ACUTE TOXICITY OF CHROME ELECTROPLATING WASTES TO MICROORGANISMS: ADSORPTION OF CHROMATE AND CHROMIUM(VI) ON A MIXTURE OF CLAY AND SAND

MOHAMMAD AJMAL, AZHAR AMIN NOMANI,* and ASIM AHMAD**

Environmental Research Laboratory, Chemistry Section, Z. H. College of Engg. and Technology, Aligarh Muslim Univ., Aligarh-202001, India

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Abstract. Chrome electroplating wastes were collected from two industrial sites and analyzed for color, turbidity, pH, alkalinity, sulfate, chloride, N-ammonia, N-nitrate, N-nitrite, acid hydrolyzable P, dissolved oxygen, biochemical oxygen demand, chemical oxygen demand, chromate and chromium(VI). The effect of these wastes on saprophytic and nitrifying bacteria was studied with varying concentrations of the waste using sucrose substrate as a source of C chain for microorganisms. The use of clay sand mixtures as adsorbents for chromate and chromium(VI) was investigated. Mixtures high in clay content were found to be suitable media for the removal of Cr from the wastes. The clay used was characterized by determination of the following parameters: pH, electrical conductivity, water soluble salts, osmotic pressure, cation exchange capacity, $CaCO_3$ and organic matter.

1. Introduction

It has been observed that the wastes from hard chrome plating are significantly more hazardous than from bright chrome plating (Guillemin and Berode, 1978). The chronic toxicity of Cr(VI) on fathead minow was investigated by Pickering (1980) and Smith and Heath (1979) studied acute toxicity of Cu, chromate, Zn and cyanide to five fresh water fish at different temperatures. Chromium(VI) is also associated with health hazards, and causes nausea and ulceration after long term exposures (McKee and Wolf, 1963; Camp, 1963). Cr can be removed from electroplating wastes by neutralization and electrocoagulation (Grin *et al.*, 1977) and Bornovolokov and Pushkarev (1979) have discussed the use of an electrochemical process for the removal of Cr. Banerjee (1976) described the treatment of effluent from the electroplating industry which can contain unacceptable quantities of KCN and chromates and which can cause corrosion to sewers and disrupt biological treatment. Ajmal *et al.* (1980) have already reported deterimental effects of pharmaceutical industrial wastes on the microorganisms and it was thought to adopt a similar approach to the study of the hazards of chrome electroplating effluent. It was therefore decided to investigate the toxicity of these wastes to microorganisms and also to develop a cheap method for the removal of chromate and Cr(VI) from the effluents. This paper, therefore, reports toxicity of the electroplating wastes on the two types of bacteria and the removal of chromate and Cr(VI) by passing through columns containing sand: clay mixtures.

* Present address: National Institute of Oceanography, Varsova, Bombay.
** C/O ARAMCO, Dhahran, Saudi Arabia.

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2. Materials and Methods

2.1. Location of Industries

Rainbow Electroplaters (RE) and Chandra Enterprise (CE) industries are situated in the district of Faridabad, Haryana, India. The effluent is dumped into the Gurgaon Canal which flows into the Yamuna River which passes through Indian capital, Delhi.

2.2. Collection of Samples

The samples of electroplating wastes were collected in 300 mL BOD bottles and stored at 0 °C prior to the determination of physico-chemical characteristics (Standard Methods, 1975; Sawyer, 1960) using a Hach DR-EL/4 model spectrophotometer. A stock solution of sucrose (500 mg L^{-1}) was prepared in pure water (DMW) and used as C chain for microorganisms.

2.3 Microorganisms

The culture of saprophytic microbial population was developed by continuous aeration with a daily increment of sewage (Standard Methods, 1975). The nitrifying bacteria were developed as suggested by Siddiqui *et al.* (1967).

2.4. Preparation of Columns

Soil was collected from the field and sieved through a 200 mesh to obtain pure clay which was then characterized by determination of related physico-chemical properties. The sand was collected from a river in the dry season. Glass columns of diameter 3.5 cm and length 105 cm were used in the adsorption experiments, a plug of glass wool being placed in the bottom of each column and the columns then packed to the height of approximate 80 cm with mixtures of clay and sand in the ratios 0 : 100, 25 : 75, 50 : 50, 75 : 25, and 100 : 0. At first the columns were moistened with water and then 200 mL of each waste were poured in and allowed to stand for 24 hr. After 24 hr the waste was eluted at the rate of 4 drops min^{-1} and analyzed for chromate and Cr(VI).

2.5. Preparation of BOD Sets

Varying volumes of the electroplating wastes were added to the following three systems separately.

(a) SB + SS in 300 mL BOD bottle
(b) NB + SS in 300 mL BOD bottle
(c) SB + NB + SS in 300 mL BOD bottle

where SB = saprophytic bacteria; NB = nitrifying bacteria; and SS = sucrose substrate.

Finally the BOD bottles were filled upto the mark with 500 mg L^{-1} of sucrose substrate and kept for incubation for 15 days at 20 °C. The BODs were monitored at selected times over this period (Ciaccio, 1972).

3. Results and Discussion

The physico-chemical characteristics of RE and CE wastes are given in Table I. The wastes were found to be rich in sulfate, chloride, silica, N, P, chromate, and Cr(VI). The wastes were alkaline in nature and had low levels of dissolved oxygen (DO). The low BOD and COD are indicative of the inorganic nature of the wastes. High contents of chromate and Cr(VI) in these wastes led us to study their toxicity to microorganisms, and to develop inexpensive methods for their removal from the electroplating wastes prior to disposal.

TABLE I

Physico-chemical characteristics of electroplating wastes

Parameters	Rainbow Electro-platers (RE)	Chandra Enterprise (CE)
1. Color	1125 Pt-Co unit (yellowish)	875 Pt-Co unit (Pinkish)
2. Turbidity	500 FTU	200 FTU
3. pH	11.5	11.0
4. Alkalinity	2390	2380
5. Sulfate	200	320
6. Chloride	680	800
7. Silica	130	140
8. $N–NH_3$	24	10
9. $N–NO_3$	80	80
10. $N–NO_2$	4.8	ND
11. P(reactive)	ND	ND
12. P(organic)	ND	ND
13. P(hydrolyzable)	24	90
14. DO	2.5	2.5
15. BOD	9	9.5
16. COD	14	12
17. Chromate	320	170
18. Cr(VI)	400	200

All units except color, turbidity, and pH are expressed in mg L^{-1}.

The results of the investigation of the toxicity of RE and CE wastes to the microorganisms are presented in the Tables II and III. The BOD of sucrose substrate with saprophytic bacteria having no waste (control) showed a rapid stabilization. It is worth reporting that 71, 76, 83, and 98% of the BOD was observed on 5th, 8th, 10th, and 15th day of incubation in the control sets of saprophytic bacteria. Similarly 75 to 99% and 77 to 99% were observed in case of nitrifying bacteria and mixture of the two bacteria (saprophytic + nitrifying), respectively. It was observed that 0.5 mL of the RE and CE wastes showed weak toxic effects in repressing the BOD of the system on 5th to 15th days as compared to control. But a pronounced repression of the activity of saprophytic bacteria started with 2 mL of RE waste and increased with an increasing volume of waste (Figure 1). Twelve mL of the waste retarded all microbial activity. The BOD was

TABLE II

BOD studies showing toxicity of RE wastes on Microorganisms

Experimental (mL)	BOD on given days											
	5th day			8th day			10th day			15th day		
	mg L^{-1}	%	% inhibition	mg L^{-1}	%	% inhibition	mg L^{-1}	%	% inhibition	mg L^{-1}	%	% inhibition
SB + SS + 0	387	71	–	425	76	–	464	83	–	548	98	–
SB + SS + 0.5	364	65	5.9	399	71	6.1	449	80	3.2	476	85	13.1
SB + SS + 2	302	54	21.9	341	61	19.7	403	72	13.1	431	77	21.3
SB + SS + 5	257	46	33.5	208	50	51.0	347	62	25.2	386	69	38.6
SB + SS + 8	173	31	55.2	218	39	48.0	240	43	48.2	285	51	47.9
SB + SS + 10	78	14	79.8	112	20	73.6	112	20	75.8	117	21	79.5
NB + SS + 0	422	75	–	442	79	–	481	86	–	554	99	–
NB + SS + 0.5	373	66	11.6	409	73	7.4	459	82	4.57	487	87	12.0
NB + SS + 2	314	56	25.5	385	64	12.8	414	74	13.9	442	79	20.2
NB + SS + 5	269	48	36.2	296	53	33.0	358	64	25.5	382	70	31.0
NB + SS + 8	184	33	56.3	224	40	49.3	252	45	47.6	291	52	47.4
NB + SS + 10	100	18	76.3	126	23	71.4	134	24	72.1	140	25	74.7
NB + SS + 12	72	13	82.9	98	17	77.8	100	18	79.2	100	18	81.9
SB + NB + SS + 0	431	77	–	448	80	–	487	87	–	554	99	–
SB + NB + SS + 0.5	375	67	12.9	414	74	7.5	464	83	4.7	492	88	11.1
SB + NB + SS + 2	324	58	24.8	367	66	18.0	414	74	14.9	414	74	25.2
SB + NB + SS + 5	274	49	36.4	302	54	32.5	364	65	25.2	369	66	33.3
SB + NB + SS + 8	196	35	54.5	218	39	51.3	252	45	48.2	257	46	53.6
SB + NB + SS + 10	100	18	76.7	100	18	77.6	134	24	72.4	140	25	74.7
SB + NB + SS + 12	72	13	83.2	95	17	78.7	100	18	79.4	100	18	81.9

% inhibition compared to the BOD of control of corresponding day.

TABLE III

BOD studies showing toxicity of CE waste on microorganisms

Experimental conditions mL	BOD on given days											
	5th day			8th day			10th day			15th day		
	mg L^{-1}	%	% inhibition	mg L^{-1}	%	% inhibition	mg L^{-1}	%	% inhibition	mg L^{-1}	%	% inhibition
SB + SS + 0	403	72	–	425	76	–	470	84	–	549	98	–
SB + SS + 0.5	397	71	1.4	421	75	0.9	470	84	–	548	98	–
SB + SS + 2	369	66	8.4	392	70	7.7	442	79	5.9	487	87	11.2
SB + SS + 5	313	56	22.3	347	62	18.3	392	70	16.5	421	75	23.3
SB + SS + 8	263	47	34.7	285	51	32.1	352	63	25.1	380	68	30.7
SB + SS + 12	190	34	52.8	224	40	47.2	246	44	47.6	291	52	46.9
SB + SS + 20	72	13	82.2	106	19	75.0	112	20	76.1	112	20	79.5
NB + SS + 0	425	76	–	431	77	–	476	85	–	548	98	–
NB + SS + 0.5	417	75	1.9	425	76	1.41	470	84	1.2	543	97	0.9
NB + SS + 2	375	67	11.7	397	71	7.8	442	79	7.1	481	86	12.2
NB + SS + 5	324	58	23.7	347	62	19.4	397	71	16.5	421	75	23.1
NB + SS + 8	274	49	35.5	296	53	31.3	358	64	24.6	375	67	31.5
NB + SS + 12	201	36	52.7	235	42	45.4	252	45	47.0	302	54	44.8
NB + SS + 20	128	23	69.8	190	34	55.9	235	42	50.6	296	53	45.9
NB + SS + 25	78	14	81.6	100	18	76.7	112	20	76.4	123	22	77.5
SB + NB + SS + 0	425	76	–	431	77	–	481	86	–	554	99	–
SB + NB + SS + 0.5	425	76	–	425	76	1.3	470	84	2.2	543	97	0.1
SB + NB + SS + 2	375	67	11.7	392	70	9.0	448	80	6.8	487	87	12.09
SB + NB + SS + 5	330	69	22.3	352	63	18.3	403	72	16.2	431	77	22.2
SB + NB + SS + 8	280	50	34.1	291	52	32.4	364	65	24.3	380	68	31.4
SB + NB + SS + 12	207	37	51.2	240	43	44.31	257	46	46.5	308	55	44.04
SB + NB + SS + 20	128	23	69.8	196	35	54.5	240	43	50.1	291	52	47.4
SB + NB + SS + 25	72	13	83.0	95	17	77.9	106	19	77.9	117	21	78.8

% inhibition compared to the BOD of control of corresponding day.

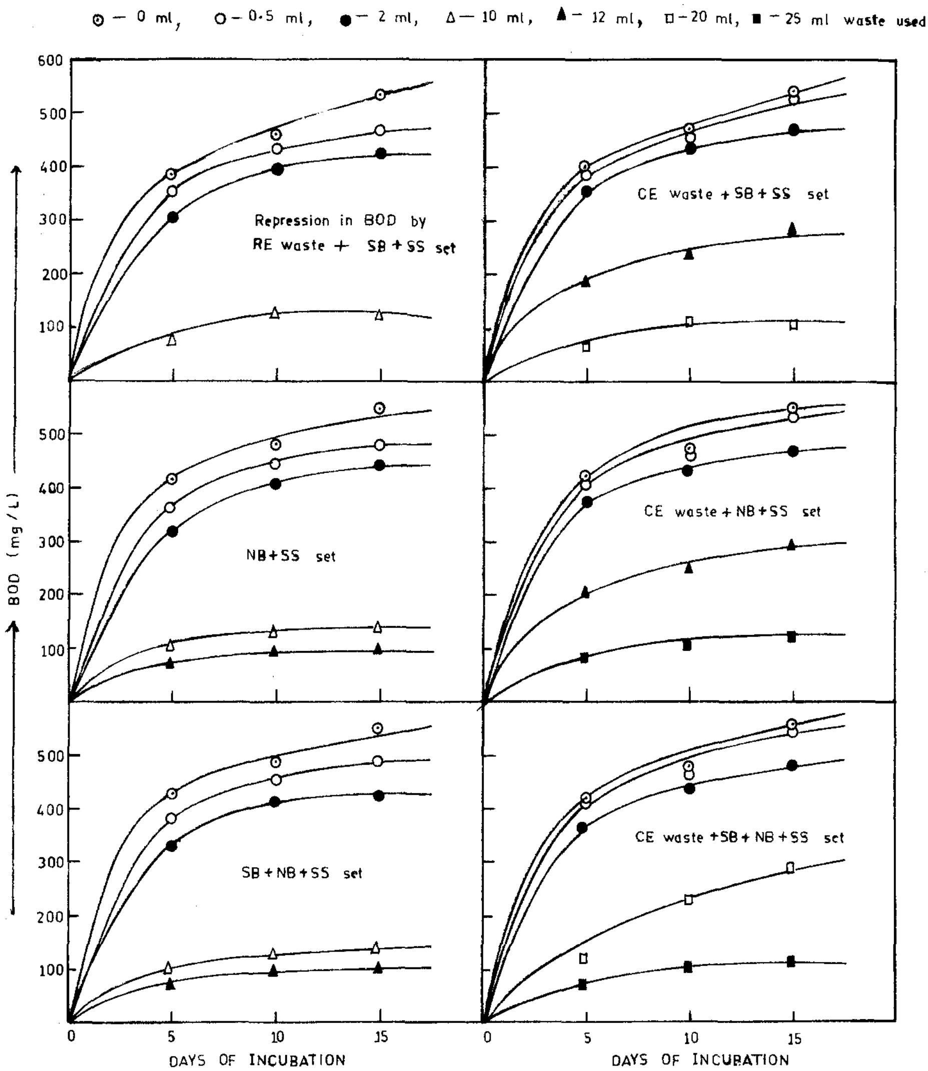

Fig. 1. BOD as a function of days of incubation.

repressed upto 14, 20, 20, and 21% on 5th, 8th, 10th, and 15th day in the sets containing 10 mL of RE waste. In general the percent inhibition decreased with the increase in the time of incubation, whereas the inhibition increased with the increase in the volume of waste. The inhibition in the sets of saprophytic bacteria ranged from 5.9 to 79.8% on the 5th day and 13.1 to 79.5% on the 15th day of incubation. Similarly the same volumes of the waste were added for nitrifying bacteria but in this case inhibition in bacterial activity was only observed when 15 mL of waste was used. The same volumes of the wastes were added to the mixture of saprophytic and nitrifying bacteria and it was found that only when 15 mL of the waste had been added the microbial activity was retarded.

TABLE IV

Physico-chemical analyses of clay

Type of soil	pH	Electrical conductivity in mhos cm^{-1}	Water soluble salts meq per 100 g	Cation exchange capacity meq per 100 g of soil	Osmotic pressure	$CaCO_3$ %	Organic matter %	No. of individual samples analyzed
Clay	7.9–8.0	3.5×10^{-4} 4.0×10^{-4}	10.8–10.95	192.4–195.5	0.79–0.82	8.14–10.7	0.84–0.86	8

The studies conducted with the CE waste under the identical conditions showed similar results to those with RE waste but the volume of waste which inhibited the microbial activity of saprophytic, nitrifying and a mixture of both were 25, 30, and 30 mL, respectively. The reason for this high volume required for the inhibition may be attributed to the low concentration of chromate and Cr(VI) in the CE waste (Table I).

It is clear from the percent inhibition data (Tables II and III) that the nitrifying bacteria can mildly tolerate effects of wastes as compared to the saprophytic bacteria. In the sets of saprophytic bacteria with 10 mL of RE waste on 5th, 8th, 10th, and 15th day the percent inhibition observed was 79.8, 73.6, 75.8, and 79.5% as compared to the 76.3, 71.4, 72.1, and 74.4% of corresponding days in the sets of nitrifying bacteria. A similar trend was found in the sets of CE waste.

The physico-chemical analysis of the clay is presented in Table IV. The cation exchange capacity of the clay ranged between 192.4 and 195.5 meq per 100 g of clay determined as per Ganguly (1952). The clay used for the studies had pH 7.9 to 8.0, electrical conductivity 3.50×10^{-4} to 4.0×10^{-4} mhos cm^{-1}, osmotic pressure 0.79 to 0.82, calcium carbonate 8.14 to 10.7% and organic matter 0.84 to 0.86%. The soil used was low in organic matter and also had a low cation exchange capacity (Alexander, 1961). The eluted wastes (RE and CE) from different columns were analysed and compared with the initial chromate and Cr(VI) concentrations (Table V). The first column (clay : sand, 0 : 100) showed slight adsorption of chromate and Cr(VI). However, the adsorption increased with an increasing proportion of clay. The fifth column filled with pure clay adsorbed nearly 95.6 to 96% chromate and 99 to 99.2% Cr(VI) (Table V). The eluant so obtained was free from color, chromate and Cr(VI). So the clay appears to provide a good and cheap means for the removal of chromate and Cr(VI) from electroplating waste before discharge to the sewer or onto the land.

TABLE V

Adsorption of chromate and Cr(VI) on clay : sand in five different ratios for 24 hr

Chromate and Cr(VI) before adsorption	Adsorbed chromate and Cr(VI) (clay : sand)				
	0 : 100	25 : 75	50 : 50	75 : 25	100 : 0
(i) RE waste					
Chromate (320 mg L^{-1})	6.4 (2)	96 (30)	214 (67)	265 (83)	307 (96)
Cr(VI) (400 mg L^{-1})	7.6 (1.9)	140 (35)	304 (76)	356 (89)	396 (99)
(ii) CE waste					
Chromate (170 mg L^{-1})	3.06 (1.8)	52.7 (31)	113 (67)	141 (83)	161 (95)
Cr(VI) (200 mg L^{-1})	3.00 (1.5)	69.4 (35)	152 (76)	178 (89)	98 (99)

Values in parenthesis shows percent adsorption.

4. Conclusion

These studies clearly indicated that the electroplating waste which contains chromate and Cr(VI) contents is inimical to the saprophytic and nitrifying bacteria. RE waste was much toxic as it contained higher concentration of chromate and Cr(VI) in comparison to CE waste. Clay proved to be a good absorpent for the chromate and Cr(VI) due to high cation exchange capacity and strong binding force. This needs further research as it may be proved to be cheapest treatment of electroplating wastes in the forth coming future.

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