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PHYSIOCHEMICAL STUDY OF NSSC EFFLUENTS AND ASSESSMENT OF PRINCIPAL POLLUTANTS

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Abstract: Waste effluents collected from different processing units of a pulp-mill were analyzed for various physiochemical parameters i.e. appearance, pH, conductance, total dissolved and suspended solids (TDS & TSS), chemical oxygen demand (COD) and 5-days biochemical oxygen demand (BOD_5). Various ions with reference to pulping process were investigated in these effluents which include Cl^-, SO_4^{2-}, SO_3^{2-}, CO_3^{2-} HCO_3^{1-}, Na^+, K^+, Mg^{+2} and Ca^{+2}. Heavy metals like Hg, Pb, Fe, Cr, Cu and Zn was also determined by atomic absorption spectrometry. The results were compared with National Environmental Quality Standards for industrial effluents. Most of the parameters were found outside the permissible limits except the temperature, pH and few cations. Effluents from NSSC process exhibited highest values of TDS, TSS, COD and BOD_5 (these are 103174, 31866, 23340, 6864 mg/l respectively). Chief polluting characteristics of these effluents were found to be the dissolved chemicals and suspended organic matter, which are responsible for very high COD & BOD_5 values. This study was an effort to monitor the concentration of various pollutants in the waste effluents of pulp & paper industry with special emphasis on NSSC effluents and their contribution in environmental pollution. The hazardous effects of these effluents and different treatment methodologies have also been discussed.

Keywords: Neutral sulfite semi-chemical pulping (NSSC), waste effluents, suspended matter, chemical oxygen demand and biochemical oxygen demand.

Introduction:

The process of isolation of cellulose from wood is called as pulping[1, 2]. Wood consists of approximately 57% cellulose, 28% lignin, 10% pentosans and 5% solvent extractions [1]. Other cellulosic raw materials are straw, jute, rope, cotton, linen rags etc. Pulping is achieved by chemical or mechanical methods or combination of the two. In mechanical pulping the original chemical constituents of the fibrous material remain unchanged, except for the removal of water soluble. Chemical pulping selectively removes lignin to a varying degree with a minimum solution of hemicelluloses and the celluloses[2, 3].

Neutral sulfite semi-chemical pulping process (NSSC)

NSSC is one of the most common pulping methods in Pakistan and wheat straw is used as a raw material. The pulping liquor used in NSSC process is a solution of sodium sulfite containing sodium bicarbonate or sodium hydroxide as a buffer to keep the pH around 7. The buffering agent is used to control the corrosion of equipment; and it neutralizes the organic acids that are formed when wood is heated to 120-160 ^oC. The NSSC process consist of four steps (a) steaming of raw material for 30 min at atmospheric pressure, (b) addition of pulping chemical and application of 100 psi pressure at a temperature of 120-125 ^oC for 60 min, (c) third step is the removal of excess liquor not absorbed by the raw material, (d) lastly digestion at 140-160^oC for 1-6 h. The yield of this process is 65-90% depending upon raw material, buffering

1-For Proof and Correspondence: **Naveed Akhtar** agent and cooking time [1, 2].

Wastes of NSSC process

The major waste effluents of NSSC process are strong spent liquor blown from digester and weak spent liquor discharged by pulp washer. The objectionable features of these effluents are their oxygen demand and color. Salts of lower fatty acids and pentosans are responsible for most of the oxygen demand, lignin and tannates for the color [1, 3]. Usually an appreciable amount of finely divided fiber is lost in the process which raises the amount of suspended matter in waste effluents.

Some other wastes which are associated with pulp & paper mill and these contribute significantly towards total mill-wastes includes the bleachery wastes, deinking wastes and paper machine over-flow water [3].

Experimental Work

Sampling Procedures

Waste-water samples were collected in appropriate containers provided by R&D Department of Packages Limited Lahore. All the samples were immediately transported to Environmental Protection Study Center, PCSIR Lahore, in accordance with appropriate procedures and holding times [4]. Waste water analyses were started immediately and the remaining proportions of the samples were kept tight and stored below 10^{o}C.

Analytical Methods

Physical parameters i.e. pH, conductivity & temperature analysis were performed by electrometric methods. The pH was measured with Crison digital model PH2001 and Jenway conductivity meter model 4010 was used to measure the conductivity. TDS and TSS were determined by weight and drying method. Total hardness, calcium hardness and magnesium hardness was determined by complexometric titrations [5]. The amount of CO_3^{2-} and HCO_3^{1-} was measured via phenolphthalein alkalinity and methyl orange alkalinity tests respectively. Chlorides were measured with standard silver nitrate solution using potassium chromate as an indicator[5,6]. Sulfates were determined by adding standard barium chloride solution in excess and then titrating against standard EDTA solution[6]. Sulfites were determined by titration against standard sodium thiosulfate using starch solution as an indicator[5,6].

Biochemical oxygen demand was measured by dilution method[6]. Known amount of waste-water sample was diluted with BOD water and kept for 5 days at 20^{o}C. The residual oxygen was measured after 5 days (120 h) by titrating against standard sodium thiosulfate solution.

Chemical oxygen demand was determined by potassium dichromate method. The sample was digested with excess of standard $K_2Cr_2O_7$ in acidic medium and in the presence of silver sulfate and mercury sulfate. Excess of potassium dichromate was determined by titrating against standard ferrous ammonium sulfate (Mohr's salt) using ferroin solution as a redox indicator[6].

Cations like Na^{+}, K^{+} and Ca^{+2} were measured by flame photometry[7] using Jenway PFP-7 flame emission photometer. Heavy metals like Cu, Cr, Fe, Pb, Al and Zn was determined by atomic absorption spectrometry[7]. The equipment used was Varian AA-127 spectrophotometer.

Results & Discussion

Waste effluents from NSSC pulping process of Packages Limited Lahore was investigated along with some other processes in the factory. A total number of 5 sampling points were selected which includes NSSC pulping effluents (black liquor), chemithermo mechanical pulping effluents (CTMP), fiber line plant effluents (NFL), waste paper plant effluents (WPP) and machine room effluents (M/R).

All the waste water samples were examined for about 26 parameters and the results are summarized in table-1 to table-5. When we compare the results of these effluents with National Environmental Quality Standards (NEQS) of Pakistan[8] reproduced in table-6, it is revealed that all the five samples contain very high quantities of TDS, TSS, COD and BOD_5. The black liquor from NSSC process showed highest values of these parameters cited in table-1. The objectionable color and bad odor of back liquor is due to the large quantities of suspended organic matter & dissolved chemicals.

Figure 1 to 4 further illustrates that NSSC waste effluents have enormous problem of dissolved solids, suspended mater and oxygen demand, those appear to be the main pollutants of the pulping wastes. CTMP and NFL waste effluents contain relatively less load of oxygen demand, TDS and TSS as compared to NSSC black liquor. Mainly due to the change in pulping methodology and process employed in CTMP and NFL units.

Waste effluents from WPP and M/R showed considerably less load of oxygen demand. TDS in these effluents were found in line with NEQS but suspended solids exceeded the limits. It is notable that WPP effluents contain high values of COD & BOD^5 as compared to the NFL and M/R effluents; because WPP is a waste recycling plant and relatively much stronger chemicals are applied for the production of pulp. The WPP effluents contain fiber debris together with a considerable amount of organic matter which accounts for high BOD_5 values.

It is evident from the above discussion that pragmatically it is convenient to characterize these effluents in terms of biological oxygen demand, chemical oxygen demand and color. These parameters appear to be the principal polluting characteristics of the subject effluents. In case of NFL, WPP and M/R waste effluents, these pollutants may become inside the NEQS limits on 1:10 dilution upon entering the water bodies. However NSSC and CTMP waste effluents definitely need a treatment before discharging into the environment. When we examine cations and anions in these effluents, sulfur containing species are found to be the main issue and their large quantity is a serious threat to environment. NSSC effluents contain large amount of sulfite ions and sodium ions, well expected because of pulping agent. All the rest of cations and anions are within the limits or will become on 1:5 times dilution upon entering the water bodies.

Heavy metals were also examined in the waste-waters of Packages Limited Lahore. The principal metals of concern to pulp & paper industry are Al, Cr, Ni, Ti, Fe, Hg and Zn. These metals that might be present in waste effluents originate[3] from three potential sources; (a) chemical used in pulping, (b) additives used in paper making and (c) products of equipment corrosion. When we compared the results of all the five samples with NEQS, heavy metals were found inside the upper limits. Iron was the only metal which crossed the limit; we found 1.2-3.5 mg/l of Fe in our samples whereas the maximum permissible limit is 2.0 mg/l. Effluents from WPP contains relatively higher amount of metal ions, possibly due to recycling process (used paper, board paper & products, newspaper and printed books etc are recycled in this plant). The WPP utilizes drastic chemicals for deinking and pulping of mixed type of raw material. Therefore it is always a possibility of metal ions in greater amounts in these effluents. The harmful effects of these metals on environment and human health are elaborately discussed in[9, 10].

Pulp and paper mill effluents are toxic to aquatic organisms and exhibits strong mutagenic effects and psychological impairment[11]. Varieties of responses were reported in fish population living downstream near a pulp & paper mill discharge. This includes delayed sexual maturity, smaller gonads and changes in fecundity[12, 13, 14].

Treatment techniques for pulp & paper mill wastes i.e. activated sludge process, aerated stabilization, storage oxidation etc has been discussed in detail[15, 16]. Diverse treatment methodologies for pulp mill effluents have been proposed, particularly treatments based upon the use of calcium hydroxide and active charcoal for suspended matter and color removal. Traditionally biological treatment is being applied for treating these wastes to reduce their BOD. Irrigation disposal[17] of weak NSSC wastes can be successful if properly installed and managed. Fodder crops are grown on the disposal area and this is a particularly economical and effective system for small mills.

Researcher in Thailand and Japan demonstrated 52–86% decolourization of pulp mill waste water using thermotolerant white rot fungi[18] and they achieved 59-83% COD reduction. The cationic and anionic polyelectrolytes were applied on pulp & paper mill waste effluents resulted in 95% of turbidity removal, 98% of TSS removal and 89% of COD removal[19]. Researchers are also working for energy[20] because pulp and paper mills generate large quantities of energy-rich biomass as wastes. Recovery of energy from wastes of different origin has become a generally accepted alternative to their disposal.

Conclusion

This study revealed that objectionable color, bad odor and high values of COD and BOD_5 along with TDS and TSS are the major problems of NSSC effluents and chiefly contribute to the total mill-waste. Due to high oxygen demand these effluents can cause potential toxicity to the fish and microorganism upon which fish feed. Therefore proper treatment techniques should be employed before discharging such effluents into the environment.

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Table 1: Physiochemical analysis of NSSC effluents

Sr. #	Parameter Studied	Results	
1	*Description / Color*	*Blackish brown color & objectionable odor*	
2	*pH at 29.6* ^oC	*8.87*	
3	*Conductivity*	*3830*	*µs/cm*
4	*Total solids*	*135040*	*ppm*
5	*TDS*	*103174*	*ppm*
6	*TSS*	*31866*	*ppm*
7	*Total hardness as* $CaCO_3$	*2813*	*ppm*
8	*Ca hardness as* $CaCO_3$	*1801.2*	*ppm*
9	*Mg hardness as* $CaCO_3$	*1011.8*	*ppm*
10	*Sodium as* Na^+	*25500*	*ppm*
11	*Potassium as* K^+	*1300*	*ppm*
12	*Calcium as* Ca^{++}	*720.48*	*ppm*
13	*Magnesium as* Mg^{++}	*245.86*	*ppm*
14	*Chlorides* (Cl^-)	*50*	*ppm*
15	*Sulfate* (SO_4^{2-})	*1420.8*	*ppm*
16	*Sulfite* (SO_3^{2-})	*12531*	*ppm*
17	*M-alkalinity* (HCO_3^{1-})	*3421.1*	*ppm*
18	*P-alkalinity* (CO_3^{2-})	*1872.3*	*ppm*
19	*COD*	*23340.3*	*ppm*
20	BOD_5	*6864.7*	*ppm*
21	*Aluminum (Al)*	*BDL*	*ppm*
22	*Copper (Cu)*	*BDL*	*ppm*
23	*Chromium (Cr)*	*0.9*	*ppm*
24	*Iron (Fe)*	*2.2*	*ppm*
25	*Lead (Pb)*	*0.4*	*ppm*
26	*Zinc (Zn)*	*BDL*	*ppm*

Note. The results are mean of triplicate readings
BDL = below detection limit

Table 2: Physiochemical analysis of CTMP effluents

Sr. #	Parameter Studied	Results	
1	Description / Color	Dark brown appearance	
2	pH at 29.4 ^oC	6.33	
3	Conductivity	3750	µs/cm
4	Total solids	13084	ppm
5	TDS	10160	ppm
6	TSS	2924	ppm
7	Total hardness as $CaCO_3$	2532	ppm
8	Ca hardness as $CaCO_3$	2094	ppm
9	Mg hardness as $CaCO_3$	438	ppm
10	Sodium as Na^+	2300	ppm
11	Potassium as K^+	1000	ppm
12	Calcium as Ca^{++}	837.6	ppm
13	Magnesium as Mg^{++}	106.4	ppm
14	Chlorides (Cl^-)	3011	ppm
15	Sulfate (SO_4^{2-})	1275.3	ppm
16	Sulfite (SO_3^{2-})	1052.7	ppm
17	M-alkalinity (HCO_3^{1-})	1830	ppm
18	P-alkalinity (CO_3^{2-})	-	ppm
19	COD	6758.3	ppm
20	BOD_5	2310	ppm
21	Aluminum (Al)	BDL	ppm
22	Copper (Cu)	BDL	ppm
23	Chromium (Cr)	0.7	ppm
24	Iron (Fe)	3.5	ppm
25	Lead (Pb)	0.3	ppm
26	Zinc (Zn)	BDL	ppm

Table 3: Physiochemical analysis of NFL effluents

Sr. #	ParameterStudied	Results	
1	*Description / Color*	*Light brown color & objectionable odor*	
2	*pH at 28.8 ^oC*	*6.78*	
3	*Conductivity*	*2870*	*µs/cm*
4	*Total solids*	*13130*	*ppm*
5	*TDS*	*6732*	*ppm*
6	*TSS*	*6398*	*ppm*
7	*Tot al hardness as $CaCO_3$*	*725*	*ppm*
8	*Ca hardness as $CaCO_3$*	*376*	*ppm*
9	*Mg hardness as $CaCO_3$*	*349*	*ppm*
10	*Sodium as Na^+*	*358*	*ppm*
11	*Potassium as K^+*	*740*	*ppm*
12	*Calcium as Ca^{++}*	*150.4*	*ppm*
13	*Magnesium as Mg^{++}*	*84.81*	*ppm*
14	*Chlorides (Cl^-)*	*601.2*	*ppm*
15	*Sulfate (SO_4^{2-})*	*81.23*	*ppm*
16	*Sulfite (SO_3^{2-})*	*179.3*	*ppm*
17	*M-alkalinity (HCO_3^{1-})*	*915*	*ppm*
18	*P-alkalinity (CO_3^{2-})*	*-*	*ppm*
19	*COD*	*1536.4*	*ppm*
20	*BOD_5*	*590.76*	*ppm*
21	*Aluminum (Al)*	*1.0*	*ppm*
22	*Copper (Cu)*	*BDL*	*ppm*
23	*Chromium (Cr)*	*0.5*	*ppm*
24	*Iron (Fe)*	*1.2*	*ppm*
25	*Lead (Pb)*	*BDL*	*ppm*
26	*Zinc (Zn)*	*0.4*	*ppm*

Table 4: Physiochemical analysis of WPP effluents

Sr. #	ParameterStudied	Results	
1	Description / Color	Grayish look & lots of settleable solids	
2	pH at 29.0 ^oC	6.86	
3	Conductivity	1552	µs/cm
4	Total solids	2968	ppm
5	TDS	978	ppm
6	TSS	1890	ppm
7	Tot al hardness as $CaCO_3$	1602	ppm
8	Ca hardness as $CaCO_3$	1147	ppm
9	Mg hardness as $CaCO_3$	455	ppm
10	Sodium as Na^+	900	ppm
11	Potassium as K^+	10	ppm
12	Calcium as Ca^{++}	458.8	ppm
13	Magnesium as Mg^{++}	110.6	ppm
14	Chlorides (Cl^-)	3500	ppm
15	Sulfate (SO_4^{2-})	53.76	ppm
16	Sulfite (SO_3^{2-})	350.1	ppm
17	M-alkalinity (HCO_3^{1-})	610	ppm
18	P-alkalinity (CO_3^{2-})	-	ppm
19	COD	1921.4	ppm
20	BOD_5	800.56	ppm
21	Aluminum (Al)	1.2	ppm
22	Copper (Cu)	0.8	ppm
23	Chromium (Cr)	0.65	ppm
24	Iron (Fe)	2.7	ppm
25	Lead (Pb)	0.5	ppm
26	Zinc (Zn)	0.45	ppm

Table 5: Physiochemical analysis of M/R effluents

Sr. #	Parameter Studied	Results	
1	*Description / Color*	*Pulp color with lot of settleable solids*	
2	*pH at 28.7 ^oC*	*7.21*	
3	*Conductivity*	*1360*	*µs/cm*
4	*Total solids*	*2767*	*ppm*
5	*TDS*	*683*	*ppm*
6	*TSS*	*2084*	*ppm*
7	*Total hardness as $CaCO_3$*	*227.3*	*ppm*
8	*Ca hardness as $CaCO_3$*	*173.1*	*ppm*
9	*Mg hardness as $CaCO_3$*	*54.24*	*ppm*
10	*Sodium as Na^+*	*541*	*ppm*
11	*Potassium as K^+*	*20*	*ppm*
12	*Calcium as Ca^{++}*	*90.94*	*ppm*
13	*Magnesium as Mg^{++}*	*13.18*	*ppm*
14	*Chlorides (Cl^-)*	*75.2*	*ppm*
15	*Sulfate (SO_4^{2-})*	*169.2*	*ppm*
16	*Sulfite (SO_3^{2-})*	*70.5*	*ppm*
17	*M-alkalinity (HCO_3^{1-})*	*381.2*	*ppm*
18	*P-alkalinity (CO_3^{2-})*	*-*	*ppm*
19	*COD*	*1347*	*ppm*
20	*BOD_5*	*481.1*	*ppm*
21	*Aluminum (Al)*	*1.1*	*ppm*
22	*Copper (Cu)*	*BDL*	*ppm*
23	*Chromium (Cr)*	*0.3*	*ppm*
24	*Iron (Fe)*	*2.0*	*ppm*
25	*Lead (Pb)*	*BDL*	*ppm*
26	*Zinc (Zn)*	*BDL*	*ppm*

Table 6: National environmental quality standards [8] for municipal and liquid industrial effluents

Sr. #	Parameters	Standards	
1	*Temperature*	*40 °C*	
2	*pH value*	*6 – 10 pH*	
3	*Total dissolved solids (TDS)*	*3500*	*mg/l*
4	*Total suspended solids (TSS)*	*150*	*mg/l*
5	*Chloride (Cl^-)*	*1000*	*mg/l*
6	*Fluoride (F^-)*	*20*	*mg/l*
7	*Sulfate (SO_4^{2-})*	*600*	*mg/l*
8	*Sulfide (S^{2-})*	*1.0*	*mg/l*
9	*COD*	*150*	*mg/l*
10	*BOD_5*	*80*	*mg/l*
11	*Cadmium (Cd)*	*0.1*	*mg/l*
12	*Copper (Cu)*	*1.0*	*mg/l*
13	*Chromium (Cr)*	*1.0*	*mg/l*
14	*Iron (Fe)*	*2.0*	*mg/l*
15	*Lead (Pb)*	*0.5*	*mg/l*
16	*Zinc (Zn)*	*5.0*	*mg/l*
17	*Total toxic metals*	*2.0*	*mg/l*

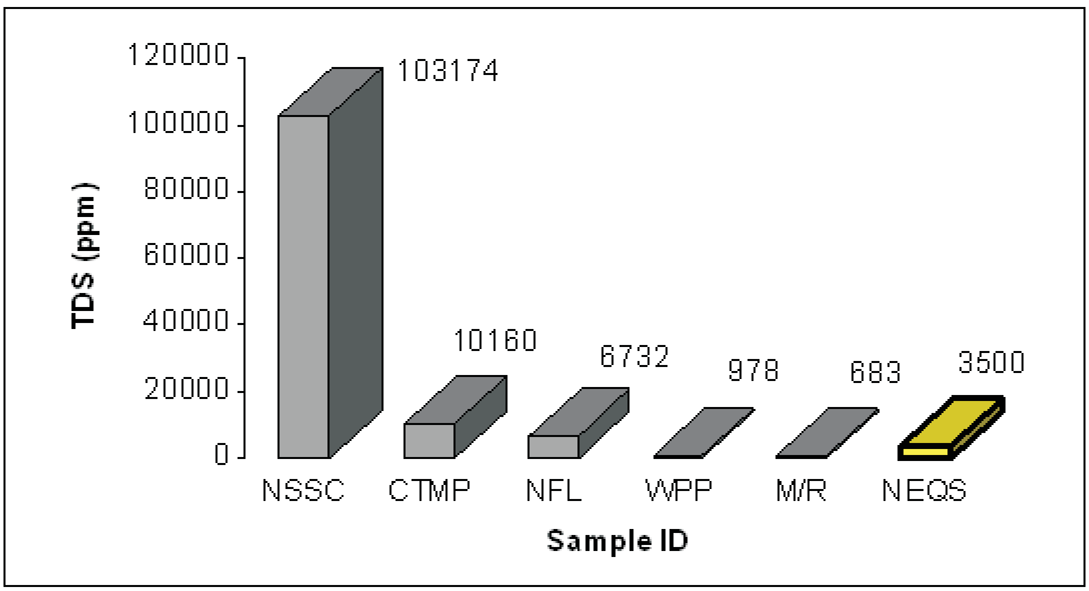

Fig-1: Comparison of TDS in various effluents with NEQS

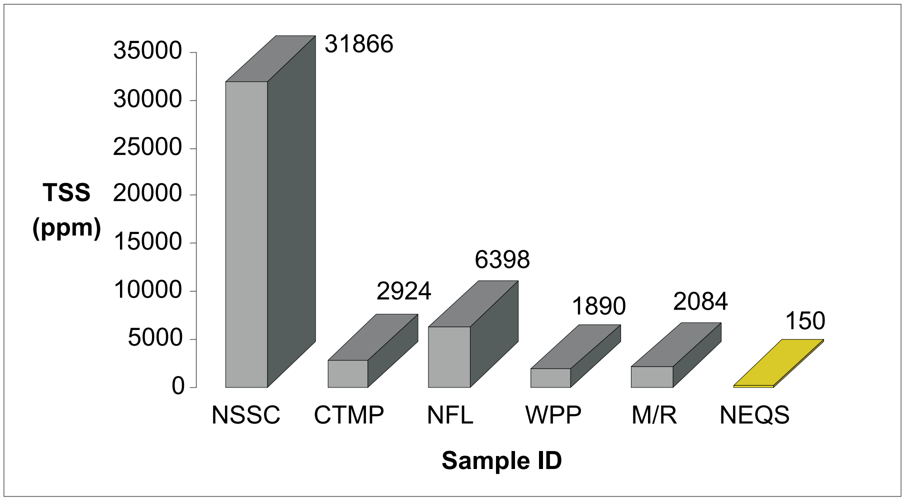

Fig-2: Comparison of TSS in various effluents with NEQS

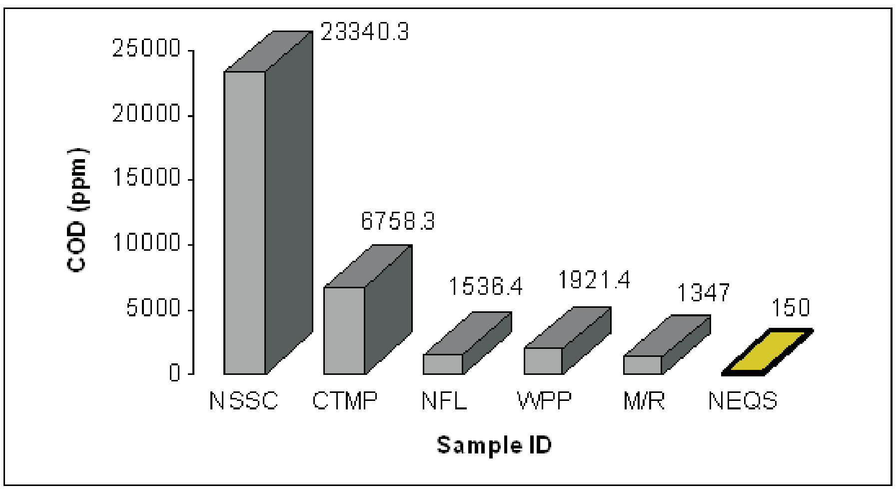

Fig-3: Comparison of COD in various effluents with NEQS

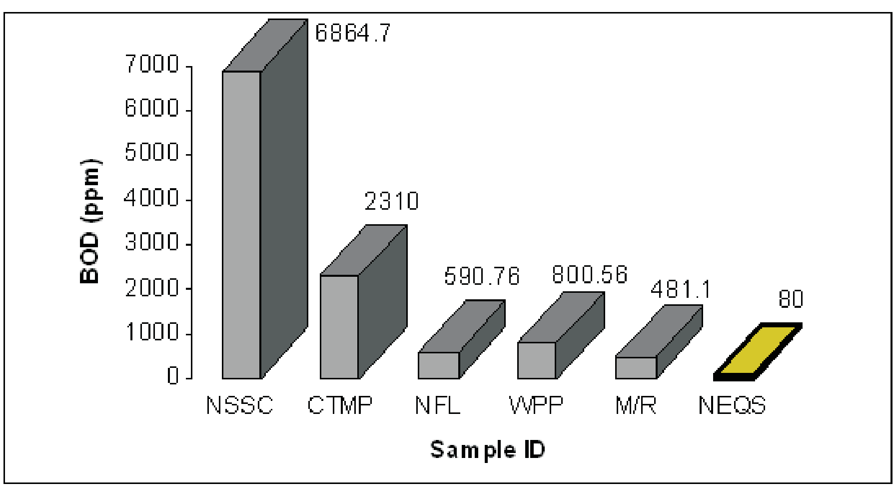

Fig-4: Comparison of BOD in various effluents with NEQS