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Combined Aerobic and Physicochemical Treatment of Pharmaceutical Industry Sludge

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Abstract. Composite samples of sludge obtained from a pharmaceutical factory were analysed for their pollution characteristics. The samples were then treated by integrated aerobic biological and physicochemical methods. The analysis revealed that the BOD and COD of the sludge liquor were high, as well as were the levels of solids concentration, nitrogen, phosphorus and bacterial count. These showed that sludge from this industry had a high pollution potential, and therefore needed treatment before disposal or reuse in other applications. Percentage solids reduction achieved were in the range of 26.1 to 29% of total soluble solids, 26.1 to 33% of suspended solids, and 43 to 52% of volatile solids. BOD and COD reductions were in the range of 96.1 to 98.2%, and 96.8 to 98.4%, respectively. Ammonia nitrogen reductions in this sludge were about 85.2 to 93.3%. Total nitrogen and phosphorus were also found to be appreciably reduced by the combined aerobic and physicochemical treatment methods.

Keywords: aerobic biodegradation, physicochemical degradation, pollution, wastewater treatment, euprophication, pharmaceutical sludge

Introduction

Industry requires large supplies of water for their processes. Only a small fraction of it is incorporated in their products and some is lost by evaporation, while the rest of it is released as the wastewater containing sludge. This sludge contains organic pollutants as the major constituent and inorganic salts as dissolved solids. If this sludge is released into the water bodies untreated, it severely affects the quality of water. This sludge may contain toxic metals that directly affect the aquatic life, or it may contain plant nutrients, such as nitrates and phosphates that may stimulate the growth of aquatic weeds, or it may have a high demand for dissolved oxygen thus resulting in anaerobic conditions. Under anaerobic conditions, H_2S gas is generated, which produces offensive odours. In order to protect the environment from the undesirable toxic materials, therefore, the wastewater is required to be suitably treated before its discharge to natural water streams. Many of the steps taken to treat the wastewater result in further concentration of the dissolved pollutants in the sludge (Priestly, 1991). The sludge, as a consequence, becomes unstable, putrescine and pathogenic. Sludge must, therefore, be treated before disposal or for reuse in order to alleviate pollution problems and thus not become a burden on the environment.

Pharmaceutical sludge contains biodegradable organic matter. Bacteria may be used to bring about its degradation, so as to stabilize the waste for ultimate disposal or reuse. However, non-biodegradable substances remain unaffected during the process of bacterial biodegradation. That is why a combination of biological and physicochemical methods was investigated in the present study, during which the wastewater sludge from the pharmaceutical industry was characterized and treated by integration of the two procedures. For this purpose, the physicochemical methods of coagulation and flocculation were used in conjunction with the aerobic biological method. This approach was considered adequate to produce a well-treated effluent and sludge, having better efficiency for reuse than was achievable with either method when used singly.

Materials and Methods

Industrial sludge used. The source of sludge used in the present study was obtained from a pharmaceutical factory located in Ikeja, Lagos. The factory produces a variety of drugs, including, Trosyl cream, Tetramycine, Ergonovine, Uvacin, Combantrin, Obron, Oxytetracyclin, Diflucan and Diphenydramine. The average wastewater generated per day by this factory was $3.1x10^4$ litres at optimum production. The wastewater from which the sludge was obtained originated from a combination of various processes, including syrup preparation, malt preparation, production of pastilizers, and from tablet rejection. The effluent was heterogeneous in nature and included water used for washing equipment, from braken vessels containing the pharmaceutical preparations, rejected tablets that were crushed and washed down the drain, starch

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washed from the equipment and starch moulds, a wide range of chemicals arising from different processing units, oils, emulsions, and a variety of ether extractable materials. All these found their way into the effluent tank, which was ultimately emptied into the drain. Wastewater flowchart of the pharmaceutical factory is as shown in Fig. 1.

Sampling of sludge. Samples of sludge were obtained from the sedimentation tank of the industry. The samples were stored in a refrigerator to prevent biodegradation. Stock solutions of alum, iron (III) chloride, hydrated lime, and polyacrylamide partially hydrolysed with soda, used as coagulants, were prepared fresh at the time of the test. For coagulation studies, jar tests were conducted. The objective of the jar test was to determine the optimum dose and the pH value at which a coagulant should be introduced to the sludge.

Combined aerobic and physicochemical treatment procedure. The sludge samples were first treated using the aerobic biological systems as described below, but without dewatering and disinfection. The resultant sludge was then treated by the physicochemical method as described earlier (Asia and Ademoroti, 2002; Ademoroti, 1982). The flow chart for the combined aerobic and physicochemical treatment is shown in Fig. 2.

Aerobic treatment procedure. Two litres of the sludge was placed in a four litre plastic container, which served as the digester (Fig. 3). Natural air served as the aeration system. Five ml of phosphate solution was added as the buffer. One ml each of magnesium sulphate, calcium chloride, and iron (III) chloride solutions were added as the nutrient source for the bacterial population in the sludge. One ml of 50% hydrogen peroxide was also added so as to keep the dissolved sulphide below 0.6 mg/l and to eliminate odour. The plastic container was covered with loose plastic cap so as to allow air to enter the digester system. The sludge was stirred at an interval of 6 h and was allowed to digest the sludge for 45 days (Asia, 2000; Ademoroti, 1983). The digestion was deemed to have been completed, as the pH at this stage was noted to have stabilized. The digested sludge was then analysed to determine the compositional changes that had occurred. The sludge was then treated with bleaching powder (calcium oxochloride) until the level of residual chlorine was between 0.2 and 0.7 mg/l (Henry and Heinke, 1989). This was done to ensure

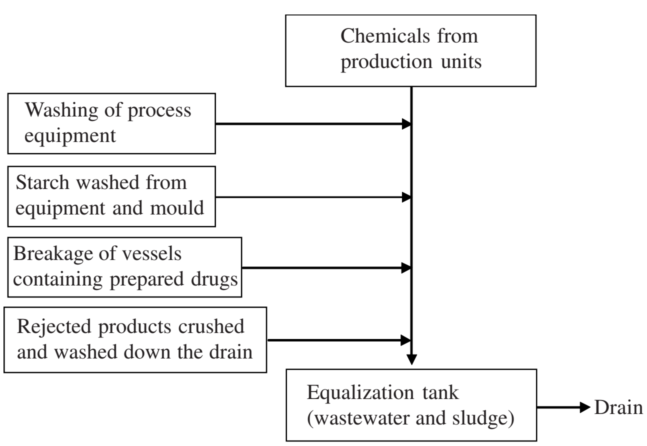

Fig. 1. Wastewater flowchart of the pharmaceutical factory located at Ikeja Lagos, Nigeria, which was investigated for the treatment of the generated sludge.

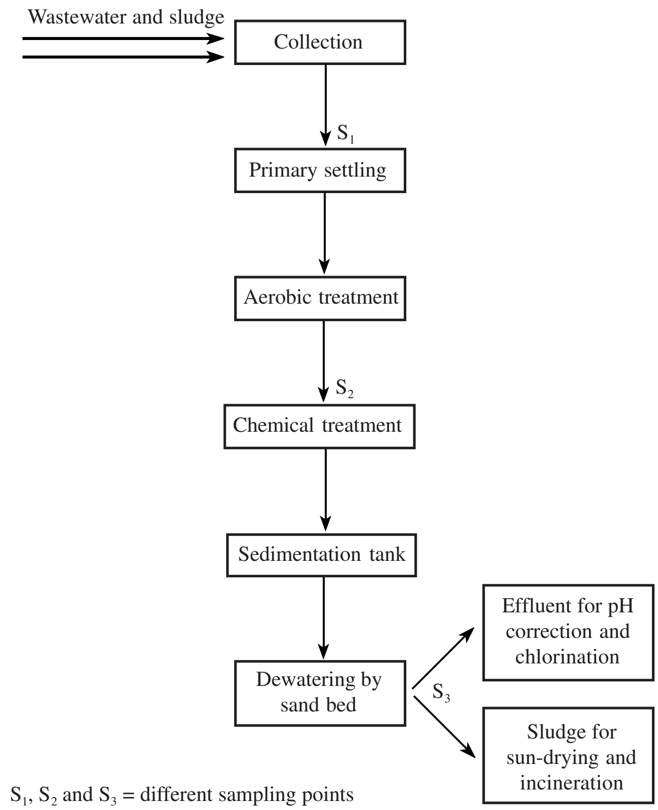

Fig. 2. Flowchart for combined aerobic and chemical treatment of pharmaceutical sludge.

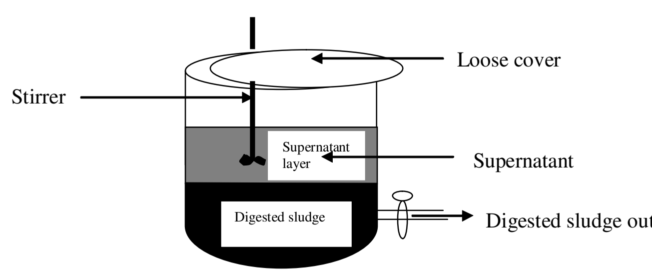

Fig. 3. Laboratory apparatus (digester) for conducting aerobic digestion studies on the sludge generated by a pharmaceutical factory.

obtaining the maximum level of bacterial kill before dewatering. Dewatering was done by sand bed filtration, using teflon as the filter medium. The wet sludge was pasteurized for 30 min at 100 °C, followed by sun-drying for three days.

Analytical procedures. All samples were analyzed, as per the standard methods for wastewater and effluent analysis (Ademoroti, 1996; APHA, 1985). Where analysis was not immediately possible, the digested sludge samples were preserved to inhibit biodegradation. All the reagents used for the analysis were of analytical grade obtained from BDH Chemicals Limited, Poole, England.

Results and Discussion

Characterization of the sludge under study. The results of the characterization carried out on the fresh sludge obtained from a pharmaceutical industry are shown in Tables 1 and 2. These results showed that the pH value for fresh pharmaceutical sludge was 6.7, indicating that fresh pharmaceutical sludge was slightly acidic. The average turbidity of 980 NTU showed that the colloidal matter in the sludge was high and by implication the sludge contained high concentration of solids. The total solids, suspended solids and the volatile solids were 14,031 mg/kg, 1,231 mg/kg and 10,800 mg/kg, respectively. The BOD_5, COD and the total bacterial count of the fresh sludge were 452 mg/l, 1446 mg/l and 3.8 x 10^6 CFU, respectively. These values are quite high when compared with the WHO standards. These indicate a strong pollution potential, and therefore call for treatment of the sludge before disposal, or for any further application. The results also showed that the ratio of COD : BOD was 3.20, indicating that the sludge was capable of undergoing about 50-90% substrate biodegradation (Quano *et al.,* 1978).

As is evident from these results, most of the nitrogen present in the sludge was more in the form of ammonium-nitrogen. Consequently, if these sludge samples, containing such high concentrations of ammonium-nitrogen are discharged to the environment, depletion of oxygen in the receiving water resources may occur, as the ammonia is oxidized to nitrates by some groups of aerobic bacteria. Also, nitrates and phosphates, derived from the sludge are inorganic nutrients, which promote plant and algal growth. Although the amounts necessary to trigger algal blooms are not well established, yet concentrations as low as 0.01 mg/1 of phosphorus and 0.1 mg/1 of nitrates may be sufficient for eutrophication when other elements are in excess (Henry and Heinke, 1989). In addition to having a detrimental aesthetic effect on lakes (odour and appearance), algae can be toxic to cattle, spoil the taste for use as potable water, block filtration units, and increase chemical requirements in the water treatment procedures (Henry and Heinke, 1989).

Table 1. Characteristics of fresh sludge liquor from a pharmaceutical factory

Sludge liquor characteristics	Units	Range of values	Mean
pH		5.21-7.20	6.70
Temperature	°C	27-29.5	28.0
Conductivity	Scm^{-1}	90-130	120
Specific gravity		1.01-1.03	1.02
Turbidity	NTU	740-1145	980
Dissolved oxygen	mg/1	1.9-2.8	2.3
BOD_5	mg/1	410-480	452
COD	mg/1	1010-1640	1446
Total alkalinity	mg/1	490-555	530
Bicarbonate alkalinity	mg/1	38.4-45.3	42
Ammonia-nitrogen	mg/1	41.4-66.0	50.7
Nitrate-nitrogen	mg/1	23.3-40.1	38.2
Organic-nitrogen	mg/1	10.1-14.9	12.5
Chloride	mg/1	127-159	134.2
Sulphate	mg/1	117-159	134.2
ABS	mg/1	13.2-24.3	21
Total bacterial count	cfu/100ml	3.1-4.1 x 10^6	3.8 x 10^6

cfu = colony forming units

Table 2. Characteristics of fresh settled sludge from a pharmaceutical factory

Sludge liquor characteristics	Units	Range of values	Mean
Settleable solids	mg/kg	840-1580	1231
Moisture	%	95-98	97
Volatile solids	mg/kg	8199-12010	10800
Total solids	mg/kg	10900-14390	14031
Ash	mg/kg	16.5-24.7	23.0
Total nitrogen	mg/kg	51.44-80.9	66.80
Phosphorous	mg/kg	10.1-14.9	14.67
Potassium	mg/kg	1.80-4.2	3.03
Oil and grease	mg/kg	3.2-6.7	5.0
Iron	mg/kg	0.11-0.17	0.13
Calcium	mg/kg	50.1-80.4	68.1
Magnesium	mg/kg	41.7-57.6	49.5
Manganese	mg/kg	nil	nil
Copper	mg/kg	0.22-0.32	0.28
Cadmium	mg/kg	nil	nil
Chromium	mg/kg	nil	nil
Lead	mg/kg	0.9-1.5	1.2
Zinc	mg/kg	1.01-1.31	1.2

On the basis of an earlier study (Tables 3, 4; Fig. 4), Asia (2000) had determined 5 g/l of alum, 4 g/l of iron (III) chloride, 15.5 g/l of lime and 400 mg/l of polyelectrolyte as the optimum coagulant/flocculant doses for the treatment of pharmaceutical industry sludge.

The reduction in solids contents. The amount of solids present in the raw and treated sludge are shown in Fig. 5. It is evident from these observations that the pharmaceutical industry sludge treated by combined aerobic and physicochemical methods had undergone the total solids reductions of 26.1-29%, suspended solids of 26.1-33%, and volatile solids of 43-52%.

Oxygen demand values. The results of the study on oxygen-demand of raw and treated sludge are shown in Fig. 6. It may

Table 3. Results of a pharmaceutical sludge liquor analysis, after treatment with different doses of alum and iron (III) chloride

Alum			Iron (III) chloride		
dosage (g/l)	pH	COD reduction (%)	dosage (g/l)	pH	COD reduction (%)
-	6.7	-	-	6.7	-
2	5.9	48.1	2	6.2	37.9
2.5	5.7	51.5	2.5	5.9	54.1
3	5.4	55.4	3	5.7	64
3.5	5.1	59.2	3.5	5.1	71.6
4	4.8	67.5	4	4.9	79
4.5	4.7	68.7	4.5	4.7	72.5
5	4.7	69	5	4.4	69.6
5.5	4.4	53.7	5.5	4.3	47.4

Table 4. Results of a pharmaceutical sludge liquor analysis, after treatment with different doses of lime and polyelectrolyte

Lime			Polyelectrolyte		
dosage (g/l)	pH	COD reduction (%)	dosage (mg/l)	pH	COD reduction (%)
7.5	6.7	-	-	6.7	-
9.5	8.1	49.9	100	6.2	41.9
11.5	9.4	53.8	200	5.9	64.7
13.5	10.3	64.7	300	5.8	70.7
15.5	11.1	72.4	400	5.6	77
17.5	11.8	70.3	500	5.6	66.8
19.5	12.2	71.6	600	5.4	66.8
21.5	12.6	69.9	700	5.3	63.3
23.5	12.8	68.2	800	4.9	59.4
25.5	12.8	64	900	4.9	56.4
			1000	4.8	53.4

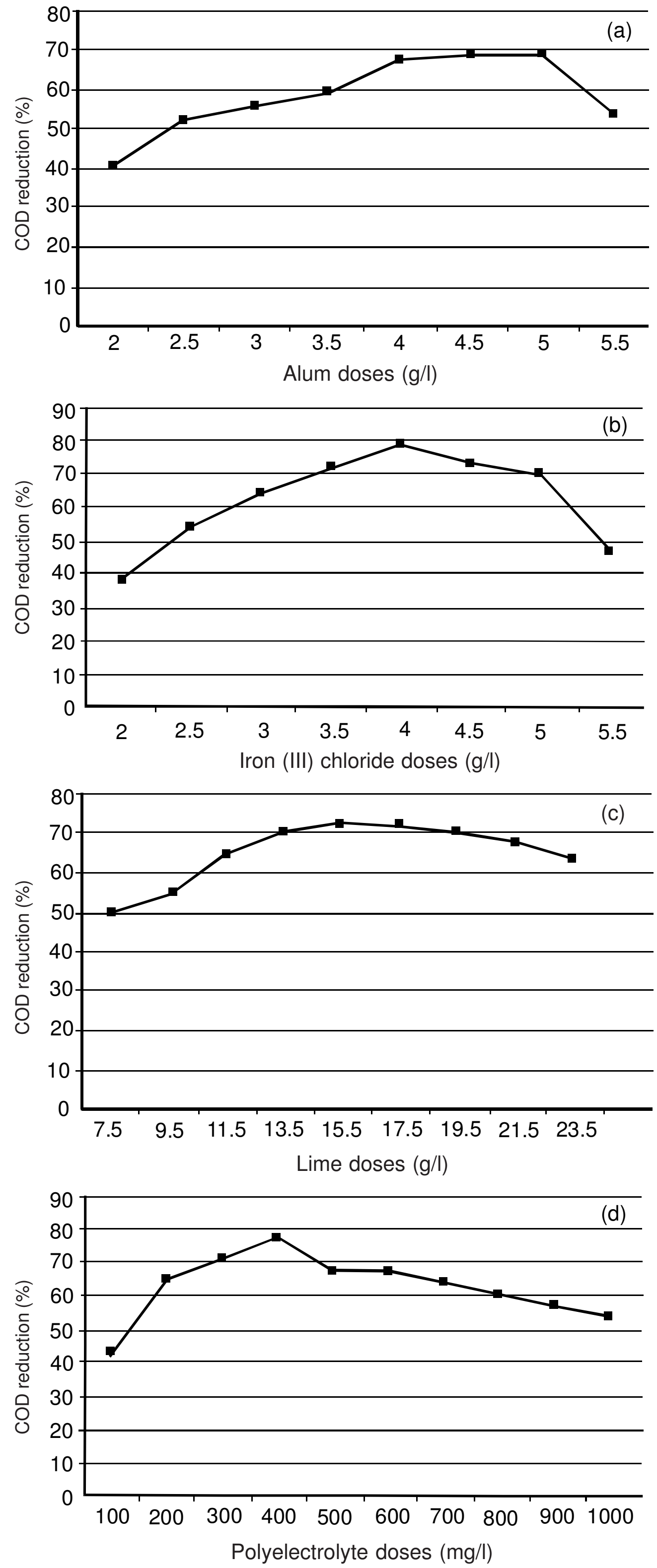

Fig. 4. The treatment of pharmaceutical sludge using various methods: (a) alum treatment; (b) iron (iii) chloride treatment; (c) lime treatment; polyelectrolyte treatment; optimum values for (a), (b), (c), (d), respectively, were 5 g/l, 4 g/l, 15.5 g/l, 400 mg/l.

be noted from these observations that the combined biological and physicochemical treatment methods had proved to be more efficient than either the biological, or the physicochemical method alone in terms of BOD and COD reduction. About 96.1-98.2% BOD and 96.8-98.4% COD reductions were achieved by the combination of these treatment methods.

Reduction in nitrogen. Nitrogen concentrations in the combined aerobic and physicochemically treated sludge is shown in Fig. 7. These results show that there was considerable reduction in the nitrogen contents of the treated sludge. The highest reductions were noticed in the aerobic lime-treated sludge. Ammonia nitrogen reductions in this sludge were about 85.2-93.3%. This may be due to the nitrification process during the digestion stage in which some of the ammonia present was converted to nitrates, while more ammonia was further reduced by the physicochemical treatment processes. Total nitrogen was also found to be reduced in all the sludge samples treated by the combined aerobic and physicochemical methods. Reductions were in the range of 64.8-86.7%.

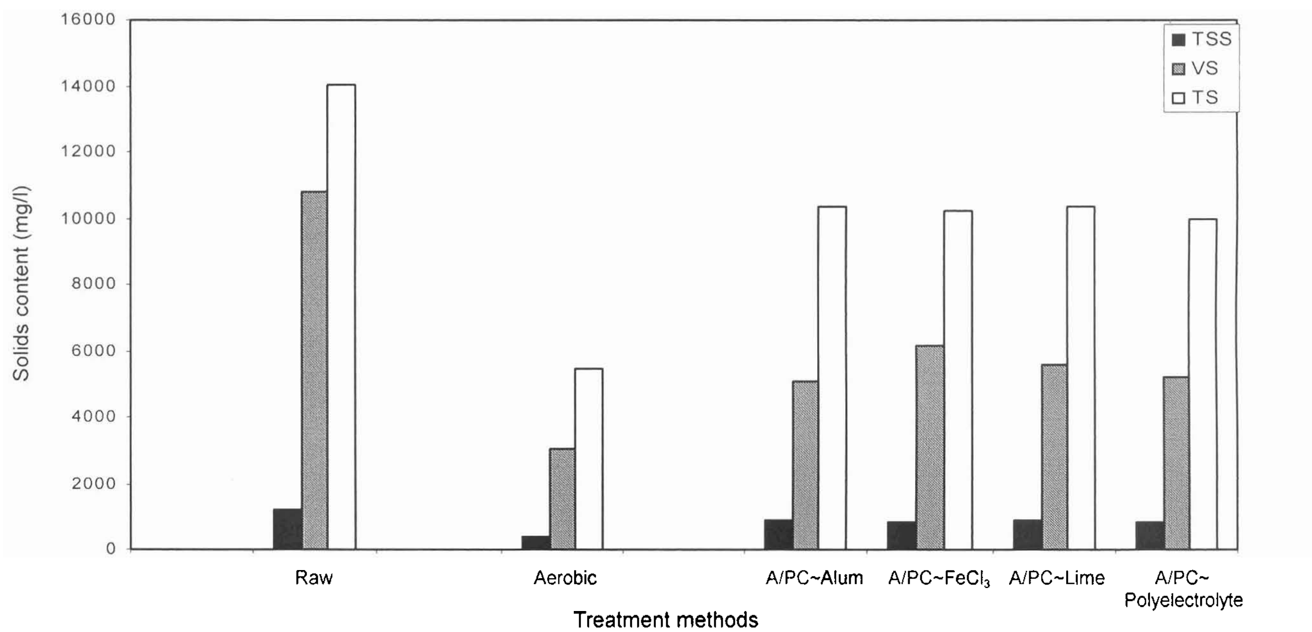

Fig. 5. Solids contents of raw and variously treated sludge from a pharmaceutical factory; TSS = total suspended solids, TS = total solids, VS = volatile solids, A/PC = aerobic/physicochemical combined treatments.

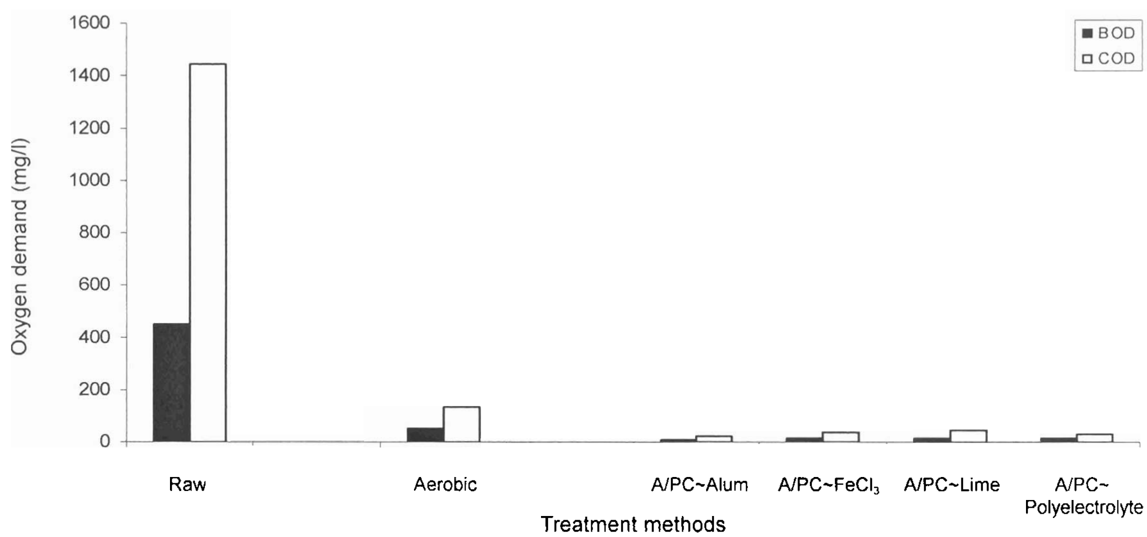

Fig. 6. BOD and COD of raw and variously treated sludge from a pharmaceutical factory; BOD = biological oxygen demand, COD = chemical oxygen demand, A/PC = aerobic/physicochemical combined treatments.

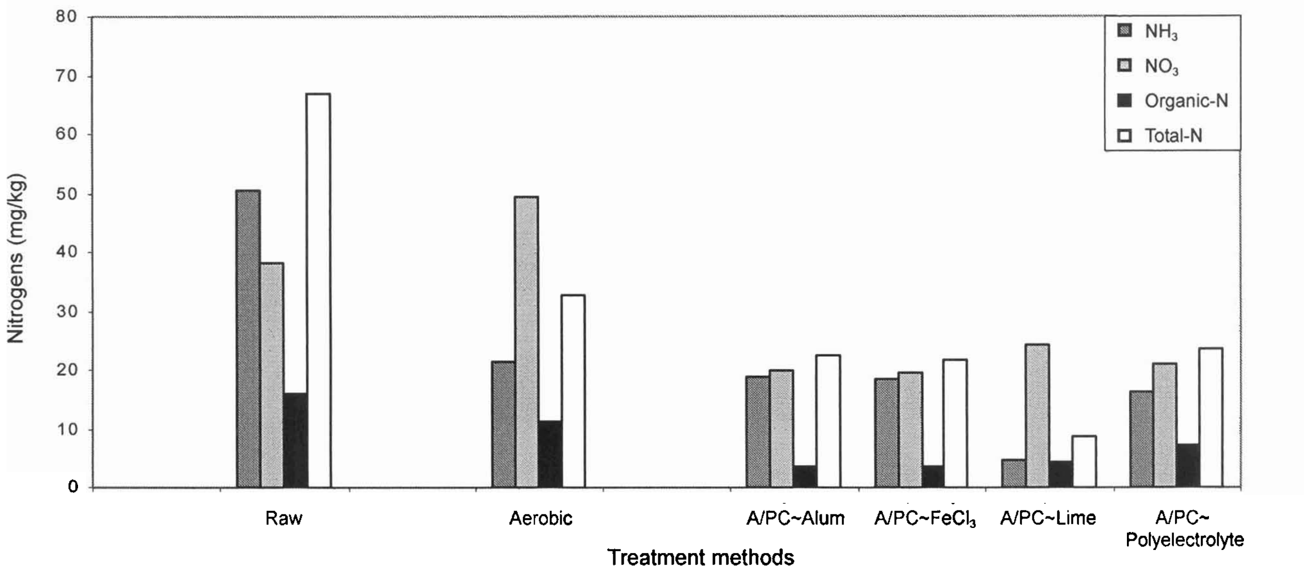

Fig. 7. Nitrogen concentration of raw and variously treated sludge from a pharmaceutical factory; A/PC = aerobic/physicochemical combined treatments.

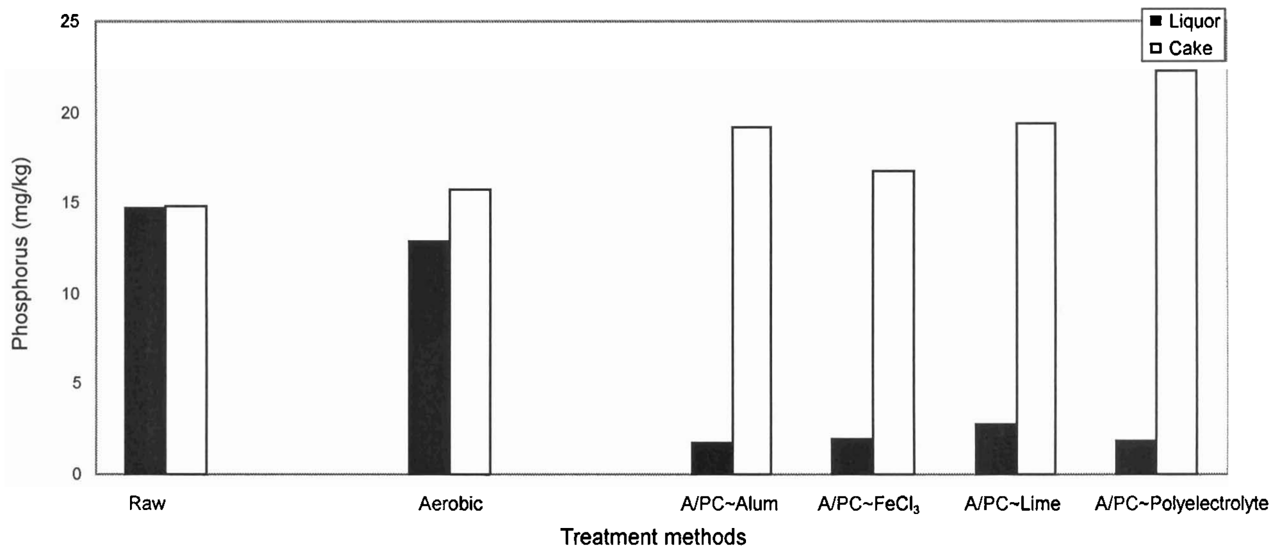

Fig. 8. Phosphorus concentration of raw and variously treated sludge from a pharmaceutical factory; A/PC = aerobic/pharmaceutical combined treatments.

The highest reductions were also found in the lime-treated aerobic sludge. This study revealed that lime was a better coagulant, if the nitrogen removal was the focus of treatment from the aerobically digested sludge.

Reduction in phosphorus concentration. The results on the reduction of phosphorus concentrations are shown in Fig. 8, which revealed that the combined aerobic and physicochemical methods can be used to reduce phosphorus from the sludge liquor. The phosphorus was adsorbed by the sludge solids which could in turn be used to condition soil, for the purposes of agricultural applications.

Conclusion

The present study has revealed that the combined aerobic and physicochemical methods are efficient for the treatment of pharmaceutical industry sludge. The choice of an aerobic method over an anaerobic system lies in the fact that pharmaceutical industries produce a large volume of water-containing sludge coupled with high values of BOD and COD, and high concentration of volatile solids. Keeping in view the economics, time and efficiency, an aerobic treatment system is recommended for the treatment of pharmaceutical sludge. This is due to the presence of aerobic organisms with a high respiratory rate, which acclimatize and treat the sludge in a short period of time. In addition, in the combination methods, while the aerobic biological system converts almost all the ammonia present in the sludge to nitrates, the physicochemical method removes the nitrates from the solution by denitrification.

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