



Soil washing with Surfactants to remove heavy metals contaminants of Agra District, UP India

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Abstract

The purpose of this work was to remove heavy metal contaminants (Cr^{3+} , Mn^{2+} , Fe^{2+} , Ni^{2+} , Zn^{2+} , C^{2+} and Pb^{2+}) from soil samples using micellar wash liquids. Five contaminated soil samples from Kitham, St. John's, Shahganj, Shahadra and Nunhai areas with low, moderate, high, higher and highest metal concentrations respectively were collected from top horizons (0-20 cm deep). Three types of the wash liquid were 4 CMC (above critical micelle concentration, CMC) of each of sodium dodecyl sulfate (SDS), Criton X-100, i.e., iso-octylphenoxy-hexaethoxyethanol (CTX) and N-cetyl N, N, N-trimethyl ammonium bromide (CTAB). Total metal content in the sample (before and after 1, 4, 7 and 10 washings) extracted with 60% perchloric acid was determined with a Perkin-Elmer Analyst 100 AAS. The micellar enhancement in removal was entirely different for various types of surfactants as well as different chemical species. However, surfactants were able to enhance the removal of contaminants 2-3 times greater than filtration without surfactants. Anionic surfactants removed more cationic contaminants and vice versa. The order of metal removal by surfactants was $\text{SDS} > \text{CTX} > \text{CTAB}$. In case of A and B type soils the order of removal % was $\text{Zn} > \text{Cr} > \text{Fe} > \text{Ni} > \text{Cu} > \text{Pb} > \text{Cd} > \text{Mn}$. The removal order for C, D and E with 4 CMC of all the three surfactants was $\text{Cr} > \text{Fe} > \text{Ni} > \text{Cu} > \text{Pb} > \text{Zn} > \text{Cd} > \text{Mn}$. Since SDS had higher removal, it should be preferred for metal removal from soil or water. Investigations at below and above CMCs are suggested.

Keywords: Heavy metal contamination, soil sample, soil pollution, surfactants, Agra district

Introduction

Major anthropogenic inorganic soil pollutants with their important oxidation states are Be(II), F(-1), Cr(III-VI), Ni(II-III), Zn(II), As(III-V), Cd(II), Hg(0- I-II) and Pb(II-IV). They enter in the environment due to their various applications and byproducts. Pb, Cd and Hg are used in batteries. Cd, Cr, Cu and Zn are used in metal plating. Besides natural sources, As pollution occurs due to its agricultural and other chemicals, ceramics and glass. Rubber tyres can contain 0.09 mm/g of Cd due to use of ZnO and zinc dialkylcarbamates in the vulcanization process and Cd occurs with Zn in nature. The abrasion of tyres on the road adds Cd to street dust that comes to soil by wet and dry deposition processes. Though Cd^{2+} movement and plant availability in soils are small, its extreme toxicity can be a serious problem in soils. Hg is used in chloralkali industry, electrical apparatus, fungicides and in seed dressing. Hg (0), Hg(I), Hg (II) and Cd (II) are retained less strongly by soils than the other toxic cations, and hence pose a more serious problem. Hg (II) can be reduced to Hg(I) and more significantly to Hg (0) that is volatile and can diffuse as a gas through soil pores. Thus, Hg is the most mobile toxic metal in soils. Roadside soil becomes enriched with Pb from leaded petrol having concentrations in the order of 1000-

4000 mg/kg on busy streets. The accumulation and toxicity of As, Cd, Hg and Pb have also been reported from different segments of biosphere. Incidents of poisoning from heavy metals and radionuclides are innumerable from different parts of India including Agra ^[1]. The purpose of this work was to remove heavy metal contaminants (Cr^{3+} , Mn^{2+} , Fe^{3+} , Ni^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+}) from soil samples using micellar wash liquids.

Materials and Methods

Five contaminated soil samples from Kitham, St. John's, Shahganj, Shahadra and Nunhai areas of Agra district of U.P. (India) with low, moderate, high, higher and highest metal concentrations respectively were collected from top horizons (0-20 cm deep) with a 5-cm diameter sampler in zig-zag along different transects of a field until a representative area was covered. About 2 kg composite sample from 10-20 subsamples were taken in plastic bags of 4-kg capacity by quartering technique. After removing silica with 40% HF in plastic vessels as silica and silicates can adsorb metals, the total metal content in the sample extracted with 60% perchloric acid was determined with a Perkin-Elmer Analyst 100 AAS for all the 8 metals to be remediated.

Table 1: Properties of surfactants used in soil washing

Name of Surfactant	Abbreviation	Type*	CMC in M	Formula and Mol. Wt.
Sodium dodecyl sulphate	SDS	AS	8.3×10^{-3}	$\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$, 288
Criton X-100	CTX	APE	2.1×10^{-4}	$\text{CH}_3(\text{CH}_2)_7\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_{10}$
N-Cetyl N, N, N-trimethyl ammonium bromide	CTAB	CTAB	9.2×10^{-4}	$[\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3] \text{Br}$, 364

*Type indicates AS = alkyl sulphates, AES = alkyl ethoxy sulphate, LAS = linear alkylbenzene sulphonates, AE alkyl ethoxylates and APE = alkyl phenol ethoxylates.

Batch soil washing studies were conducted by placing a constant ratio of soil to wash liquid (1:5 = 20 g/100 ml) at room temperature. In of 250-ml capacity PVC bottles, 20 g of soil was added to each of eight sets each having two bottles for different concentrations of a metal and 100 ml of the wash solution was added to each bottle. A control without surfactant was taken for each concentration. Three types of the wash liquid were 4 CMC (above CMC, critical micelle concentration) of each of SDS, CTX and CTAB. The bottle was be shaken by hand for about 30 seconds to disperse the soil particles and then at in a rotating shaker at 120 rpm for 2 h. The foam was removed by decantation. The soil suspension was centrifuged at 4000 rpm for 10 min and the residue was extracted with perchloric acid. The extract was used for the determination of metals by Perkin-Elmer AAnalyst 100 AAS. A series of 10 washings.

Criton X-100, i.e., iso-octylphenoxy- hexaethoxyethanol (CTX)

It was performed by washing the soil for 2 h each time with a fresh lot of same amount of the wash liquid containing surfactant and metals were determined in duplicate after 1, 4, 7 and 10 washings and the results were averaged. The final concentration for a washing became the initial metal concentration for the next washing.

Results and Discussion

The removal % of metal ions at 4 CMC were calculated. The results, listed in Tables- 1,2,3,4, show the impact of micelle on the removal of chemical species in single system surfactants. The removal was considerably enhanced due to the presence of micelles. The micellar enhancement in removal was entirely different for various types of surfactants as well as different chemical species.

However, surfactants were able to enhance the removal of contaminants 2-3 times greater than filtration without surfactants. Anionic surfactants removed 2,34 more cationic contaminants and vice versa [2, 3, 4]. The molecular structure plays a key role in the interaction of surfactants also considering the nature of type of surfactant. Metal removal by anionic surfactant was maximum, nonionic alone should be insignificant and cationic minimum. However, nonionic surfactants help to solubilize and form anionic species to bind metals. The order of metal removal by surfactants was SDS > CTX > CTAB.

The attraction between opposite charged species may be the cause for different extents of removal of cationic inorganic species with anionic surfactants and cationic surfactants. It totally depends on the interaction between sorbate and surfactant [5, 6, 7]. The enhancement in removal of anionic inorganic species with cationic surfactants were more than that of anionic surfactants due this reason only.

Surfactants enhanced results are 2 to 3 orders of magnitude greater than water only and occur both below and above the CMC. With water only 1-5% removal was recorded. Surfactants in single washing removed 5-15% and after 10 washings 40- 70% decontamination was obtained. Since SDS had higher removal at lower concentration, it should be preferred for metal removal from soil or water.

The experimental findings indicate that at surfactant concentration lower than CMC, monomers fail to bind soluble contaminants. However, as the concentration of a surfactant reaches upto its CMC level, the formation of micelle starts and as the concentration increases the micelle structure grows to give more giant and more efficient micelles to strongly bind up contaminants at their hydrophobic ends.

Table 2: Metal removal % from contaminated soils (each 20 g of 2 mm size) after 1,4,7 and 10 washings (each of 2 h) with 100 ml water + 4 CMC SDS at pH 6.8 and temp. 25°C

Soil type	Location	Metal concentration (in mg/kg)	No of washings	Metal removal %							
				12.0	13.3	12.2	19900.3	31.2	14.3	22.0	0.9
A	Kitham	Concentration		12.0	13.3	12.2	19900.3	31.2	14.3	22.0	0.9
		Low	1	31.53	22.54	25.46	27.53	12.74	28.67	18.6	13.55
			4	43.17	30.86	34.86	37.69	17.44	39.26	25.46	18.55
			7	45.59	32.59	36.82	39.81	18.42	41.46	26.89	19.59
			10	48.55	34.67	39.17	42.35	19.6	44.11	28.61	20.84
B	St. John's	Concentration		58.8	52.6	43.2	22190	108	36.00	98.0	1.5
		Moderate	1	28.69	20.51	23.17	25.05	11.6	26.09	16.93	12.32
			4	39.28	28.08	31.72	34.3	15.88	35.72	23.18	16.87
			7	41.49	29.66	33.5	36.23	16.77	37.73	24.48	17.82
			10	44.14	31.55	35.64	38.54	17.84	40.14	26.04	18.96
C	Shahganj	Concentration		496.5	365.2	201.7	68350.6	800.2	201.2	298.5	4.3
		High	1	13.56	18.66	21.08	22.8	10.55	23.74	15.41	11.21
			4	18.57	25.55	28.86	31.21	14.44	32.51	21.09	15.35
			7	19.61	26.99	30.48	32.97	15.26	34.34	22.28	16.22
			10	20.86	28.71	32.43	35.07	16.23	36.53	23.7	17.25
D	Shahadra	Concentration		595.5	498.7	251.8	89000.1	836.5	293.3	320.8	5.2
			1	11.67	16.98	19.18	20.74	9.65	21.61	14.02	10.21
			4	15.98	23.26	26.26	28.4	13.15	29.58	19.2	13.97
			7	16.87	24.56	27.74	30.45	13.88	31.25	20.28	14.76
			10	17.95	26.13	29.51	31.91	14.77	33.24	21.57	15.7
A	Nunhai	Concentration		690.0	376.3	191.5	78000.1	930.4	216.7	339.6	5.5
		Highest	1	9.78	15.46	17.45	18.88	8.74	19.66	12.76	9.29
			4	13.39	21.16	23.9	25.85	11.96	26.92	17.47	12.72
			7	14.14	22.35	25.24	27.3	12.63	28.44	18.45	13.43
			10	15.04	23.78	26.85	29.04	13.44	30.25	19.63	14.29

Table 3: Metal removal % from contaminated soils (each 20 g of 2 mm size) after 1,4,7 and 10 washings (each of 2 h) with 100 ml water + 4 CMC SDS at pH 6.8 and temp. 25°C

Soil type	Location	Metal concentration (in mg/kg)	No of washings	Metal removal %							
				12.0	13.3	12.2	19900.3	31.2	14.3	22.0	0.9
A	Kitham	Concentration		12.0	13.3	12.2	19900.3	31.2	14.3	22.0	0.9
		Low	1	16.08	11.49	12.99	14.04	6.5	14.63	9.48	6.91
			4	22.02	15.74	17.78	19.22	8.9	20.03	12.99	9.46
			7	23.26	16.62	18.78	20.3	9.4	21.15	13.71	9.99
			10	24.74	17.68	19.98	21.6	10	22.5	14.59	10.63
B	St. John's	Concentration		58.8	52.6	43.2	22190	108	36.00	98.0	1.5
		Moderate	1	14.63	10.46	11.82	12.78	5.92	13.31	8.63	6.29
			4	20.03	14.32	16.18	17.05	8.1	18.23	11.82	8.61
			7	21.16	15.12	17.09	18.48	8.55	19.25	12.48	9.09
			10	22.51	16.09	18.18	19.66	9.1	20.48	13.28	9.67
C	Shahganj	Concentration		496.5	365.2	201.7	68350.6	800.2	201.2	298.5	4.3
		High	1	6.92	9.52	10.75	11.63	5.38	12.12	7.85	5.72
			4	9.47	13.03	14.72	15.92	7.37	16.59	10.75	7.83
			7	10	13.76	15.55	16.82	7.78	17.52	11.36	8.27
			10	10.64	14.64	16.54	17.89	8.28	18.64	12.08	8.8
D	Shahadra	Concentration		595.5	498.7	251.8	89000.1	836.5	293.3	320.8	5.2
			1	5.95	8.66	9.78	10.58	4.89	11.02	7.14	5.21
			4	8.14	11.85	13.39	14.49	6.7	15.09	9.78	7.13
			7	8.6	12.52	14.15	15.3	7.08	15.94	10.33	7.53
			10	9.15	13.32	15.05	16.28	7.53	16.96	10.99	8.01
A	Nunhai	Concentration		690.0	376.3	191.5	78000.1	930.4	216.7	339.6	5.5
		Highest	1	4.99	7.88	8.91	9.63	4.45	10.03	6.5	4.74
			4	6.83	10.79	12.19	13.18	6.1	13.73	8.9	6.49
			7	7.21	11.39	12.88	13.92	6.44	14.5	9.4	6.85
			10	7.67	12.12	13.7	14.81	6.85	15.43	10	7.29

Table 4: Metal removal % from contaminated soils (each 20 g of 2 mm size) after 1,4,7 and 10 washing (each of 2 h) with 100ml water + 4 CMC CTAB at pH 6.8 and temp. 25°C

Soil type	Location	Metal concentration (in mg/kg)	No of washings	Metal removal %							
				12.0	13.3	12.2	19900.3	31.2	14.3	22.0	0.9
A	Kitham	Concentration		12.0	13.3	12.2	19900.3	31.2	14.3	22.0	0.9
		Low	1	8.2	5.86	6.62	7.16	3.32	7.46	4.84	3.52
			4	11.23	8.03	9.07	9.81	4.54	10.22	6.99	5.09
			7	11.86	8.48	9.58	10.36	4.79	10.79	6.99	5.09
			10	12.62	9.02	10.19	11.02	5.12	11.48	7.44	5.42
B	St. John's	Concentration		58.8	52.6	43.2	22190	108	36.00	98.0	1.5
		Moderate	1	7.46	5.34	6.03	6.52	3.02	6.79	4.42	3.23
			4	10.22	7.31	8.25	8.93	4.13	9.3	6.03	4.39
			7	10.79	7.72	8.71	9.43	4.36	9.82	6.36	4.63
			10	11.48	8.21	9.27	10.03	4.64	10.45	6.77	4.93
C	Shahganj	Concentration		496.5	365.2	201.7	68350.6	800.2	201.2	298.5	4.3
		High	1	3.53	4.86	5.49	5.93	2.74	6.18	4	2.92
			4	4.83	6.65	7.51	8.13	3.76	8.46	5.48	4
			7	5.1	7.02	7.93	8.58	3.97	8.94	5.79	4.22
			10	5.43	7.47	8.44	9.13	4.22	9.51	6.16	4.49
D	Shahadra	Concentration		595.5	498.7	251.8	89000.1	836.5	293.3	320.8	5.2
			1	3.04	4.42	4.99	5.4	2.5	5.62	3.65	2.66
			4	4.16	6.05	6.84	7.4	3.42	7.7	4.99	3.64
			7	4.39	6.39	7.22	7.81	3.61	8.13	5.27	3.84
			10	4.67	6.8	7.68	8.31	3.84	8.65	5.61	4.09
A	Nunhai	Concentration		690.0	376.3	191.5	78000.1	930.4	216.7	339.6	5.5
		Highest	1	2.54	4.02	4.54	4.91	2.27	5.12	3.32	2.42
			4	3.48	5.51	6.22	6.73	3.11	7	4.55	3.31
			7	3.68	5.82	6.57	7.11	3.28	7.4	4.8	3.5
			10	3.91	6.19	6.99	7.56	3.49	7.87	5.11	3.72

Surfactants enhanced results are 2 to 3 orders of magnitude greater than water only and occur both below and above the CMC. With water only 1-5 % removal was recorded. Surfactants in single washing removed 5-15% and after 10 washings 40-70% decontamination was obtained. Since SDS had higher removal from soil or water.

The experimental findings indicate that at surfactant concentration lower than CMC, monomers fail to bind soluble contaminant reaches upto its CMC level, the formation of micelle starts and as the concentration increases the micelle structure grows to give more giant and more efficient micelles to strongly bind up contaminants at their hydrophobic ends.

Conclusions

From the foregoing results the impact of micelle on the removal of chemical species in single system surfactants is obvious. The removal is considerably enhanced due to the presence of micelles. Metal removal by anionic surfactant is maximum, nonionic alone should be insignificant and cationic minimum. However, nonionic surfactants help to solubilize and form anionic species to bind metals. The order of metal removal by surfactants is anionic such as SDS > nonionic like CTX > cationic CTAB. Surfactants enhanced results are 2 to 3 orders of magnitude greater than water only and occur above S the CMC. With water only 1-5% removal is possible. Surfactants in single washing can remove 5-15% and after 10 washings 40-70% decontamination can be obtained. Since SDS had 6 higher removal, it should be preferred for metal removal from soil or water. Investigations at below and above CMCs are suggested.

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