Characterization of Effluents from Marble Industries Located in the Industrial Estates of NWFP (Pakistan)

[1]M. KHAN, [1]U. KALSOOM, [1]A. R. KHAN, [1]F. KHAN AND [2]IMDADULLAH
[1]*PCSIR Laboratories Complex, Jamrud Road Peshawar*
[2]*Department of Chemistry University of Peshawar*

(Received 7th August, 2002, revised 25th June, 2003)

Summary: Effluent samples were collected from some of the marble industries located in the Industrial Estates of NWFP and were chemically evaluated for the parameters like TSS, TDS, BOD, COD, and metals like Cr^{+3}, Fe^{+2}, Zn^{+2}, Pb^{+2}, Cu^{+2} and Ni^{+2}, These values were compared with the National Environment Quality Standards, (NEQS) and it was found that most of the values are higher then the standard limit of NEQS.

The TSS values are in the range of 1915 to 2915 mg/L for the samples collected from Industrial Estate Hayatabad. Its values ranges from 985-2219 mg/L for Industrial Estate Hattar and from 675-2212 mg/L for Industrial Estate Gadoon 525-1612 mg/L (or G.T.Road and 824-4010 mg/L for scattered Industries. Similarly the TDS values ranges from 2617-2840 mg/L for Industrial Estate Hayatabad, 2328-3955 mg/L for Industrial Estate Hattar, 2140-3688 mg/L for I.E. Gadoon, 1523-3880 mg/L for G. T. Road and 1617-2280 mg/L for scattered Industries. The COD values ranges from 50-75 mg/L for Industrial Estate Hayatabad, 96-160 mg/L for Industrial Estate Hattar, 110-240 mg/L for Industrial Estate Gadoon, 82-210 mg/L for G.T. Road and 96-128 mg/L for scattered Industries. The BOD values in almost all the samples of the Industrial Estates were found to be within the permissible limits of 43-59 mg/L Trace toxic metals were also found to be within the permissible range, however in some samples they exceed the NEQS.

Introduction

Wastes from the Marble Industries normally carry loads of suspended and dissolved solids, which are harmful to both aquatic and human life. Marble is mostly composed of carbonates of calcium and Magnesium, which impart an important role in contaminating the soil after being discharged in the form of effluents resulting in the hazardous effects on aquatic, wildlife and agricultural activities.

Several studies have been made in the past on characterization of industrial effluents and their contribution towards the aquatic pollution. Studies have been carried out on the monitoring of industrial effluents from the industries of different localities of NWFP [1-2]. Similarly Inorganic contaminant in the potable water of Karachi has also been reported [3]. Studies were also undertaken on the environmental impacts of Industrial Effluents from woolen & Sugar Mills situated in D. I. Khan [4] that render the potable water unfit for drinking purpose due to contamination from these industries. Wastewaters of tanneries, fertilizers and textile industries in Multan region has also been reported [5] which reveals that the waste from these industries are highly polluted and are hazardous to the mankind and environment. The adverse effects of industrial effluents on soil and vegetation have also been reported [6-7] The pollution of Kabul River by the receiving discharges from the industries located along its way has been discussed [8-9] and it was concluded that Kabul River is no longer fit for drinking due to the indiscriminate discharges of the industrial effluents in the river [10]. The studies have also been undertaken on the textile effluents [11] and it was reported that the discharges from these industries are responsible for reduction of fish population due to the alarmingly high concentration of sulphide in Kabul river.

Besides the harmful effects of marble wastes, studies have also been carried out on the possible uses of these wastes in cement industries. Effect of marble wastes on the physico-chemical properties of Portland cement have been discussed and the possible uses of marble waste as a mineral filler in the manufacturing of Portland cement has been reported [12]. The possibility of using marble waste in cement manufacturing with significant economic effect and for prôducing quality cement has also been reported [13].

Results and Discussion

The determination like temperature, pH, Total Suspended Solids (TSS), Total Dossolved Solids

Table-1: Results of Effluent Samples (mg/L) Collected from Marble Industries in Industrial Estate Hayatabad

PARAMTERS	INDUS-TRY # 1	INDUS-TRY # 2	INDUS-TRY # 3	INDUS-TRY # 4	AVERAGE	S.D
Temperature (°C)	27.00	27.00	27.00	26.00	26.75	±0.40
pH	8.20	7.82	7.22	8.42	7.915	±0.45
Total Suspended Solids (TSS)	2151.00	2400.00	1915.00	2915.00	2345.25	±370.90
Total Dissolved Solids (TDS)	2840.00	2617.00	2623.00	2700.00	2695.00	±89.90
Biochemical Oxygen Demand (BOD)	60.20	75.20	54.00	50.00	59.85	±9.57
Chemical Oxygen Demand (COD)	125.00	145.40	148.00	250.00	167.10	±48.67
Chromium as Cr	1.10	0.55	0.54	0.50	0.672	±0.25
Copper as Cu^{+2}	0.62	0.38	0.58	0.80	0.595	±0.149
Lead as Pb^{+2}	BDL	0.28	0.35	0.25	0.293	±0.042
Iron as Fe^{+2}	3.34	1.13	2.13	4.30	2.725	±1.19
Zinc as Zn^{+2}	5.16	2.80	3.28	4.13	4.28	±0.96
Nickel as Ni^{+2}	0.42	0.10	0.52	BDL	0.346	±1.179

BDL = Below detection limits.
S.D = Standard Deviation

Table-2: Results of Effluent Samples (mg/L) Collected from 3 Marble Industries in Industrial Estate Hattar (Haripur)

PARAMTERS	INDUSTRY # 1	INDUSTRY # 2	INDUSTRY # 3	AVERAGE	S.D
Temperature (°C)	30.00	28.00	26.00	28.00	±1.63
pH	8.11	8.10	8.21	8.14	±0.049
Total Suspended Solids (TSS)	1230.00	985.00	2219.00	1478.	±533.4
Total Dissolved Solids (TDS)	2328.00	3955.00	3780.00	3354.30	±729.2
Biochemical Oxygen Demand (BOD)	64.50	55.00	45.30	54.93	±7.83
Chemical Oxygen Demand (COD)	160.00	120.30	96.20	125.33	±26.39
Chromium as Cr	BDL	0.54	0.24	0.44	±0.81
Copper as Cu^{+2}	BDL	0.85	0.68	0.765	±0.085
Lead as Pb^{+2}	BDL	0.25	0.20	0.225	±0.025
Iron as Fe^{+2}	1.23	4.35	3.34	2.973	±1.29
Zinc as Zn^{+2}	1.46	5.13	4.88	3.823	±1.674
Nickel as Ni^{+2}	BDL	0.50	0.23	0.365	±0.135

BDL = Below detection limits.
S.D = Standard Deviation

Table-3: Results of Effluent Samples (mg/L) Collected from 4 Marble Industries in Industrial Estate Gadoon Amazai

PARAMTERS	INDUS-TRY # 1	INDUS-TRY # 2	INDUS-TRY # 3	INDUS-TRY # 4	AVERAGE	S.D
Temperature (°C)	26.00	28.20	27.00	28.00	27.30	±0.877
pH	7.12	7.62	8.02	7.88	7.66	±0.343
Total Suspended Solids (TSS)	2212.00	899.00	915.00	675.00	1175.26	±606.04
Total Dissolved Solids (TDS)	2842.00	3688.00	2140.00	2668.00	2834.50	±556.45
days Biochemical Oxygen Demand (BOD)	62.20	46.80	N.D	56.80	55.26	±6.38
Chemical Oxygen Demand (COD)	122.40	100.60	240.00	110.00	143.25	±56.39
Chromium as Cr	0.42	0.28	0.65	0.43	0.445	±0.132
Copper as Cu^{+2}	0.62	BDL	0.62	0.35	0.53	±0.127
Lead as Pb^{+2}	0.22	0.16	0.45	0.41	0.31	±0.127
Iron as Fe^{+2}	2.42	3.36	4.43	3.34	3.337	±0.719
Zinc as Zn^{+2}	6.13	3.16	2.56	2.25	3.525	±1.539
Nickel as Ni^{+2}	2.21	0.18	BDL	0.50	1.195	±1.015

BDL = Below detection limits.
S.D = Standard Deviation

(TDS), Biochemical Oxygen Demand (BOD), and the Chemical Oxygen Demand (COD) were determined in the industrial effluent samples. The heavy metals like chromium $(Cr)^{+3}$, Copper $(Cu)^{+2}$, Lead $(Pb)^{+2}$, Iron $(Fe)^{+2}$, and Nickel $(Ni)^{+2}$ were also determined in these samples. These parameters are represented in Tables 1-5 whereas the Standard values of NEQS are shown in Table-6.

The temperature ranges from 26-31°C in the effluents samples collected from the marble industries in all the Industrial Estate of NWFP which

Table-4: Results of Effluent Samples (mg/L) Collected from 6 Marble Industries in Industrial Estate at G.T. Road Peshawar

PARAMTERS	INDUS-TRY # 1	INDUS-TRY # 2	INDUS-TRY # 3	INDUS-TRY # 4	INDUS-TRY# 5	INDUS-TRY # 6	AVER-AGE	S.D.
Temperature (°C)	26.00	29.00	22.00	27.00	29.00	31.00	27.33	±2.867
pH	7.68	7.62	7.60	8.08	7.76	7.33	7.678	±0.223
Total Suspended Solids (TSS)	625.00	924.	1125.00	1612.00	725.00	525.00	922.67	±365.59
Total Dissolved Solids (TDS)	2553.00	3722	1523.00	3600.00	2828.00	3888.00	3019.00	±824.47
Biochemical Oxygen Demand (BOD)	46.80	66.80	76.00	38.00	56.00	65.00	58.10	±12.78
Chemical Oxygen Demand (COD)	110.00	129.20	210.00	82.20	120.00	122.60	129.00	±39.23
Chromium as Cr	0.23	0.28	0.45	0.25	0.55	0.52	0.378	±0.132
Copper as Cu^{+2}	0.39	0.64	0.38	0.26	0.26	0.28	0.368	±0.133
Lead as Pb^{+2}	0.49	0.62	0.28	BDL	0.24	0.42	0.412	±0.137
Iron as Fe^{+2}	4.42	3.46	4.36	1.42	3.36	3.12	3.356	±0.996
Zinc as Zn^{+2}	3.15	4.80	4.14	2.18	2.34	2.02	3.105	±1.046
Nickel as Ni^{+2}	BDL	0.70	0.21	0.55	0.51	BDL	4.92	±0.182

BDL = Below detection limits.
S.D = Standard Deviation

Table-5: Results of Effluent Samples (mg/L) Collected from some Scattered Industries in Peshawar

PARAMTERS	INDUSTRY # 1	INDUSTRY # 2	INDUSTRY # 3	AVERAGE	S.D
Temperature (°C)	27.00	29.00	28.00	28.00	±0.816
pH	7.11	6.82	7.60	7.17	±0.322
Total Suspended Solids (TSS)	4010.00	220.00	824.00	2344.67	±1304.70
Total Dissolved Solids (TDS)	2232.00	1617.00	2121.00	1990.00	±267.6
Biochemical Oxygen Demand (BOD)	40.80	48.00	40.20	43.00	±3.544
Chemical Oxygen Demand (COD)	128.00	100.20	96.50	108.20	±14.05
Chromium as Cr^{+2}	0.65	BDL	0.12	0.385	±0.265
Copper as Cu^{+2}	0.48	0.78	BDL	0.63	±0.15
Lead as Pb^{+2}	0.24	0.55	BDL	0.395	±0.155
Iron as Fe^{+2}	2.38	2.28	1.13	1.93	±1.567
Zinc as Zn^{+2}	4.21	6.04	2.28	4.17	±1.535
Nickel as Ni^{+2}	0.34	BDL	BDL		

BDL = Below detection limits.
S.D = Standard Deviation.

Table-6: National Environmental Quality Standards (NEQS) for Industrial Effluents of Pakistan [15]

PARAMTERS	STANDARDS
Temperature (°C)	40.00 °C
pH	6.5-9.2
Total Suspended Solids (TSS)	150.00 mg/L
Total Dissolved Solids (TDS)	3500.00 mg/L
Biochemical Oxygen Demand (BOD)	80.00 mg/L
Chemical Oxygen Demand (COD)	150.00 mg/L
Chromium as Cr	1.00 mg/L
Copper as Cu^{+2}	1.00 mg/L
Lead as Pb^{+2}	0.50 mg/L
Iron as Fe^{+2}	2.00 mg/L
Zinc as Zn^{+2}	5.00 mg/L
Nickel as Ni^{+2}	1.00 mg/L

indicate that the temperature of the effluent samples are within the permissible limit (40 °C) of the NEQS. The pH varies from 6.82 - 8.42 in the samples from different localities of NWFP, which are also considered to be within the permissible range (6.5 – 9.2). The Total Suspended Solids (TSS) varies from 525 – 4010 mg/L, which are alarmingly high than the permissible limits of 150 mg/L, which causes high turbidity and prevent light from entering into the water and therefore effects the normal growth of aquatic plant. The Total Dissolved Solids (TDS) are also higher than the permissible limits of 3500 mg/L in some samples from G. T. Road, Industrial Estate Hattar, and Industrial Estate Gadoon Amazai whereas the rest of samples are below the permissible limits. The excess of this parameter above the permissible limit may disturb the aquatic life.

The values of Biochemical Oxygen Demand (BOD) varies from 38 – 76 mg/L which are within the permissible limit of 80 mg/L. The high values of the BOD may cause depletion of dissolved oxygen. The Biochemical Oxygen Demand (BOD) of the industrial effluents is the quantity of dissolved oxygen required for the stabilization of decomposable organic matter by aerobic biochemical action. The value for Chemical Oxygen Demand (COD) varies from 82 – 250 mg/L whereas its permissible

value is 150 mg/L. The COD is considered as indicating the amount of carbonaceous organic matter present in the effluent. This is an important parameter for industrial effluents since it determines the oxidizable organic matter. In some of the samples its values are higher than the permissible limits.

Toxic and heavy metals like chromium, Copper, Lead, Iron, Zinc and Nickel are commonly used in the industry and are often present in industrial effluents. The chromium content varies from traces to 0.65 mg/L, except for sample from industry No. 1 from Industrial Estate Hayatabad which has a chromium content of 1.10 (above the permissible limit of 1 mg/L), rest of the samples are within the permissible range for chromium content. Similarly copper content ranges from traces to 0.80 mg/L and are within the permissible limits of NEQS (1 mg/L) The Iron content ranges from 1.13 – 4.43 mg/L. The reddish colour and unpleasant taste and odour of water is mainly due to the excessive concentration of iron resulting in the corrosion of pits. The zinc content varies from 1.46 – 6.13 mg/L and are higher than the permissible limits of 5 mg/L in some samples. The nickel content varies from traces to 2.21 mg/L and its content is higher than the permissible limit of 1 mg/L in a sample from Industrial Estate Gadoon. The Nickel content in rest of the samples lies within the permissible limits of NEQS.

Experimental

Sampling

Samples were collected from various industries in 1 Liter Polythene containers. The containers were washed with the cleaning mixture and detergent before sampling. After sampling, the container were kept air tight till analysis. Samples were collected from the drain at different distances from the Industries.

Procedure

Temperature and pH of each sample was measured by a Centigrade thermometer and Coring 240 digital pH meter respectively on the spot. The Total Suspended Solids (TSS) and Total Dissolved Solids (TDS) were determined by standard methods [14].

The biochemical oxygen demand (BOD) was determined by diluting suitable portion of the sample with water, followed by saturation with oxygen. The dissolved oxygen was measured in the mixture both immediately and after a period of incubation for 5 days at 20 °C [14]. The chemical oxygen demand (COD) is measured by refluxing a suitable portion of the sample with standard (0.25N) potassium dichromate solution and concentrated sulphuric acid (H_2SO_4). After refluxing the mixture at 150°C for two hours, the solution is cooled and titrated the excess dichromate with standard Ferrous Ammonium Sulphate solution using ferroin as indicator.

The metal ions like Cr^{+3}, Cu^{+2}, Pb^{+2}, Fe^{+2}, Zn^{+2} and Ni^{+2} were determined by Flame atomized Atomic Absorption Spectrophotometer Z-2000 (Hitachi Japan). Stock standard solutions (1000 mg/L) were prepared for each element from their respective salts. These solutions were further diluted for preparing working standards in the measuring ranges. The instrument was operated under Flame atomization mode and absorbance measurements were recorded for each element using their respective cathode lamp. Calibration of the instrument was periodically repeated during operation and their concentrations were recorded on a compatible personal computer.

Conclusions

On the basis of the studies undertaken it has been concluded that effluents from the marble industries carry loads of suspended and dissolved solids, which are harmful both for agriculture & general environment. This situation also contributes significantly in threatening the local aquatic population in water without any proper treatment into the receiving streams and canals. However application of treatment procedures to such wastes are essential to minimize their harmful effects. Further, implementation of NEQS must be strictly implimented.

References

1 M. Rasul Jan, Haider Shah, *Jour. Chem. Soc. Pak*, **20**(1), 41 (1998).
2 Yousaf Iqbal, Sultan Alam and Miraj Muhammad, *Jour. Chem. Soc. Pak.* **20**(1), 46 (1998)
3 Sneedon Ceguan, A. Sajif Bari, Zahida Begum and S.A. Malik, *Jour. Chem. Soc. Pak.*, **20**(I), 38 (1998).
4 Muse Kaleem, Muhammad Ishaq, *Pak. J. Anal. Chem.*, **2**(1) 48 (2001).

5 T.M. Ansari, S.A. Malik and M Naeem, *Pak. J. Anal. Chem.*, 2(1) 59 (2001)
6 "A.R. Khan and M.Akif: Environmental Degradation in Haripur Hazara" Technical report PCSIR Labs., Peshawar (1994).
7 M.H. Bukhari and S.A. Malik "Effects of Industrial Effluents on Soil & Vegetation in and around Multan" Tech: report, Institute of Pure and applied biology, Bahuddin Zakria University Multan (1994-97).
8 "Environmental Profile of Pakistan" Environmental and urban affair Division Government of Pakistan Islamabad (1987)
9 I.A.V., DIJK and M. H. Hussain "Environmental Profile of NWFP Pakistan, Government of NWFP" pp 47 (1994)
10 K. Khan, M. Akif, M. A. Khattak, *J. Engg App Sci.* 4, 111 (1985).
11 M. Akif, A. R. Khan, Mumtaz Khan, *Jour. Chem. Soc. Pak* (In press).
12 Turdieva, R. M. Mingu lova, F.A. Atakuziev, *T.a. U3 b Khain, Zh*, 3, 51 (1998) Russ.
13 Turdielva, R.M. Meangulova, F.A. Atakuziev, *T.a. U3 b Khain Zh*, 4, 52 (1998) Russ.
14 A.P. H.A., A.W.W.A. "Standard Methods for the examination of water, sewage and industrial wastes" 10th Ed. 1955, N.Y. 19, N.Y.
15 "National Environmental Quality Standards The Gazette of Pakistan, Notification SRO No. 742(I)/92, Pak, EPA, Islamabad (1993).