

Chemical Investigation of the Effluents of Selected Industries of NWFP, Pakistan

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(Received 12th May, 1997, revised 29th November, 1997)

Summary: 150 samples of effluents were collected from the drain mouths and at different distances from the waste water drain for physico-chemical properties and heavy metals like Pb, Ag, Cu, Zn, Fe, Ca, Cr, Cd, Mn and Ni, using spectroscopic techniques. The results of our investigation are presented and discussed.

Introduction

In addition to its function in carrying off sewage produced by workers, water plays two main roles in manufacturing industries, it may serve as a source or sink for heat or it may be directly involved in some chemical processes as a reactant, product or solvent. Depending on the type of industry, a wide variety of hazardous substances may be dissolved, suspended or adsorbed on suspended particles in its effluents.

There are different types of water pollution. Among these are acid mine drainage, thermal pollution, effluents from petroleum refining and oil spills, radioactive materials, solids, and acids resulting from air pollution control, spent pickle liquor, effluents associated with steel production and contamination from other metal processing. Sulfuric acid is widely used in a great many chemical processes as well as in the manufacture of rubber and

plastics. The same is true of NaOH, used in vegetable processing. Food processing also release high concentration of BOD, often in the form of objectionable materials, such as blood, entrails, grease and fat or hair, which degrade slowly. Small quantities of a variety of metals are released by almost every industry. Since many of them are toxic and relatively little is known about their cycling in the biosphere, they constitute a real problem [1-4].

A variety of methods are available for the determination of suspended solids dissolved solids and trace metals, reported in this paper [5-11].

Results and Discussion

In this paper, effluents of Match factories, Marble, Ceramics, Paper and Board and Ghee industries were investigated for physico-chemical properties like pH, temperature, TSS, TDS and heavy metals like Pb, Cu, Zn, Cd, Fe, Cr, Ca, Mn and Ni. As can be seen from Tables 1-6, the effluents of match factories were found to have higher concentration of TDS, Zn, Fe, Cr, and Mn. The effluents of ceramics industries were found to have higher concentration of TSS, amongst all the industries studied. The presence in high concentration of Zn, Fe, Cr and Mn in the effluents of Match industries is because of using Fe_2O_3 and ZnO as filler, $\text{K}_2\text{Cr}_2\text{O}_7$ as oxidising agent and MnO_2 as a catalyst respectively. We believe that Cr is

present in the effluents of Match factories as Cr(VI) which is highly undesirable.

Among the Match factories, as can be seen from Table-1, Match factory-4, liberates higher concentration of TSS, TDS, Zn and Ca in its effluents which may be due to its defective technology. The effluents of Match factory-2 shows a higher concentration of Cr, which may be due to defective handling of $\text{K}_2\text{Cr}_2\text{O}_7$.

As can be seen from Table-5, the ghee mills release liberate Ni at its drain mouth in higher concentration than the NEQS which is undesirable. Ni is dumped into the effluents, because of its use during hydrogenation process and defective filtration. Table-6 shows, the chemical investigation of the effluents of main drain of SDA, industrial state. As shown in this table, the concentrations of all of the pollutants except Fe, are in permissible limits, showing that nature takes care itself of the effluents of the industries, not allowing them to flow into rivers, canals and finally entering into the food chain of animals and humans.

Experimental

Apparatus and instruments

Corning, 240 digital pH meter and Philips flame atomic-absorption spectrometer PU-9100X, were used during this investigation.

Table-1: Investigation of the Effluents of Match Factories for Physicochemical Properties

| Match Factory | Location | | | | | |
|------------------|-------------|------------------|------------------|------------------|------------------|-------------------|
| | Drain Mouth | 10' from D.Mouth | 30' from D.Mouth | 50' from D.Mouth | 70' from D.Mouth | 100' from D.Mouth |
| Factory 1 | | | | | | |
| Temperature °C | 20 | 20 | 19 | 18 | 18 | 18 |
| pH | 7.17 | 7.75 | 7.46 | 7.48 | 7.27 | 7.50 |
| TSS (mg/1) | 127 | 184 | 2182 | 223 | 1023 | 140 |
| TDS (mg/1) | 684 | 744 | 882 | 604 | 564 | 580 |
| Factory-2 | | | | | | |
| Temperature °C | 14 | 13 | 13 | 13 | - | - |
| pH | 7.52 | 7.52 | 7.41 | 7.35 | - | - |
| TSS (mg/1) | 118 | 70 | 200 | 210 | - | - |
| TS (mg/1) | 578 | 686 | 830 | 832 | - | - |
| Factory-3 | | | | | | |
| Temperature °C | 18 | 18 | 17 | 17 | 17 | 17 |
| pH | 7.25 | 7.36 | 7.35 | 7.42 | 7.35 | 7.36 |
| TSS (mg/1) | 20 | 12 | 50 | 15 | 30 | 15 |
| TS (mg/1) | 1466 | 514 | 590 | 506 | 540 | 530 |
| Factory-4 | | | | | | |
| Temperature °C | 20 | 19 | 18 | 18 | 18 | 18 |
| pH | 7.44 | 7.46 | 7.46 | 7.45 | 7.48 | 7.45 |
| TSS (mg/1) | 2470 | 990 | 1084 | 492 | 752 | 745 |
| TS (mg/1) | 2028 | 2528 | 2574 | 2204 | 2490 | 2310 |

Table-2: Investigation of the Effluents of Match Factories for Heavy Metals (ppm)

| Industry | Location | | | | | |
|------------------|-------------|---------------------|------------------|------------------|------------------|-------------------|
| | Drain Mouth | 10' from D.Mouth | 30' from D.Mouth | 50' from D.Mouth | 70' from D.Mouth | 100' from D.Mouth |
| Factory 1 | | | | | | |
| Zn | 4 | 3.3 | 13 | 4.8 | 14 | 4.5 |
| Fe | 1.5 | 3.6 | 16 | 5.5 | 13 | 2.45 |
| Ca | 60 | 80 | 75 | 68 | 62 | 70 |
| Cr | 1.8 | 2 | 4.9 | 0.68 | 3.4 | B.D* |
| Mn | 0.1 | 0.18 | 1.1 | 0.25 | 0.5 | 0.22 |
| Factory-2 | | | | | | |
| Zn | 2.3 | 3 | 5.8 | 4.3 | - | - |
| Fe | 2.2 | 2.4 | 3.25 | 2.1 | - | - |
| Ca | 60 | 56 | 60 | 62 | - | - |
| Cr | 3.7 | 6.7 | 5.45 | 4.38 | - | - |
| Mn | 0.1 | 0.1 | 0.15 | 0.18 | - | - |
| Factory-3 | | | | | | |
| Zn | 12.5 | 3.7 | 2.7 | 2.7 | 2.5 | 2.6 |
| Fe | 2 | 2 | 2 | 2 | 1.4 | 1.28 |
| Ca | 76 | 60 | 60 | 60 | 52 | 65 |
| Cr | B.D | B.D | B.D | B.D | B.D | B.D* |
| Mn | 0.16 | 0.1 | 0.1 | 0.1 | 0.1 | 0.12 |
| Factory-4 | | | | | | |
| Zn | 22 | 26 mixing with 3 | 24.5 | 20 | 22 | 20 |
| Fe | 1.4 | 1.3 | 1.3 | 1.6 | 8.4 | 2.1 |
| Ca | 115 | 76 | 77 | 65 | 70 | 65 |
| Cr | 1.14 | 1.1 | 0.58 | 0.14 | 0.3 | B.D* |
| Mn | 0.54 | 0.4 | 0.35 | 0.24 | 0.29 | 0.32 |

B.D*:- Below detection limit.

Table-3: Investigation of the Effluents of Marble, Paper and Ceramics Industries for Physicochemical Properties.

| Industry | Location | | | | | |
|-----------------|-------------|--|------------------|------------------|------------------|-------------------|
| | Drain Mouth | 10' from D.Mouth (mixing with main drain) | 30' from D.Mouth | 50' from D.Mouth | 70' from D.Mouth | 100' from D.Mouth |
| Marble | | | | | | |
| Temperature °C | 17 | 17 | 12 | 12 | 12 | 12 |
| pH | 8.3 | 7.31 | 7.24 | 7.25 | 7.23 | 7.26 |
| TSS (mg/l) | 674 | 136 | 24 | 14 | 25 | 40 |
| TDS (mg/l) | 356 | 710 | 730 | 678 | 685 | 672 |
| Paper | | | | | | |
| Temperature °C | 24 | 24 | 24 | 24 | 23 | 23 |
| pH | 7.52 | 7.5 | 7.5 | 7.5 | 7.25 | 7.52 |
| TSS (mg/l) | 858 | 844 | 367 | 78 | 596 | 235 |
| TDS (mg/l) | 598 | 504 | 584 | 520 | 488 | 504 |
| Ceramics | | | | | | |
| Temperature °C | 21 | 21 | 20 | 20 | 20 | 20 |
| pH | 8.5 | 8.3 | 8.3 | 8.35 | 8.38 | 8.32 |
| TSS (mg/l) | 2640 | 2519 | 2681 | 2561 | 4570 | 2660 |
| TS (mg/l) | 518 | 420 | 584 | 526 | 506 | 450 |

Chemicals and reagents

All chemicals used were of analytical reagent grade purity and were used without further purification.

Sampling

Samples of the effluents were collected from the drain mouth at different distances from the drain

mouth, at the mixing of drains and at different distances from the mixing of drains, of different industries. These samples were collected in 250 mL polyethylene bottles.

Procedure

Temperature of each sample was measured on the spot, whereas pH of each sample was recorded in laboratory using corning 240 digital pH meter.

Table-4: Investigation of the Effluents of Match, Marble, Paper and Ceramics Industries for Heavy Metals (ppm)

| Industry | Location | | | | | |
|-----------------|-------------|--|------------------|------------------|------------------|-------------------|
| | Drain Mouth | 10' from D.Mouth (mixing with main drain) | 30' from D.Mouth | 50' from D.Mouth | 70' from D.Mouth | 100' from D.Mouth |
| Marble | | | | | | |
| Zn | 0.8 | 3.6 | 4.0 | 4.0 | 3.9 | 3.8 |
| Fe | 1.7 | 2.4 | 2.0 | 2.7 | 2.4 | 2.2 |
| Ca | 220 | 65 | 70 | 72 | 75 | 72 |
| Cr | 8.0 | 0.6 | 0.3 | 0.25 | 0.18 | 0.14 |
| Mn | 0.30 | 0.38 | 0.38 | - | 0.35 | 0.43 |
| Paper | | | | | | |
| Zn | 1.5 | 1.4 | 0.7 | 0.8 | 0.8 | 1.0 |
| Fe | 2.5 | 2.4 | 2.6 | 2.3 | 2.8 | 6.5 |
| Ca | 85 | 87 | 80 | 75 | 73 | 150 |
| Cr | B.D* | B.D* | B.D.* | B.D* | B.D* | B.D* |
| Mn | 0.26 | 0.31 | 0.2 | 0.15 | 0.13 | 0.14 |
| Ceramics | | | | | | |
| Zn | 0.9 | 0.9 | 1.0 | 1.10 | 1.2 | 1.2 |
| Fe | 2.4 | 3.0 | 2.6 | 4.0 | 2.3 | 5.2 |
| Ca | 100 | 65 | 75 | 70 | 98 | 65 |
| Cr | B.D* | B.D* | B.D* | B.D* | B.D* | B.D* |
| Mn | 0.2 | 0.15 | 0.16 | 0.12 | 0.2 | 0.12 |

*BD = below detection limit

Table-5: Investigation of the Effluents of Ghee Mills for Physicochemical Properties

| | Location | | | | | |
|------------|-------------|------------------|------------------|------------------|------------------|-------------------|
| | Drain Mouth | 10' from D.Mouth | 30' from D.Mouth | 50' from D.Mouth | 70' from D.Mouth | 100' from D.Mouth |
| Temp. (°C) | 24 | 24 | 23 | 23 | 23 | 22 |
| pH | 8.14 | 8.14 | 8.18 | 8.22 | 8.3 | 7.9 |
| TSS (mg/l) | 390 | 50 | 5 | 6 | 2 | 33 |
| TDS (mg/l) | 426 | 428 | 362 | 392 | 400 | 448 |
| Zn(ppm) | B.D* | B.D | B.D | B.D. | B.D. | B.D. |
| Ca(ppm) | 90 | 65 | 57 | 42 | 44 | 46 |
| Cr(ppm) | B.D. | B.D | B.D | B.D | B.D | B.D |
| Mn(ppm) | 0.2 | 0.2 | 0.28 | 0.3 | 0.29 | 0.1 |
| Ni(ppm) | 0.34 | 0.34 | 0.30 | 0.2 | 0.17 | 0.3 |
| Fe(ppm) | 2.3 | 2.3 | 8.0 | 9.5 | 3.8 | 3.8 |

B.D* = Below detection limit.

Table-6: Investigation of the Effluents of Main Drain of SDA for Physicochemical Properties.

| | Location | | | | | |
|------------|-----------------------------------|------------------|------------------|------------------|------------------|-------------------|
| | Main Drain near Rehman Industries | 10' from D.Mouth | 30' from D.Mouth | 50' from D.Mouth | 70' from D.Mouth | 100' from D.Mouth |
| Temp. (°C) | 19 | 19 | 19 | 18 | 18 | 18 |
| pH | 7.95 | 7.95 | 7.95 | 7.72 | 7.9 | 7.9 |
| TSS (mg/l) | 69 | 121 | 100 | 115 | 121 | 90 |
| TDS (mg/l) | 428 | 384 | 388 | 375 | 368 | 385 |
| Zn(ppm) | B.D* | B.D | B.D | B.D | B.D. | B.D |
| Fe(ppm) | 4.7 | 2.0 | 3.0 | 3.0 | 1.6 | 2.4 |
| Ca(ppm) | 93 | 68 | 90 | 100 | 92 | 85 |
| Cr(ppm) | B.D | B.D | B.D | B.D | B.D | B.D |
| Cd(ppm) | B.D | B.D | B.D | B.D | B.D | B.D |
| Mn(ppm) | B.D | B.D | B.D | B.D | B.D | B.D |
| Ni(ppm) | B.D | 0.18 | 0.2 | 0.18 | 0.14 | 0.12 |

B.D* = Below detection limit.

Determination of total dissolved solids (TDS)

Ignited an evaporating dish for one hour at 550°C, cooled it in a desiccator and measured its mass. Filtered a volume, somewhat in excess of 100 cm³ of well mixed sample under vacuum through whatman 540 filter paper. Maintained the vacuum for at least three minutes after filtration is complete, to remove as much water as possible. Transferred 100 cm³ of the filtrate to the prepared evaporating dish and evaporated to dryness on hot plate. Cooled in desiccator. Dried the residue in an oven at 180°C for at least one hour. Cooled in desiccator and measured the mass.

$$\text{Total dissolved solids (mg/dm}^3\text{)} = \frac{(m_1 - m_2) \times 1000}{V}$$

where

m_1 = is the mass of dried residue and dish in mg.

m_2 = is the mass of prepared dish in mg.

V = is the volume of filtered sample in cm³.

Determination of total suspended solids (TSS)

Dried a Whatman 540 filter paper in an Oven at 105°C for 1 hour, cooled in a desiccator and measured its mass immediately before use. Assembled the filtration apparatus with Whatman 540 filter paper in position. Transferred 100 cm³ of well mixed sample to the filter funnel, applied vacuum and washed the residue with three successive 20 cm³ portions of distilled water. Removed the filter paper, dried in an oven at 105°C for one hour, cooled in a desiccator and measured the mass.

Total suspended

$$\text{solid (mg/dm}^3\text{)} = \frac{(m_1 - m_2) \times 1000}{V}$$

where

m_1 = is the mass of filter paper with residue in mg.

m_2 = is the mass of dried filter paper in mg.

V = is the sample volume in cm³.

Determination of heavy metals

100 cm³ of the unfiltered well mixed sample was taken in a breaker to which 10 mL of concentrated HNO₃, HCl mixture (1:3) was added. This mixture was evaporated, to 100 mL and then subjected to flame atomic absorption spectrometer PU 9100x for determination of metals, like Pb, Ag, Cu, Zn, Fe, Ca, Cr, Cd, Mn, and Ni, under the following operating parameters.

| Metals | Wavelength (nm) | Lamp Current (m-Amperes) | Band Pass (nm) |
|--------|-----------------|--------------------------|----------------|
| Pb | 217 | 10 | 0.5 |
| Ag | 328.1 | 04 | 0.5 |
| Cu | 324.8 | 05 | 0.5 |
| Zn | 213.9 | 10 | 0.5 |
| Fe | 248.3 | 15 | 0.2 |
| Ca | 422.7 | 06 | 0.5 |
| Cr | 357.9 | 12 | 0.5 |
| Cd | 228.8 | 08 | 0.5 |
| Mn | 279.5 | 12 | 0.5 |
| Ni | 232 | 15 | 0.2 |

The flame used was air acetylene flame.

Conclusion

Amongst the industries studied Match factories were found responsible for polluting the industrial effluents with Zn, Fe, Cr, Mn and TDS. Ceramics industries increase the concentration of total suspended solids, whereas ghee mills pollute water with Ni. Control measures for the decrease in concentration of Zn, Fe, Cr, Mn and TDS in the effluents of Match industries, TSS in the effluents of ceramics and Ni in the effluents of ghee mills are suggested.

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