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Industrial Wastewater Treatment Using Local Natural Soil in Abu Dhabi, U.A.E

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Abstract: Local soil from the Emirate of Abu Dhabi, United Arab Emirate is investigated for its efficiency in removing heavy metals from industrial wastewater. Eight different industrial water effluents from different industries were treated. Pb, Zn, Fe, Cu and Mn were removed from industrial wastewaters yielding treated water with heavy metal concentrations well below the maximum limits enforced by environmental protection agencies.

Key words: Industrial wastewater, treatment, heavy metals, natural soils

INTRODUCTION

Disposal of industrial wastewater has always been a major environmental issue. Pollutants in industrial wastewater are almost invariably so toxic that wastewater has to be treated before its reuse or disposal in water bodies. Maximum allowed limits for contaminants in "treated" wastewater are enforced in developed and many developing countries. Treatment methods that use simple techniques and make use of locally available treatment materials will result in reducing the cost of treatment to the point that polluting industries will not find it inhibitive or discouraging. Previous investigations on the removal of heavy metals from wastewater[1,2,3] suggest that systems containing calcium in the form CaO or $CaCO_3$ and carbonates in general, are particularly effective in the removal of heavy metals from wastewater. Thus, natural soils of high calcium and carbonate contents may prove to be useful in this respect. A significant number of industries in the United Arab Emirates (U.A.E.) discharge their wastewater in nearby water bodies or waste dumps without any treatment. Pending the enforcement of proper environmental protection regulations, the development of inexpensive methods of treatment will hopefully entice such industries to exercise greater environmental responsibility and thus contribute to environmental protection. Eight representative industries were thus selected in the Emirate of Abu Dhabi which contributes 89% of the total area of the U.A.E. for the purpose of the investigation of the feasibility of the treatment of their wastewaters using suitable local natural soils. The industrial activities of these companies are:

1. Dates Preservation
2. Pharmaceuticals
3. Vegetable Preservation
4. Paints Manufacturing
5. Organic Fertilizers
6. Iron and Steel Processing
7. Soaps and Detergents Manufacturing
8. Cardboard Manufacturing.

MATERIALS AND METHODS

Instrumental: The pH measurements were done using ORION-420 pH-meter. Carbonate content of the soil was determined using a simple glass Calcitemeter. The concentrations of the major cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and heavy metals (Fe, Mn, Cu, Pb and Zn) were determined in aqueous solutions by simultaneous VISTA-MPX-CCD ICP-OES from Varian.

Wastewater sample preparation and analysis: Industrial wastewater samples were collected from the industrial wastewater effluents of eight different factories, before discharge. The pH and temperature of each were measured at the site. A portion of 200 ml of each sample was filtered through a 0.45 µm pore diameter membrane filter immediately after collection. The filtrate was then acidified with concentrated HNO_3 (65% wt/wt) to pH < 2. It was then analyzed using ICP-OES to determine the concentration of dissolved heavy metals (Fe, Mn, Cu, Pb and Zn) and the major cations of Na, K, Ca and Mg. A portion of each of the unacidified samples was digested by repeated treatment and boiling with concentrated HNO_3. The digested samples were then analyzed for heavy metals.

Soil Analysis: For measurement of pH of the soil a paste was prepared by mixing 250g of the soil with 60 ml distilled water. The paste was left to stand for one hour. A suction pump was used to extract the solution from the paste. The pH of the solution was then measured. The carbonate content of the soil was determined (as % $CaCO_3$) using a simple Calcitemeter with HCl as the acid. The soil was analyzed for metals by digesting the sample of the soil with hot

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concentrated HNO_3, hot H_2O_2 (30%) solution and hot, concentrated HCl, consecutively. The soil sample solution was then filtered, diluted and analyzed for the metal ions using ICP-OES.

Wastewater treatment: Industrial wastewater treatment was carried out using a simple apparatus consisting of a water reservoir connected to a plastic column (40 cm long, 2 cm diameter) and a water receiver. The lower end of the column was fitted with a cotton plug, then packed with 225g of the soil.

Treated wastewater samples were collected and then their pH was measured. They were then acidified to pH < 2 using concentrated HNO_3 and analyzed for metal ions using ICP-OES.

Others: Synthetic wastewater was prepared by mixing known volumes of standard solutions of the metals, under investigation. Each of the standard solutions is prepared from the corresponding metal salt or by dissolving the corresponding metal in the proper strong acid. Calcium-oxide-treated soil was prepared by adding dried CaO to the soil sample to make up a 5% (wt/wt) mixture of CaO-soil.

RESULTS

Soil Composition: The soil used in the treatment of industrial wastewater in this investigation had a pH of 7.8 and a total carbonate, as $CaCO_3$, of 18.9%. The metal ion content of the soil is shown in Table 1.

Major ions in the wastewater: The pH values and the concentrations of the major ions (Na^+, K^+, Ca^{2+} and Mg^{2+}) in the industrial effluents are shown in Table 2 before and after treatment.

Heavy metals from industrial wastewater: Table 3 lists the concentrations of dissolved heavy metals in the industrial effluents of the industries investigated, before and after treatment by soil filtration.

Table 4 lists the concentrations of total heavy metals in the digested samples of industrial effluents.

Table 5 lists the percentage removal of selected heavy metals from industrial effluents. The table includes metals whose concentrations in the effluent, before treatment, exceeded the maximum allowed limits (MCL) for treated industrial wastewater according to the Federal Environmental Agency of the U.A.E. (Table 6).

Treatment of synthetic wastewater sample: The efficiencies of untreated and CaO-treated soils in the removal of heavy metal from a synthetic wastewater sample are compared in Table 7.

Table 1: Analysis of the soil used for industrial wastewater treatment

Cation	Concentration (mg kg^{-1})
Ca^{2+}	5.099×10^3
Mg^{2+}	1.470×10^4
Na^+	1.161×10^2
K^+	5.040×10^2
Fe^{3+}	4.232×10^3
Mn^{2+}	8.220×10
Cu^{2+}	4.600×10^0
Zn^{2+}	6.490×10
Pb^{2+}	1.130×10^{-1}

Table 2: Concentrations of the major cations and pH values in industrial wastewater before and after treatment

#	Na^+ (mg L^{-1})		K^+ (mg L^{-1})		Ca^{2+} (mg L^{-1})		Mg^{2+} (mg L^{-1})		pH	
	Before	After	Before	After	Before	After	Before	After	Before	After
1	121	220	35	143	53	198	11	65	7.2	8.3
2	702403	5830	3717	3637	45	1568	80	643	9.8	8.2
3	1241	967	64	284	260	551	179	247	7.6	8.7
4	296	256	27	115	63	154	32	70	7.8	8.5
5	13698	12689	1825	879	525	151602	162	662	8.1	7.1
6	284	323	25	190	6	301	21	85	5.6	8.4
7	1332	397	10	222	29	733	32	196	7.8	8.4
8	106	330	6	175	335	29	29	130	8.2	7.7

Table 3: Concentrations of dissolved heavy metals in the industrial effluents before and after treatment

#	Fe (mg L^{-1})		Mn (mg L^{-1})		Cu (mg L^{-1})		Pb (mg L^{-1})		Zn (mg L^{-1})	
	Before	After	Before	After	Before	After	Before	After	Before	After
1	0.04	*	0.03	*	0.05	*	*	*	0.15	*
2	0.50	0.04	*	*	0.22	0.02	0.02	*	0.85	*
3	0.12	*	0.16	0.02	*	*	*	*	0.17	*
4	0.33	0.10	0.04	*	0.42	0.01	0.44	*	1.42	0.35
5	4.96	0.04	0.03	0.01	*	*	*	*	*	*
6	24.32	0.01	1.50	*	0.09	*	0.01	*	4.58	0.12
7	2.55	*	0.50	0.10	0.10	0.04	0.05	*	5.18	0.34
8	8.80	0.61	0.42	*	166.69	0.02	0.10	*	8.85	0.28

* Below detectable limit

Table 4: Concentrations and pH values of total heavy metals in the industrial effluents (in the digested samples)

#	pH	Fe (mg L^{-1})	Mn (mg L^{-1})	Cu (mg L^{-1})	Pb (mg L^{-1})	Zn (mg L^{-1})
1	2.0	0.22	0.049	0.11	0.08	0.15
2	1.7	1.16	0.02	0.5	0.51	0.85
3	1.9	2.37	0.17	0.28	0.19	0.17
4	2	0.65	0.06	1.43	3.84	8.77
5	1.8	66.85	8.43	1.19	1.92	0.22
6	1.9	62.73	1.37	0.45	0.03	1.23
7	1.7	7.25	0.3	0.23	0.19	10.57
8	1.6	24.25	1.32	170.76	1.03	12.65

Table 5: Percentage removal of heavy metals from industrial wastewater using local natural soil

Heavy Metal	Concentration range of heavy metals in untreated wastewater (mg L^{-1})	Range of percentage of removal
Fe	0.12 - 24.32	93-100%
Mn	0.16 - 1.5	80-100%
Cu	0.10 - 166.7	100%
Pb	0.10 - 0.4	100%
Zn	0.85 - 8.85	75-100%

Table 6: Maximum allowed concentrations (MCL) of heavy metals discharged in treated industrial wastewater set by FEA # 24/1999*

Heavy metal	Concentration (mg L^{-1})
Fe	2.00
Cu	0.50
Zn	0.50
Mn	0.20
Total Cr	0.20
Co	0.20
Ni	0.10
Pb	0.10

*Reference: Federal Environmental Agency (FEA), Abu Dhabi, UAE, 1999

Table 7: Concentrations of heavy metals in synthetic wastewater samples before and after treatment using normal and CaO-treated soils& percentages of their removal

	Fe		Mn		Cu		Pb		Zn	
	mg L^{-1}	Removal %	mg L^{-1}	Removal %	mg L^{-1}	Removal %	mg L^{-1}	Removal %	mg L^{-1}	Removal %
Before treatment	1027		65		498		4.0		1738	
After treatment with normal soil	21	98.0	10	84.6	9	98.2	0.06	97.5	32	98.2
After treatment with soil and 5% CaO	0.37	100	1.8	97.2	0.12	100	<0.01	100	12	99.3

DISCUSSION

Soil composition: The soil used in the treatment of industrial wastewater had a pH of 7.8 and a total carbonate, as $CaCO_3$, of 18.9%. The high Ca^{2+} and Mg^{2+} content of the soil (Table 2) suggest that the carbonate in the soil is mainly Ca- and Mg-carbonate. The high carbonate content also suggests that some heavy metals may be removed from wastewater by the precipitation of their carbonates. The high Fe and Mn content suggests that a significant amount of metal oxides is present in the soil, which in addition to silica, may suggest that an adsorption mechanism will supplement the carbonate precipitation mechanism in removing heavy metals from wastewater. The pH of the soil (7.8) is optimal for adsorption on the oxides of manganese and iron[4] . The pH range of 7.1-8.7 for the treated wastewater (Table 2) is compatible with the pH range for carbonate precipitation. Carbonate precipitation mechanism is more dominant than adsorption on oxides.

Major ions in wastewater: The most dominant cation in the industrial wastewater (before treatment) is Na^{+}. This is followed by Ca^{2+} then Mg^{2+} and to a lesser extent, K^{+}. The concentrations of Ca^{2+} and Mg^{2+} always increased after treatment due to the exchange of Ca^{2+} with the ions of the heavy metal pollutants. This is consistent with observations made in the investigation of the removal of heavy metals using lime ($Ca(OH)_2$) and calcium carbonate[1,2] . Sodium and potassium ions behaved differently. They increased upon treatment if their concentration before treatment was low, probably due to leaching out some of the excessive Na^{+} and K^{+} in the soil. However, their concentration decreased upon treatment, when their concentrations before treatment were high, due to exchange with Ca^{2+} and Mg^{2+}.

Removal of heavy metals from industrial wastewater: Heavy metals investigated for their removal from industrial wastewater by local soil were selected on the basis of their occurrence in the wastewaters of the industries investigated. Ions of Fe, Mn, Cu, Pb and Zn were thus investigated. Table 3 lists the concentrations of dissolved heavy metals in industrial effluents of the industries investigated, before and after treatment by soil filtration.

Consideration of maximum allowed limits for the concentration of heavy metals in treated industrial wastewater (Table 6), suggests that treatment of the industrial wastewater by filtration through soil has resulted in the significant removal of heavy metals in the wastewater bringing their concentrations well below the allowed limits. The efficiency of their removal ranged between 75 and 100 % (Table 5). These results compare favorably with the results of other investigations[5] using hydroxide and sulfide precipitation. Hydroxide precipitation is more efficient only at high pH values > 9.0[6]. Incorporating 5% CaO in the soil resulted in enhancing heavy metal removal (Table 7). However, the enhancement is not very significant and the use of high pH soil requires pH adjustment after treatment, an effort that is not economically justified.

CONCLUSION

Local soil with high carbonate content is efficient in removing several heavy metals that commonly occur in industrial wastewater bringing their concentrations well below the allowed limits and their pH to within the accepted range. The application of this effective and inexpensive technique may encourage polluting industries to be more environment-protective at extremely affordable cost. A pilot-plant unit will be designed and tested at field sites.

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