Characterization and Treatment of Industrial Effluent from Sugar Industry

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Summary: Effluent samples were collected from a sugar industry at Peshawar (Pakistan) in the sugar-cane season (Dec-March, 2002) and beat season (May-August 2002). The samples were chemically evaluated for different parameters. Total suspended solids (TSS), chemical oxygen demand (COD) and biological oxygen demand (BOD) values were found higher than the threshold limits and can therefore create aquatic problems in the Kabul River. A treatment process (mainly physicochemical) has been developed to reduce the harmful effects of the sugar mills effluent and to safeguard the aquatic habitat of the Kabul River. The efficiency of the treatment process in terms of BOD and COD reduction was found to be 96% and 95% respectively, which signifies its suitability to be used as an appropriate process. The process has the potential to protect the water bodies from further deterioration.

Introduction

Sugar industry is one of the main sources of pollutants to surface water bodies and the adverse impacts of sugar mills effluents are well known. These effluents carry loads of oxygen demanding wastes and suspended matters, which may result in depletion of dissolved oxygen and chocking of fish gills resulting in the extinction of aquatic life. The daily discharges of such harmful effluents from a sugar mills are around 5000 cubic metres per day. These discharges are threatening the quality of surface water, which demand to be treated for reducing their harmful effects before their discharge into receiving water channels. The sugar effluent is the most complex, caramelised and cumbersome waste having very high BOD, COD, TSS and TDS contents.

Several chemicals are used in sugar industries mainly for coagulation of impurities and refining of the end products. $Ca(OH)_2$ is used to clarify and to increase pH of juices. A small quantity of H_3PO_4 is added prior to liming to improve clarification. CO_2 gas is bubbled through the defecated juice to lower pH, which result in the improvement of precipitation of impurities. Polyelectrolytes, which are polymer based chemicals are also used for the coagulation of impurities during defecation and carbonation process. SO_2 is bubbled through the defecated raw sugar to remove colour. Dilute solutions of NaOH or Na_2CO_3 are used for the periodic descaling of heaters followed by neutralizing it with dilute HCl. Lead sub-acetate is used for the analysis of sugar content. All these chemicals, one-way or another, are contributing towards increasing the organic strength, dissolved solids and suspended matter.

Tremendous work on the characterization of the sugar mills wastes has been undertaken in the past, but no efforts have been undertaken so far in Pakistan to minimize their harmful effects. Previously [1] the studies conducted include analyses of effluents of the four sugar mills in NWFP, which had higher values of COD, BOD and TSS than the threshold limits. These studies [1] suggest that suspended solids come mainly from beat root/sugar-cane washing, lime cake, slurry and other sources like pulp screen, pulp press, pulp silo, lime cake, etc. Most of the sugar mills in NWFP utilize press mud, which are converted into slurry and ultimately discharged into nearby water channel [2]. The comprehensive treatment of organic liquor discharged from a sugar industry in China was studied which includes multistage flash evaporation system, resulting in a zero discharge of organic wastes [3]. The solid waste (bagasse), a part of which ends up as suspended matter in liquid effluent can be utilized as reinforcement in polyester matrix composites [4]. In another study [5], vacuum distillation techniques were applied for the treatment of wastewater which removes virtually all the contaminants like TSS, COD, BOD, heavy metals and mineral compounds. Studies on low temperature, conversion of sugar-cane by-products into oil, char, water and non-combustible gases have also been carried out [6].

In the past effluent samples from selected chemical industries of small industrial estate, Kohat Road Peshawar (Pakistan) [7] were evaluated for physico-chemical properties and heavy metals like Pb^{+2}, Ag^{+2}, Cu^{+2}, Zn^{+2}, Fe^{+2}, Cr^{+3}, Cd^{+2}, Mn^{+2} and

Ni^{+2}. Results based on one year data [7] have indicated that marble industries increased TSS, plastic industries increased iron concentration, food industries increased Mn and aluminium industries increased Cr concentration in their effluents, which were above the threshold limits of NEQS [8].

A case study on distillery waste treatment of Indian molasses to produce alcohol via fermentation and recovery of rectified spirit was also undertaken [9]. Anaerobic distillery-waste treatment studies were undertaken [10] in which BOD was reduced from 25000 to 2800 mgO_2/L, 10,000 to 900 mgO_2/L and 800 to 50 mgO_2/L. Treatment of low strength wastewater was studied by anaerobic sludge blanket whose COD removal efficiency was greater then 95% [11]. Thermophilic anaerobic degradation studies on the treatment of concentrated industrial wastewater were also carried out in which 82.5% reduction in COD was observed [12].

The present studies are focussed to develop a practical treatment process in order to minimize the harmful effects of sugar mills effluent. These studies were intended to control eutrophication, aesthetic look and above all to protect the fish crop from further damage due to the continued discharge of high oxygen demanding wastes of the sugar mills. Devising a treatment technology means providing an alternative to industries for the treatment of their effluents within the premises before discharging them into water bodies.

Results and Discussion

a. Characterization of effluents

The data in Table 1 show the chemical analysis of sugar mills effluent and river water at confluence point. The parameters of these samples have also been compared with that of National Environmental Quality Standards (NEQS) [8]. The results reveal that organic strength (COD and BOD) of the sugar mills effluent was significantly higher than the threshold limits [8]. COD and BOD values of the effluent were 80 and 39 times higher than the NEQS respectively. The river water at the confluence point (Table 1) was respectively found to have COD and BOD values 19 and 22 times higher than the permissible limits in-spite of significant dilution. Industrial effluent from different industries of I-9 Sector of Islamabad [13] were chemically evaluated previously. These studies [13] have pointed out that COD, Cl^-, I^- and cations like Cu^{+2}, Zn^{+2}, Mn^{+2} and Cd^{+2} were higher than the permissible limits of NEQS [8]. COD was in the range 321-956 mgO_2/L

Table 1. Chemical analyses of water and waste water samples

	Parameters	Sample		NEQS
		Effluent	River water at confluence point	
1.	pH	9.5	8.35	6-10
2.	Total Hardness as $CaCO_3$ (mg/L)	3900	880	-
3.	Calcium as $CaCO_3$ (mg/L)	2460	400	-
4.	Magnesium as $CaCO_3$ (mg/L)	1440	480	-
5.	M-alkalinity as $CaCO_3$ (mg/L)	5520	2200	-
6.	P-alkalinity as $CaCO_3$ (mg/L)	800	320	-
7.	Chloride as Cl^- (mg/L)	3195	585	1000
8.	Sulphate as SO_4^{-2} (mg/L)	825.6	460	600
9.	Chemical oxygen demand, COD (mgO_2/L)	12211.44	2915.3	150
10.	Biochemical oxygen demand, BOD (mg/L)	3131.84	1766.3	80
11.	Sodium as Na^+ (mg/L)	1100	765	-
12.	Potassium as K^+ (mg/L)	11250	975	-
13.	Total suspended solids, TSS (mg/L)	9212	1776	150
14.	Total dissolved solids, TSS (mg/L)	21498	2336	3500
15.	Sodium as Na^+ (mg/L)	1100	765	-
16.	Potassium as K^+ (mg/L)	11250	975	-
Heavy Metals				
17.	Zinc as Zn^{+2} (mg/L)	0.8	BDL	5.0
18.	Nickel as Ni^{+2} (mg/L)	3.9	BDL	1.0
19.	Copper as Cu^{+2} (mg/L)	1.6	BDL	1.0
20.	Manganese as Mn^{+2} (mg/L)	3.4	2.4	1.5
21.	Lead as Pb^{+2} (mg/L)	BDL	BDL	0.5
22.	Cadmium as Cd^{+2} (mg/L)	BDL	0.2	0.1
23.	Chromium as Cr^{+3} (mg/L)	BDL	BDL	1.0
24.	Iron as Fe^{+2} (mg/L)	2.00	0.50	2.0

NEQS: *National Environmental Quality Standards* [8] BDL: *Below detection limit*

Cl^- 382-1385 mg/L, and iodine were in the range 121-1983 mg/L [13].

It was observed that the effluent discharged into Kabul River has also contributed in increasing the suspended solids concentration significantly. Effluent (Table 1) contained 61 times more suspended solids than the threshold limit of NEQS [8], whereas its concentration in the river water at the confluence point was almost 12 times higher than the permissible limits. Higher organic strength and suspended matter in water bodies adversely affect the dissolved oxygen level and the spawning and hatching process of fish [14]. Furthermore, higher concentration of suspended matter in water bodies also prevents penetration of sunlight and consequently retards the growth of algae and microplanktins in the river bed. These two effects create a suffocating environment and food shortage to fish population. Besides, these effluents may contain some of the organics, which after combining with other analytes might be directly or indirectly toxic to the aquatic life and becomes a probable cause for the extinction of fish population in Kabul River [15].

Most of the heavy metals (Zn^{+2}, Ni^{+2}, Cu^{+2}, Pb^{+2}, Cd^{+2}, Cr^{+3} and Fe^{+2}) both in effluent and river water samples (Table 1) were within the permissible limits except Mn^{+2}, which was above the threshold limit. Dilution reduced the concentration of Mn^{+2} from 3.20 mg/L in the effluent to only 2.40 mg/L in river water at confluence point. However, this does not pose a serious threat to aquatic habitat, as further dilution is certain which result in a tolerable concentration of heavy metals in the Kabul River water. Previously [13] studies have indicated that industrial effluents from Islamabad area had heavy metals in concentration higher than the threshold limits [8]. For example Cu^{+2} was in the range 2.30-4.50 mg/L, Zn^{+2} in the range 2.90-6.30 mg/L, Mn^{+2} 2.80-4.30 mg/L and Cd^{+2} 0.50 mg/L [13]. Similarly, effluent samples from match industries in NWFP [16] contained Cr^{+3} in the range of 11.00-38.91 mg/L, Fe^{+2} 11.76-21.70 mg/L and Mn^{+2} 0.06-2.28 mg/L, which were above the NEQS. Other heavy metals like Cu^{+2}, Pb^{+2}, Zn^{+2} and Ni^{+2} were below the detection limits.

b. Treatment of Effluent

Studies on the physico-chemical methods include filtration, flocculation, sedimentation, adsorption on activated charcoal and air stripping. These steps were applied in sequence on sugar mills effluent as shown in Figure 1 and the results of these treatments are presented in Table 2.

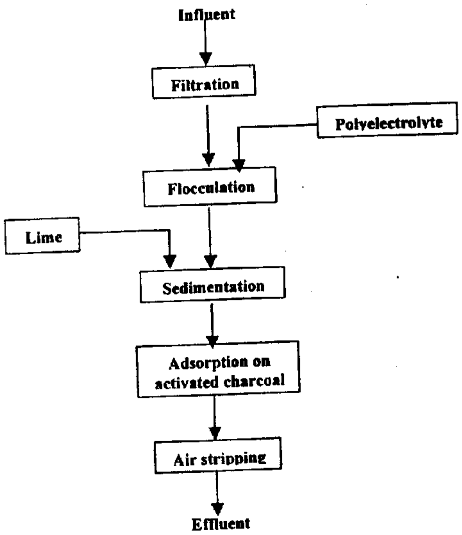

Fig. 1: Flow sheet for the treatment of sugar mills effluent.

Data (Table 2) on effluents have been compared with the upstream Kabul River water sample and water sample of Kabul River at the confluence point so that a clear picture of the status of water could be drawn. Several features of the data in Table 2 are conspicuous. The quality of effluent is very poor (Table 1) and most of the parameters are above the threshold limits, yet these parameters except COD and BOD do not pose a serious threat to aquatic life. Previously [14], industrial effluents containing high demanding wastes were implicated to have been creating a suffocating environment to fish population in the Kabul River. The effluent bearing the characteristics as mentioned in Table 1 was subjected to different physico-chemical treatments using either mixed salts {$Al_2(SO_4)_3$ + $FeSO_4$} or aluminium salt {$Al_2(SO_4)_3$} and the data are presented in Table 2.

Simple filtration was carried out which removed solids resulting a decrease in the COD from 12211.44 to 9360 mg O_2/l and BOD from 3131.84 to 2508.28 mg O_2/l. The same treatment was carried out with the river water at the confluence point resulting a decrease in COD and BOD. Yet the river water was

Table 2. Characteristics of waste water after applying various treatments in sequence

	Parameters	Upstream Sample*	Filtration		Flocculation		Sedimentation		Charcoal filtration		Aeration	
			Waste-water	River** water	Mixed salts***	$Al_2(SO_4)_3$ salt	Mixed salts	$Al_2(SO_4)_3$ salt	Mixed salts	$Al_2(SO_4)_3$ salt	Mixed salts	$Al_2(SO_4)_3$ salt
1.	pH	8.2	9.2	8.1	-	8.20	8.1	8.1	7.9	8.0	7.5	7.8
2.	Total Hardness as $CaCO_3$ (mg/L)	634.87	33600	816	2100	2280	1840	1800	960	1136	784	976
3.	Calcium as $CaCO_3$ (mg/L)	167.20	2300	350	1130	1220	1020	980	496	944	384	832
4.	Magnesium as $CaCO_3$ (mg/L)	467.67	1060	464	970	1060	820	820	464	192	400	144
5.	M-alkalinity as $CaCO_3$ (mg/L)	197.7	5300	1840	3900	2700	2520	2320	1168	1360	992	1056
6.	P-alkalinity as $CaCO_3$ (mg/L)	Nil	760	288	420	380	290	180	160	176	128	136
7.	Chloride as Cl^- (mg/L)	11.30	3150	540	1890	1800	1665	1215	900	828	792	648
8.	Sulphate as SO_4^{-2} (mg/L)	30.5	806	414.7	1171.2	1267.2	1180	1104	844	691.2	783	599.04
9.	Chemical oxygen demand, COD (mg/L)	7.1	9360	2832	2148.12	2274.48	1824	1920	929.15	634.37	664.57	533.1
10.	Biochemical oxygen demand, BOD (mg/L)	12.0	2508.28	1280.37	1593.5	1698.3	1358.93	1280.3	424.37	424.42	261	97.81

*Upstream Sample [17]
**Downstream sample at the confluence point
***Mixed salt: $Al_2(SO_4)_3$ and $FeSO_4$ (5% solution of 1:1 mixture of salts) [7]

not subjected to other treatments, as removal of pollutants from the river water was considered not feasible. The effluent sample was subjected to flocculation using flocculants (poly-electrolytes). A marked decrease in COD and BOD occurred after flocculation in the resulting liquid (supernatant). Flocculation due to mixed salts ($Al_2(SO_4)_3$ + $FeSO_4$) reduced the COD from 9360 to 2148.12 mg O_2/l (77 % removal), whereas $Al_2(SO_4)_3$ caused a COD reduction of 75.7% in comparison to sample after filtration, where the COD was reduced from 9360 to 2274.48 mgO_2/l. BOD of the filtered sample was also reduced due to flocculation with mixed salts from 2508.28 to 1593.50 mg O_2/l (36.47 % removal), whereas aluminium salt caused a decrease in BOD from 2508.28 to 1698.30 mg O_2/l (32.29 % removal). Decrease in BOD and COD due to flocculation is attributed to the adsorption of organics (both biodegradable and refractory compounds), on the surface of flocculants. No appreciable change was observed in the removal of BOD and COD when sedimentation was conducted inspite of addition of lime that increased pH of the liquid. Activated charcoal was used for adsorption of organic matter in order to further reduce BOD and COD. The adsorption on charcoal, as a filtering material, was applied to the effluent, which brought a marked decrease in the organics since flocculation. Activated charcoal filtration adsorbed organics which reduced COD from 1824 to 929.15 mg O_2/l in the mixed salts regimes and from 1920 to 634.37 mg O_2/l in $Al_2(SO_4)_3$ regimes. BOD was also reduced due to adsorption during charcoal filtration (Table 2), from 1358.93 to 424.37 mg O_2/l in the mixed salt regimes and from 1280.30 to 424.42 mg O_2/l in aluminium salt regimes.

Air stripping is used to get rid of volatile organics and gaseous inorganic materials, like free NH_3 and H_2S. Air stripping removed volatile organics and some of the inorganic oxidizable matter, which further improved the quality of the effluent by reducing COD and BOD. Yet all these treatments did not reduce the organics in the wastewater to meet NEQS. The effluents after all these sequential treatment steps was still having COD in the range of 533.10-664.57 mg O_2/l and BOD in 97.81-261.0 mg O_2/l which are above the permissible limits for effluents.

The data describing the % removal of BOD and COD after carrying out the sequential treatment steps are presented in Table 3. Table 3 summarizes and substantiating the claim that flocculation step and adsorption on charcoal are the main steps to reduce the BOD and COD. The % reduction in BOD due to both flocculation and adsorption was 59.04 % (with mixed salts). Total BOD reduction caused by these two steps using $Al_2(SO_4)_3$ was found to be 53.13 %. Total COD reduction due to mixed salt was 66.39 %, of which maximum removal being due to flocculation (59.06 %). $Al_2(SO_4)_3$ reduced 68.53% COD level both in the flocculation and charcoal adsorption, of which 58.03 % removal in COD was contributed by the flocculation step. Overall, both the mixed salts and $Al_2(SO_4)_3$ reduced COD during entire steps in the range of 94.55-95.61 % and BOD in the range of 91.67-96.87 % suggesting that these salts are effectively contributing in the reduction of organic strength.

Table 3. Percent reduction in organic strength after applying various treatments

	Treatment	% Reduction in BOD		% Reduction in COD	
		$Al_2(SO_4)_3$+$FeSO_4$	$Al_2(SO_4)_3$	$Al_2(SO_4)_3$+$FeSO_4$	$Al_2(SO_4)_3$
1.	Filtration	19.92	19.92	23.35	23.35
2.	Flocculation	49.12	45.77	82.41	81.38
3.	Sedimentation	56.61	59.12	85.06	84.30
4.	Charcoal filtration	86.45	86.40	92.39	94.80
5.	Air stripping	91.67	96.87	94.55	95.61

The BOD and COD reductions trends after applying different treatments in sequence are given in Figure 2. A sample bearing COD (2900 mg O_2/l) and BOD (1750 mg O_2/l) was subjected to the sequential treatments (Figure 2). The results substantiate that maximum COD was reduced by the flocculation step.

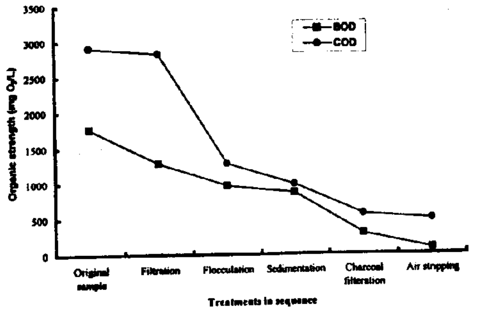

Fig.2: BOD and COD reduction trends by different treatments in sequence.

Most of the refractory substances (1450 mg O_2/l) were removed and quite less amount of biodegradable organics (250 mg O_2/l) were removed by flocculation. This was due to the adsorption of soluble organic matter on the flocculants and settling out of the particulate matter during flocculation.

Sedimentation process did not contribute significantly in removing the remaining organics where only 300 mg COD/l was removed. This is not necessarily due to fact that sedimentation does not remove organics; on the contrary, it does remove organics. That is the reason why charcoal is widely used for the removal of the colour. Another feature of Figure 2 is the air stripping, which did not support any organic removal, mainly due to the presence of very less concentration of volatile organic matter. Yet it might have removed free NH_3 and H_2S if it was originally present. However, this cannot be substantiated in the present studies. Another reason of non-removal of organics can also be linked with other processes; e.g. flocculation and charcoal adsorption. Most of the organics that include volatile and non-volatile both, were removed in the preceding steps of flocculation/charcoal adsorption. This indicates that volatile organics were absent after flocculation and charcoal adsorption steps. Therefore, air stripping at that stage did not impart a significant role. However, had the air-stripping carried out in the beginning of the proposed treatment process, it is more likely that it would have contributed significantly in the reduction of volatile organic and inorganic compounds.

Experimental

Standard methods [18] were employed in all determinations. pH was measured with a Metler Delta-320 pH meter. Suspended solids were determined by filtering an aliquot of sample through Whatman-42 filter paper followed by drying it alongwith its contents at 105°C. Total dissolved solids were determined in the filtrate by evaporating the liquid on a water bath and then drying in an oven at 105°C.

Biological oxygen demand (BOD) in water and wastewater samples were determined by finding out the difference between the initial and final dissolved oxygen (DO) concentration after incubation at 20°C for 5 days divided by the decimal fraction of sample. BOD bottles of 300 ml were used for this purpose. DO levels were measured by Azide modification Winkler's method [18]. Appropriate aliquot of sample was used and suitable dilutions were made wherever needed. Seeded dilution water was used for upstream river water samples so that a marked difference in DO levels could be found. Dilution water was aerated for about 30 minutes before use.

Chemical oxygen demand (COD) of samples was measured by open reflux method [18]. For this purpose, an aliquot of sample was digested in strong acidic environment (H_2SO_4 reagent) in the presence of standard $K_2Cr_2O_7$ solution and digesting the solution for 2 hours. The sulphuric acid reagent contained mercuric sulphate and silver sulphate that are used to catalyse the oxidation of organic matter in the sample. After digestion, the unreacted $K_2Cr_2O_7$ was titrated against standard ferrous ammonium sulphate solution using ferroin indicator. A blank was also run in parallel. Ferrous ammonium sulphate solution was standardized on the same day when COD was carried out owing to its oxidation and its subsequent decrease in concentration with the course of time.

Heavy metals in wastewater were determined by atomic absorption spectrophotometer using AAS Hitachi, model Z-2000 Japan, following the standard methods [18].

Treatment Methodology

Effluent from a sugar industry near Peshawar (Pakistan) was subjected to different treatment steps as illustrated in Figure 1. Two-litre beaker was used for the flocculation experiment, while one-litre measuring cylinder was used for sedimentation studies. Glass funnel with a Whatman filter paper filled with charcoal served as carbon adsorption bed. Aluminium sulphate [$Al_2(SO_4)_3$] and mixture of aluminium and iron sulphates [i.e. $Al_2(SO_4)_3$ + $FeSO_4$] were separately used as flocculants. A 5% (w/v) flocculent solution was used in the study. Calcium carbonate with active calcium content of 70% CaO was used as a flocculent aid. For this purpose, 20% (w/v) lime solution was utilized as was used previously [9].

A known volume of the sample was transferred to a 2-L beaker and a predetermined quantity of flocculent was added to the effluent. The mixture of flocculent and effluent was agitated for 2-3 minutes and allowed to settle for a while. The supernatant was drawn for BOD and COD determination. Lime was added to this mixture and the sample was agitated for 3-5 minutes and the supernatant was again withdrawn for BOD and COD determination.

The effluent followed by flocculation was transferred to a 1-L cylinder to settle down the suspension, COD of the supernatant was determined. The supernatant was filtered through a sand bed and the filtrate was passed over activated Charcoal and BOD and COD of the resulting solution was determined. Finally, air stripping of the solution was carried out by aeration of the sample for an hour. BOD and COD of different treatment steps were determined for monitoring the effectiveness of the process.

Conclusions

Sugar mills effluent was characterized and load of organic strength discharged into Kabul River was evaluated in terms of BOD, COD and other parameters. The results have indicated that the sugar industry discharged effluent that contained high BOD, COD and TSS into the Kabul River.

On the basis of the laboratory scale studies, the extent of pollution due to sugar mills effluent was decreased and an economical and feasible method of treatment has been developed. This method is based on filtration, flocculation, sedimentation, adsorption and air stripping in sequence. Following this sequence, colour of the effluent was improved, TSS level was reduced below the permissible limit of NEQS. Furthermore, COD level of the effluent was decreased from 12211 to 664 mg O_2/L with 95% removal and BOD from 3132 to 261 mg O_2/L with 96% removal.

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