

Evaluation of Paint Industry Effluents for Irrigation Purposes

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Abstract. Effluent samples collected from a paints factory for a period of seven months were analyzed for pH, electrical conductivity (EC), soluble cations and anions, nitrogen, phosphorus, and trace elements (Cd, B, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Pb). Compared with the natural groundwater used for washing paint wastes, the paint industry effluents were found to contain elevated concentrations of cations with the exception of Ca and moderately high concentrations of trace elements. Evaluation of the effluents was made, based on the integration of EC and both the sodium absorption ratio (SAR) and soluble sodium percent (SSP), BOD and COD values, and maximum permissible limits of heavy metals in the irrigation water. From the overall assessment, the effluents were considered suitable for use as supplement irrigation water. However, it is essential that the heavy metals in the effluents, as well as their accumulation in plants and soils, are monitored regularly.

Keywords: industry effluents, irrigation water, physicochemical properties, ICP-AES, paint industry

Introduction

In most developing countries, uncontrolled industrialization has resulted in extensive environmental pollution particularly of water and soil. Inadequate wastewater treatment due to high costs have resulted in a situation whereby most industries discharge their effluents directly to open landscapes, into rivers, canals and water drains leading to rivers, thus polluting the surrounding ecosystems. However, some industries have invested in treatment facilities for the clean-up of effluents, before their discharge into the environment. One of the possible uses of the industrial effluents is the irrigation of agricultural land. The use of municipal and industrial wastewaters for the irrigation of crops is well documented (Singh and Mishra, 1987). This has become an important part of the urban and industrial wastewaters disposal programmes.

As the effluents, on the one hand, provide plants with their essential nutrients (N, P, S, K, Ca, Mg) and various micronutrients (particularly Mn, Cu, Fe), they may on the other hand pose serious problems to the soil due to long term deposition of heavy metals and other chemicals (El-Nennah and El-Kobbia, 1983). Therefore, the use of industrial effluents on agricultural land requires a knowledge of the chemical composition of these effluents before their application for irrigation purposes.

Numerous paint factories have been built in Asian countries, including Bangladesh. This industry is expected to grow further in the next few years. Consequently, there is a need to monitor the chemical quality of industrial effluents produced

by this category of the industry, as well as to investigate their possible agricultural utilization. The present study was, therefore, undertaken to characterize the effluents originating from a paints factory and to evaluate its use for irrigation purposes.

Materials and Methods

Source and nature of effluents. Berger Paints Bangladesh Ltd., a leading paints manufacturer, was selected for effluent collection for the present investigations. The industry produces both water and solvent based paints. Paints are constituted by combining binders, pigments, fillers, solvents and additives. The major contaminants in the wastewater of the industry result from the washings of paints and the resin reactors. Before disposal, all effluents undergo treatment including neutralization with lime and alum to facilitate the coagulation of suspended matter. The supernatant from the settling tank is subjected to secondary treatment for subsequent settlement by aeration. The unused mass is taken to the sludge drying beds, while the effluents are discharged into the environment through a drain pipe (Kadam Environmental Consultants, 1999).

Effluent sampling. The sample collection containers were thoroughly washed with detergent solution, kept immersed in 5% HNO₃ overnight, and then rinsed with deionized water. During collection, the pipes from which the samples were taken were flushed several times in order to obtain representative samples. Samples of the treated effluent were collected monthly in 1 litre polyethylene bottles at the discharge point of the treatment plant for a period of seven months. The samples were then filtered through Whatman No. 41 filter pa-

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pers. Conc HNO_3 , 5 ml per litre of the effluent, was added to samples to be used for metal and other elemental analyses at the time of sample collection to minimise metal adsorption on the container walls as well as to retard chemical and biological changes. Separate non-acidified samples were collected for the measurement of other biological, chemical and physical parameters. Care was taken to handle the samples in such a way that they did not deteriorate or become contaminated before they reached the laboratory where they were stored in a refrigerator (4°C), or analysed within a week. The pH and electrical conductivity (EC) of the untreated samples were also measured in the field during collection. For a comparative study, the natural groundwater used to wash paint-manufacturing tanks, before the next batch of production, were also collected and preserved using similar procedures as described for the collection of treated effluent samples.

Analytical methods. The samples were analyzed for soluble cations (Na, K, Ca, Mg), anions (Cl^- , HCO_3^- , SO_4^{2-}), N, P, trace elements (Cd, Cr, Cu, Fe, Mn, Ni, Zn, As, Pb), and soluble and total residues. For comparison, the groundwater samples were also analysed. The cations and trace elements were determined using ICP-AES (Model: JY-2000) method. The samples were run after further acidification with 5 ml of 70% ultrapure HNO_3 (J. T. Baker, USA) per litre of the sample. These samples were diluted with deionised water as per requirement. Blank samples were run against each sample analysed. The analysis was carried out under similar experimental conditions as described elsewhere (Quraishi and Akhter, 2005).

For arsenic analysis, ICP-AES coupled with a JY model hydride generator was used. The analysis was carried out with 10 ml sample pre-reduced with 1 ml of 10% KI (AnalaR, BDH, England) and 2.5 ml of aristar grade HCl (BDH, England) for 2 h reduction time (Hering *et al.*, 1996). The sample was then transferred to the hydride generation system. Arsine gas, generated by the continuous addition of 4% basic sodium borohydride solution and HCl, was carried to the ICP by the carrier argon gas.

Two standard calibration curves, one for major elements and another for trace elements were constructed from secondary standard solutions synthesized from single element standards (SPEX Certiprep., Metuchen, NJ, USA) by dilution. Before analysis of the samples, the validity of the curves was checked by analysis of a NIST standard reference material- SRM (Tohmas, 1998) for K, Ca, Mg, Mn, Fe, Ni, Cu, Zn, Sr and Mo. Anions, BOD and COD were measured by adopting the procedures outlined in the standard methods (Michael, 1975). Nitrogen and phosphorus were measured by the Kjeldahl and colourimetric methods, respectively. A Jenway 3051 pH meter

and a Jenway 4070 conductivity meter were used for the measurements of pH and EC of the samples (Chukwuma, 1996).

Statistical analysis. For statistical analysis, t-tests were carried out to compare the data obtained monthly for all the parameters. The simple t-test formulation to make t-test between two sets of data, where true value was not known, was done using the following equation (Bassett, 1993):

$$t = \left(\frac{m_1 - m_2}{S_{12}} \right) \left(\frac{n_1 n_2}{n_1 + n_2} \right)^{\frac{1}{2}} \quad (1)$$

where:

m_1 = average of data set 1 of n_1 pieces

m_2 = the average of data set 2 of n_2 pieces

S_{12} = the standard deviation of any value in either set based on the data in both sets

If the standard deviation of each set is assumed to be the same, it can be cancelled out of the expression and then equation (1) becomes:

$$t = (m_1 - m_2) \left(\frac{n_1 n_2}{n_1 + n_2} \right)^{\frac{1}{2}} \quad (2)$$

The t-tests among all monthly data of the concerned parameters investigated were calculated using equation (2). The comparison was made between the average values of alternate months based on the t-test values obtained. For four degrees of freedom (two in one month and the other two in the immediate next month), the tabulated value of t-test at 95% confidence level was 2.78, while at 99% confidence level it was 4.60. All t-test values calculated ($t_{\text{calculated}}$) for anions, cations, pH, EC were less than either of the tabulated t-test value ($t_{\text{tabulated}}$). For BOD, COD, and dissolved and total residues, the $t_{\text{calculated}}$ values were higher than the $t_{\text{tabulated}}$ values. For Zn, almost all the $t_{\text{calculated}}$ values and two values for Mn, one value for Fe, and one value for Pb were greater than the tabulated values.

Results and Discussion

The analytical results are shown in Tables 1-3. The pH values of the paints effluents were lower than those of the natural groundwater, however, their EC values were higher. For the groundwater and effluents, the average pH values were 7.2 and 5.6, and the average EC values were 0.17 mS and 1.22 mS, respectively (Table 1). No significant variation was observed in the pH and EC values of groundwater and the monthly collected effluents. The BOD and COD determined in effluents during the period varied between 53-80 mg kg^{-1} and 86-112 mg kg^{-1} , having the average values of 66 and 100.5 mg

Table 1. pH, EC and soluble cations and anions in the Berger Paints Bangladesh Ltd., effluents and the natural groundwater used for washing

Sample	Sampling (month)	pH	EC (mS)	Cations concentrations (meq per litre)*				Anions concentrations (meq per litre)*			SAR	SSP (%)
				Na ⁺¹	K ⁺¹	Ca ⁺²	Mg ⁺²	HCO ₃ ⁻¹	Cl ⁻¹	SO ₄ ⁻²		
Treated effluents	November	5.93	1.09	2.14	0.77	10.03	0.56	0.085	0.70	0.79	0.93	4.55
	December	6.04	1.16	1.80	0.54	15.67	0.40	0.098	0.69	0.85	0.63	3.39
	January	6.07	1.34	1.94	0.71	14.17	0.48	0.095	0.71	0.83	0.72	4.40
	February	6.01	1.33	1.98	0.62	15.07	0.42	0.082	0.73	0.74	0.71	4.06
	March	5.86	1.10	2.10	0.55	14.72	0.53	0.090	0.79	0.81	0.76	4.30
	April	5.95	1.40	2.13	0.72	15.52	0.43	0.110	0.80	0.90	0.75	4.23
	May	5.88	1.05	2.00	0.66	13.23	0.50	0.079	0.75	0.80	0.76	4.51
	June	6.0	1.28	2.05	0.69	12.98	0.52	0.099	0.82	0.77	0.79	4.49
Groundwater	-	7.20	0.17	0.73	0.06	0.72	0.08	0.055	0.65	0.47	1.16	12.43

*average concentrations of duplicate measurements; SAR= sodium absorption ratio; SSP= soluble sodium percent

Table 2. BOD, COD, nitrogen, phosphorus, and dissolved and total residues in the Berger Paints Bangladesh Ltd., effluents and the natural groundwater sample used for washing (mg per litre)

Sample	Sampling (month)	BOD	COD	Soluble nitrogen	Soluble phosphorus	Dissolved residues	Total residues
Treated effluents	November	60	104	14.80	3.82	1080	1100
	December	65	107	14.71	3.14	1220	1360
	January	70	86	15.12	4.67	1010	1210
	February	68	97	15.30	5.14	1090	1270
	March	60	96	14.93	4.57	1150	1310
	April	72	103	14.74	4.85	1120	1230
	May	53	99	15.00	4.35	1020	1290
	June	80	112	14.70	4.91	1050	1180
Groundwater	-	-	-	7.10	4.86	135	145

Table 3. Trace elements concentrations in the Berger Paints Bangladesh Ltd., effluents and the natural groundwater used for washing (ppb)*

Sample	Sampling (month)	B	Cd	Cr	Mn	Fe	Ni	Cu	Zn	As	Pb
Treated effluents	November	<10	<4.5	<4	26.5	31.2	5.43	4.56	66.5	<10	22.1
	December	<10	<4.5	<4	28.0	30.0	7.0	8.5	62.6	<10	20.5
	January	10	<4.5	<4	23.3	34	10	8.2	49	<10	20.2
	February	10	<4.5	<4	24.2	27.6	5.1	7.1	56.3	<10	21.3
	March	10	<4.5	<4	30.0	31.6	6.3	7.5	68.0	<10	20.1
	April	10	<4.5	<4	25.2	28.3	6.1	6.4	59.2	<10	19.4
	May	<10	<4.5	<4	22.4	29.1	4.5	5.3	50.3	<10	17.5
	June	10	<4.5	<4	27.1	32.0	6.4	8.3	60.2	<10	23.2
Groundwater	-	<10	<4.5	<4	2	3	<5	2	<3	<10	<4

*average concentrations of duplicate measurements

kg⁻¹, respectively (Table 2). Though the concentrations of anions and cations in the effluents were more than those in the natural groundwater, the difference was not significant. Total soluble nitrogen was higher in the effluents as compared with the values in the groundwater. A similar trend was also observed for phosphorus. However, the increase in nitrogen concentration was higher than that for phosphorus. The dissolved and the total residues of the effluents dried at 105 °C were on an average 1093 and 1244 mg per litre, which were about 8.1 and 8.6 times higher than those in the groundwater, respectively. With respect to anion concentrations, effluents were found to contain higher concentrations of cations (Table 1). According to t-tests, an insignificant variance among the monthly data of pH, EC, cations, anions, N and P was observed, while the data for BOD, COD, and dissolved and total residues showed significant variations.

The concentrations of trace elements (B, Cd, Co, Cr, Cu, Fe, Fe, Mn, Ni, As, Pb), measured in the effluents and the natural groundwater used for paints waste washings are shown in Table 3. It was observed that the average elemental concentrations were much higher than those observed in the groundwater.

The higher concentrations of soluble salts and trace elements in the effluents, as compared with the groundwater, can be attributed to the pollution of the washing water with industrial wastes as well as the low-grade chemicals (lime, alum) used for effluent treatment before its disposal to the environment. The increase in cation and anion concentrations in the effluents was much less than in trace elements because the inorganic chemical compounds generally used in paints preparation are mostly oxides of Ti, Zn, Cu, Fe, Pb containing trace elements as impurities. The calcium concentrations were higher as compared to other cations. This increase was probably due to the addition of lime used for the effluent treatment. In relation to a former study on trace elements in the effluents of the Berger Paints Bangladesh Ltd., a good agreement was observed between the present and previous elemental results (Hossain, 2004).

Assessment of the effluents for irrigation purposes. The US Department of Agriculture (Richards, 1954) has classified irrigation waters based on electrical conductivity and sodium absorption ratio (SAR) as shown in Fig. 1. The SAR is determined by:

$$SAR = \frac{[Na^+]}{\sqrt{\frac{[Ca^{2+}] + [Mg^{2+}]}{2}}}$$

where all the ionic concentrations are in meq per litre.

The combination of SAR and electrical conductivity of the paints industry effluents indicates that the effluents are in the category of C₃-S₁, which relates to water of high salinity and low sodium content and is considered marginal for human consumption (El-Nennah and El-Kobbia,1983). According to Wilcox' diagram based on EC and SSP, the investigated effluents corresponded to the class of 'good to permissible' for irrigation purposes (Fig. 2). Effluents with BOD₅ values varying from 50-100 mg per litre are not recommended for biological treatment. The present effluents showed BOD and COD values in the range of 53-80 mg per litre and 86-112 mg per litre, respectively. The average ratio obtained from BOD₅ and COD values of the investigated effluents was 0.66, indicating that the effluents contained mostly biologically degradable substances (Tolgyessy *et al.*, 1993). However, according to effluents quality standard for Bangladesh, the recommended values for BOD₅ (at 20 °C) and COD are 50 and 200 mg per litre, respectively (MEF, 1997).

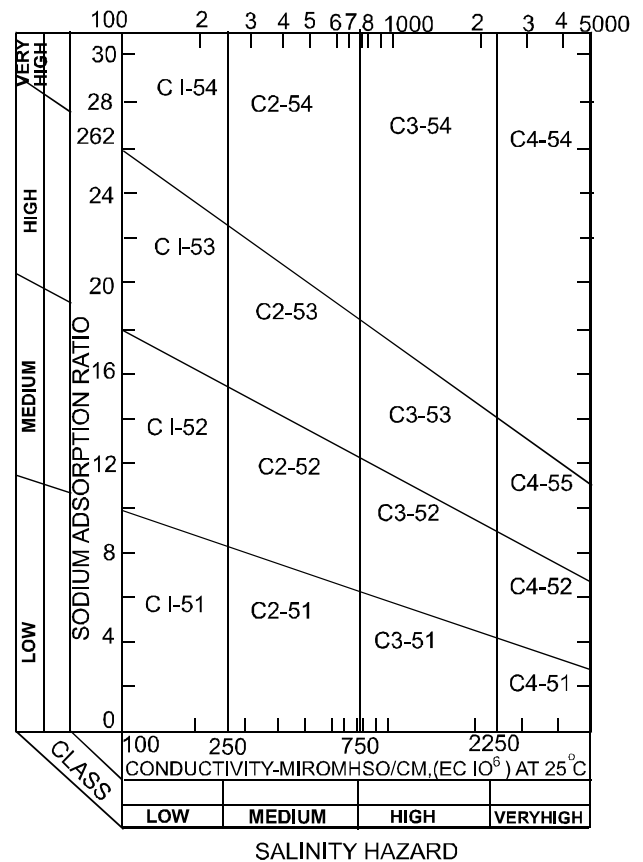


Fig. 1. Evaluation of paint industry effluents (Berger Paints Bangladesh Ltd., Savar) for irrigation purposes as per recommendations of the US Department of Agriculture (Richards, 1954).

The average concentrations of trace elements in the effluent samples were lower than the maximum permissible limits in irrigation water as recommended by National Academy of Sciences-National Academy of Engineering (NAS-NAE, 1973) by WHO (2002), and for drinking water quality by FAO/WHO (1996), as presented in Table 4. The results obtained in this study are in agreement with those recommended for trace elements in irrigation water.

Table 4. Recommended concentrations of trace elements in irrigation water*

Elements	Trace element concentrations (µg per litre)
Ni	200
Cu	200
Zn	200
Cd	10
Pb	5000

*NAS-NAE: National Academy of Science-National Academy of Engineering (1973)

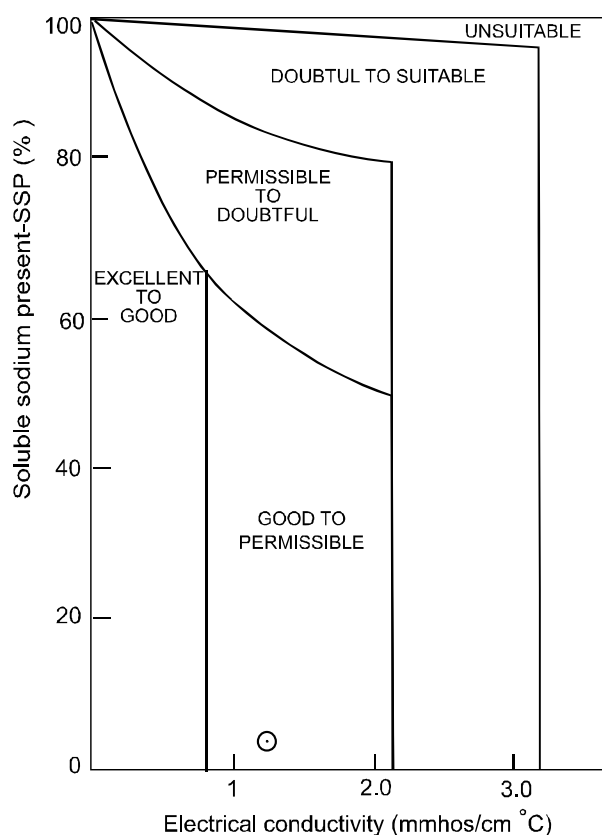


Fig. 2. Evaluation of paints industry effluents (Berger Paints Bangladesh Ltd., Savar) for irrigation purposes as described by the Wicox's diagram.

Conclusions

The discharged effluents from the paints factory were found to be suitable for irrigation purposes. These effluents can be used as a source of water for irrigating the surrounding agricultural land for crop cultivation in the dry season. The lack of micronutrients in the soil can be compensated by the application of these effluents as a good source of plant nutrients (Abdou and El-Nennah, 1980). The increase in the heavy metal contents of the soil and their uptake by plants may be a potential problem in the long term. However, according to a study, it was observed that no symptoms of toxicity appeared on the plants even from the long term use of municipal effluents in irrigation as indicated by visual observations and good crop yield (El-Nennah *et al.*, 1982). The levels of the toxic elements, Cd and As, were found to be below the detection limits of the analytical technique. Although Pb was detected, its concentration was too low to contribute any significant pollution to the soil.

This study has demonstrated that pretreated effluents from a paints factory can be used for irrigation purposes. However, it may be necessary to monitor the long term impact of heavy metals in the soil and plants to ensure that there is no build-up.

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