 ± 3.7	1260 ± 3.81

3.1. Color odor and appearance

The average color range of the untreated tannery effluent was found to be 1760 Pt–Co units; which was 117 times higher than all the recommended values of standard (15 Pt–Co units). The color appearance of untreated effluent was found yellowish-brown. The analysis results indicate that the untreated effluents contained highly colored compound which has the potential to pollute the environment. The original color of the effluent (1760 Pt–Co units) was reduced to 860 Pt–Co units after sand-stone filtration, indicating the effectiveness (50%) of the filter media. The color appearance of this filtered effluent was dull-white. The study also used saw dust filter solely and a combination of saw dust with sand-stone to access the filtration efficiency, but the results of the filtered effluents showed less effective in removing color and odor than those of the sand-stone filter (Table 1).

Reports illustrated that the yellowish brown color contained α-mesosaprobic type water might be hindering the penetration of sunlight which indicates the presence of significant amounts of algae and large numbers of bacteria [12,54]. The color value of $FeCl_3$ (150 mg/L) treated effluents was found 15 Pt–Co, which was within the permissible recommended level for ISW-BDS and other standards. Apparently clean effluents were found after treatment with different doses $FeCl_3$ (100–250 mg/L). The effluents' color have turned clear to light brownish and brownish, when the $FeCl_3$ doses increased above 250 mg/L. The study results show that 150 mg/L of $FeCl_3$ dose was the most effective for removal of coloring agent (Table 2). Color responses from all treated effluents were significantly different from those of untreated effluents. The odor was found very obnoxious smell in untreated effluent but unobjectionable odor was observed after treatment with different does of $FeCl_3$.

In this study, the average temperature was found to be 34 °C which was well below the permissible limit of National Environmental Quality Standard ([42], website). Temperature is an important indicator of water quality with regards to survival of aquatic organisms. Research reports showed that the effluents temperature depends on the process of production in the industry and it is usually with a range of 32–40 °C [30,53,46].

3.2. pH and EC

The average pH values of the untreated (control) and treated (sand-stone filter) effluents were 7.5, and 7.95, respectively (Table 1). After filtration, pH slightly increased due to add NaOH during the settling period. After filtration, the effluents were treated with different doses (50–500 mg/L) of $FeCl_3$. The study results observed that the pH of the treated effluents was decreased with increasing $FeCl_3$ dose as expected (Table 2). Similar observation was reported by Islam et al. [26]. EC (at 25 °C) values of the untreated tannery effluents (control) was observed 18.65 mS/cm which was about 7 times higher than the prescribed limit for [27] (Table 1). Reports showed that EC of untreated effluents usually contained about 20 mS/cm [37], supporting the results of this study. EC value of sand-stone filtered effluent was found to be 12.68 mS/cm, which was very high compare to [27] standard. The results show that EC values were decreased sharply with increasing $FeCl_3$ doses until EC value reached at around 5 and then it slowly increased with $FeCl_3$ concentrations (Table 2). Lofrano et al. [36] illustrated that 900 mg/L of $FeCl_3$ treated effluents showed maximum removal efficiency for EC at pH 8.5. However, the results showed that the higher coagulant ($FeCl_3$) dose was unable to remove significant amount of other toxic parameters. Similar observation was made by Naumczyk and Rusiniak [41], reported that 600 mg/L dose of $FeCl_3$ showed the best removal efficiency for majority of parameters at pH 6.35. This study results showed comparatively better removal efficiencies in removing the parameters at a lower $FeCl_3$ (150 mg/L) dose at near neutral pH.

3.3. TSS and TDS

The average TSS and TDS values of the untreated tannery effluent (control) were 6800 and 14,000 mg/L, respectively, which were very high compared to those of prescribed limits for ISI and ISW-BDS. The average TSS and TDS values after filtration were still very high indicating that sand-stone filtration process alone was not sufficient to reduce the values below the standard permissible limits (Table 1). However the treatment results illustrated that TSS decreased with increasing dose concentration until the optimum dose of 150 mg/L, but it increased once again with increasing coagulant ($FeCl_3$) dose (Table 2). But TDS values were still far above the standard limit for all treatment doses. The lowest values of these parameters (TSS and TDS) were found at a dose of 150 mg/L FeCl3 treated effluents. The study results reveal that the TSS concentration was almost zero (0) mg/L and the removal efficiency was 100% at a coagulant ($FeCl_3$) dose of 150 mg/L indication the suitability of the coagulant dose.

3.4. DO, BOD_5 and COD

The average values of DO, BOD_5 and COD of the tannery effluents (control) were 0.8, 920 and 3980 mg/L, respectively (Table 1), these values were quite unexpected for fish and other aquatic lives. DO concentration within 5–8 mg/L is fair for aquatic environment and less than 4 ppm is critical level [6,2]. Verma et al. [54] suggested that the low DO content (≤4 ppm) of untreated effluents was the result of high organic pollution indicating the high BOD_5 value. The analyzed results illustrated that DO, BOD_5 and COD values were very high than those of prescribed standards fixed for the ISI and ISW-BDS (Table 1) [19,24]. The results of theses parameters after treatment with different doses of

Table 3
Quantity of dissolved cations of tannery effluents (before and after filtration processes) and compare with standard permissible limits.

Parameters	Untreated effluents (raw effluents or control)	Sand-stone filtered effluents (SSF)	Saw-dust filtered effluents (SDF)	Combined sand –stone and saw-dust filtered effluents (CF)	Standards limits (ISI-2000)/ISW-BDS
Na(mg/L)	3840 ± 37.42	3050 ± 41.23	3000 ± 18.71	3005 ± 8.37	–
Ca (mg/L)	785 ± 4.12	750 ± 3.81	730 ± 3.81	720 ± 1.58	200
Cr (mg/L)	9.81 ± 0.63	9.78 ± 0.12	6.8 ± 0.19	7.8 ± 0.14	0.1/2
Pb (mg/L)	5.35 ± 0.19	4.55 ± 0.07	5.2 ± 0.15	4.75 ± 0.14	0.2
Cd(mg/L)	3.45 ± 0.045	3.15 ± 0.10	3.4 ± 0.16	3 ± 0.09	0.1
As (mg/L)	1.35 ± 0.12	0.85 ± 0.11	1.3 ± 0.19	1.29 ± 0.12	0.1

Table 4
Quantity of dissolved cations of treated tannery effluents.

Parameters	Coagulant doses $FeCl_3$ (mg/L)						
	50	100	150	200	250	400	500
Na (mg/L)	1230 ± 3.81	1050 ± 3.81	460 ± 1.58	860 ± 3.61	955 ± 5.43	1150 ± 3.54	1450 ± 3.81
Ca (mg/L)	360 ± 3.08	250 ± 1.58	140 ± 3.81	210 ± 3.08	560 ± 3.81	610 ± 1.41	690 ± 1.58
Cr (mg/L)	3.65 ± 0.11	1.75 ± 0.11	0.35 ± 0.01	0.65 ± 0.04	2.35 ± 0.08	3.5 ± 0.16	6.5 ± 0.14
Pb (mg/L)	2.5 ± 0.25	0.79 ± 0.01	0.67 ± 0.03	1.2 ± 0.11	2.67 ± 0.12	3 ± 0.14	3.45 ± 0.05
Cd (mg/L)	1.05 ± 0.13	0.69 ± 0.03	0.25 ± 0.06	0.75 ± 0.04	2.6 ± 0.08	3.05 ± 0.08	3.05 ± 0.06
As (mg/L)	0.80 ± 0.04	0.65 ± 0.04	0.1 ± 0.04	0.35 ± 0.08	0.5 ± 0.04	1 ± 0.01	1.23 ± 0.08

coagulant ($FeCl_3$) reduced significantly and 150 mg/L coagulant dose showed the best removing efficiency for BOD_5 (200 mg/L) and COD (300 mg/L) (Table 2), which were within the prescribed limits for ISW-BDS.

3.5. Sulfate

The average sulfate content of the untreated (control) and filtered effluents were found to be 4000 and 3350 mg/L, respectively. These values were very high compare to the standard prescribed limits for ISW-BDS. The high concentration of SO_4^{2-} in tanneries were a result of many auxiliary chemicals containing sodium sulfate as a byproduct of the manufacturer or chrome tanning powders [10]. Coagulant $FeCl_3$ removed SO_4^{2-} efficiently from effluents and the lowest SO_4^{2-}- concentration (462 mg/L) in the effluent was observed in treatment with 150 mg/L $FeCl_3$ dose (Table 2). The results showed that maximum sulfate removal efficiency achieved was 88.45% and the value was well below the standards permissible limits of ISW-BDS and other International standards.

3.6. Quantity of dissolved metal ions concentration

The average sodium (Na) and calcium (Ca) contents in the untreated effluents were 3840, and 785 mg/L, respectively (Table 3). The results of the filtrated effluents showed that the sand-stone filter was unable to remove Na, Ca and heavy metal ions below the standard limits for effluent discharged. However, the chemical treatment results show that the coagulant ($FeCl_3$) efficiently removed heavy metals (Cr, Pb, Cd and As) in an optimal coagulant dose of 150 mg/L (Table 4). The analysis results illustrate that the concentrations of Ca, Cr and As were within the prescribed standards limits for ISW-BDS. But the concentrations of other metal ions were still very high even after chemical treatment with coagulant $FeCl_3$ suggesting the need for further treatment.

3.7. Factors influencing on treatment processes

3.7.1. Effect of coagulants doses

The effect of coagulant ($FeCl_3$) dose on the removal efficiency of different parameters (TSS, EC, COD, BOD_5, SO_4^{2-}, Cr, As) are shown in Fig. 2. The figure illustrates that the graphs show a common trend, where the removal percentage (%) of different parameters are initially increased with dose until the efficiencies got maximum and then decreased with dose. The maximum removal percentage (%) obtained in 150 mg/L coagulant ($FeCl_3$) dose for all parameters. The highest removal efficiencies for different chemical parameters achieved were 78% (BOD), 92% (COD), 100% (TSS), 88% (SO_4^{2-}), 96% (Cr), 93% (As), and 93% (Cd). The results of the study revealed that the poor coagulation process was observed at lower coagulant doses as expected. The study also observed that the removal efficiency decreased when coagulant doses were above 150 mg/L, may be the cause of pH increased. Islam et al. [26] described that the effluents particles were surrounded by a large quantity of coagulant particles, when coagulant dose was very high and as a result their surfaces were saturated resulting less possibility to combine with each other and thus reach another state of stability [26]. Reports showed that the inorganic sludge production was increased with increasing $FeCl_3$ concentration [37,41]. Thus an optimum $FeCl_3$ concentration should be chosen for minimum sludge production. The study observed that 150 mg/L coagulant ($FeCl_3$) dose showed maximum removal efficiency, which kept minimum sludge production in one hand and reduce cost and environmental burden on the other hand.

3.7.2. Effect of pH on coagulation

The effect of pH on removal efficiency (%) is shown in Fig. 3. The maximum efficiencies for different parameters were found at neutral pH area and they gradually reduced on both sides of the neutral pH. The colloid substances in the leather industrial effluents usually carry negative electrical charges, whereas coagulant ($FeCl_3$) possesses a lot of Fe^{3+} ions. Around neutral pH, Fe(III) are hydrolyzed into mononuclear and multi nuclear hydroxyl complex ions, which have the capability of adsorbing particles and formed electric double layer for destabilization of the particles [45]. The study results illustrate that the maximum removal efficiencies were 78, 92, 100, 88, 96 and 92% for BOD_5, COD, TSS, SO_4^{2-}, Cr, As and Cd, respectively.

The study suggests that the lower coagulation efficiencies for the parameters observed at low pH which may be attributed to the competition between protons and cations for common binding sites and also colloidal re-stabilization caused by charge reversal at the colloidal surface. [29] stated that Fe^{3+} ions did not exist in solutions around neutral pH and a range of hydrolysis products [$Fe(OH)_2^+$ and $Fe(OH)_2^+$] are responsible for the de-stabilizing effects on colloid impurities. Different hydrolysis products can cause different treatment performances. The result of the present study agreed to the above observation and may be illustrated that at high pH (> 6.95) and coagulant dose (> 150 mg/L),

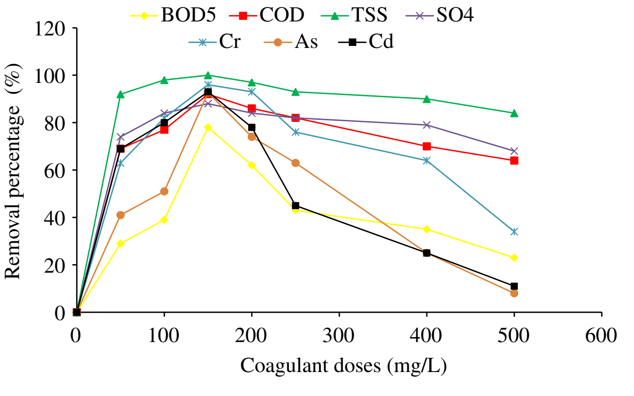

Fig. 2. Effect of coagulant dose on removal percentage (%) of some physico-chemical parameters.

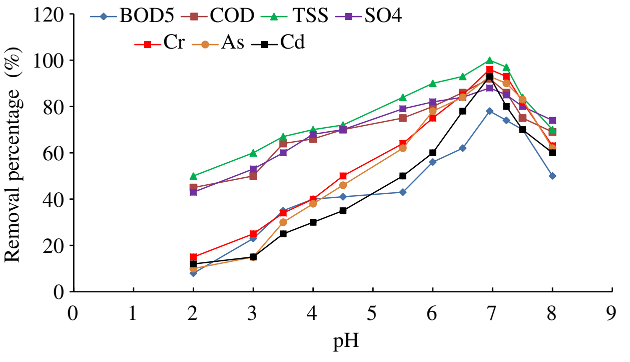

Fig. 3. Effect of pH on removal percentage (%) of some physico-chemical parameters.

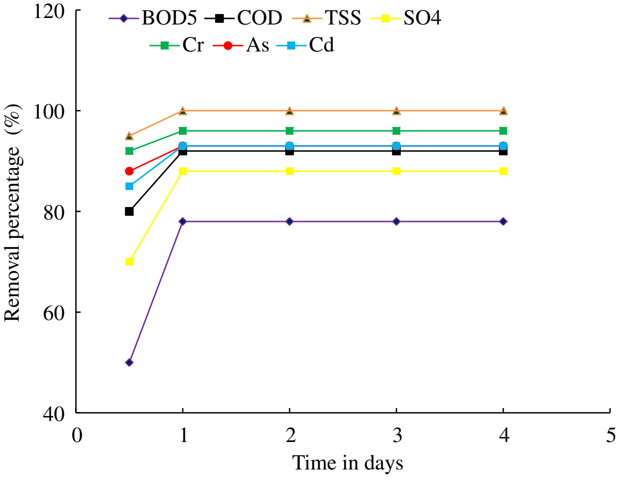

Fig. 4. Effect of time on removal percentage (%) of some physico-chemical parameters.

amorphous ferric hydroxide precipitates were formed which enmeshed and co-precipitated the colloidal impurities and settle together and thus reduced the coagulation efficiency. pH has an important role in coagulation process since it controls hydrolysis species [31]. Another report illustrated that the removal efficiency decreased at pH lower than 7 or higher than 9 [1]. The present study attributes from the above discussion that pH has a great influence on coagulation process in removing different parameters including metal cations from tannery effluents.

3.7.3. Effect of time

The dependency of removal efficiency of some physico-chemical parameters on reaction time is shown in Fig. 4. The study results indicate that the time of coagulation reaction and subsequent settling has a large effect on the removal efficiency of various parameters. The results of the chemical treatment and subsequent settling after a half day (12 h) were not enough for getting maximum removal efficiency for any pollutant, but the maximum removal efficiencies for all parameters were showed after one day treatment and they were remained the same after two or more days (Fig. 4). Stephenson and Duff [51] stated that the inorganic coagulant hydrolyzes quickly and the coagulation process is accelerated. This observation is in agreement to our study. The study suggests that one day reaction and settling time would be enough to complete the hydrolysis and sedimentation processes for the coagulant $FeCl_3$.

3.8. Comparison with other treatment processes

The maximum removal efficiencies for different parameters were compared to other treatment processes reported by others are shown in Table 5. Various chemicals and processes have been practicing for removing different inorganic and organic pollutants from tannery effluents [38,16,56]. Most commonly used chemicals are $FeCl_3$, alums, and TiO_2 as coagulants, $MgSO_4$ and NiSO4 as oxidizing agent, $FeSO_4$, and H_2O_2 in Fenton-photo process for COD, Cr and other cations removal. The removal efficiency of COD, total organic carbon (TOC), ammonia and sulfate using TiO_2/UV oxidation technique at pH 7 were found to be 3%, 8.5%, 10% and 6%, respectively (no shown in Table 5) indicating lower efficiencies [47]. The results of the present study illustrated that 150 mg/L coagulant ($FeCl_3$) dose in the pH range 6.5–7.5 has showed the maximum pollutants removal capacity from the tannery effluents. The other processes mentioned in Table 5 have used huge amount of chemicals compare to the present study. It may be suggested that few amount of coagulant could reduce sludge production and thus reducing the environmental burden. Moreover $FeCl_3$ is inexpensive compare to TiO_2, alum, sulfate salts and other commonly used coagulants. So this treatment process could be an efficient, cost effective and eco-friendly process for the removal of pollutants from leather industrial wastewater (effluents). Thus the study results showed the best removal performance among other studies indicating the suitability of its application in tannery effluents treatment.

4. Conclusion

The study showed that the untreated tannery effluents contained extremely high values of TSS, TDS, BOD_5, COD, sulfate, sodium, calcium and trace metal ions. These values were far above the standard prescribed limits for ISW-BDS and [27]. The results suggest that the leather industrial effluents were not suitable for discharging into surface water bodies which pose potential threats to human health and the environment. The study illustrate that the sand-stone filtration process could reduce certain pollution levels but not sufficient enough to consider the process alone using in effluent treatment. It is observed that chemical treatment with 150 mg/L coagulant ($FeCl_3$) dose showed the best efficiency in removing major physico-chemical parameters which are well below the standard prescribed limits for ISW-BDS. Thus the study suggests that the combined treatment process, i.e., filtration and coagulation could be promising in order to reduce pollutants from the other tannery effluents.

Table 5
Comparison of sand-stone filter combined with $FeCl_3$ treatment process with others.

Coagulants	Dose (mg/L)	Removal efficiency for considerable parameters (%)							References
		COD	TSS	TDS	EC	Cr	Pb	As	
Alum+polyelectrolyte	600+2	82	85	–	–	97	–	–	[36]
Alum+polyelectrolyte	400+2	77	85	–	–	98	–	–	[36]
$FeCl_3$+polyelectrolyte	1000+2	77	83	–	–	99	–	–	[36]
Alum	800	30–37	38–46	–	–	74–99	–	–	[50]
SBR	–	81.9	–	–	–	–	88.6	–	[58]
Fenton-photo Fenton oxidation (ferrous ions and H_2O_2)	1000+1500	90	–	–	–	76	–	–	[16]
Alum+ferric chloride	70+70	81	100	57	–	99	–	–	[26]
Ferric chloride	300	63.5	98	–	60.7	–		–	[41]
Fenton oxidation (H_2O_2 and $FeSO_4$)	111000+6000	77	–	–	–	23	–	–	[37]
$FeCl_3$(after sand-stone filtered)	150	92	100	71	75	96	87.5	93	This study

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