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Integrated Biological and Chemical Treatment of Brewery Sludge

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Composite samples of sludges obtained from a brewery in Benin City were analysed for their pollution characteristics. The samples were then treated by integrated biological and chemical methods. The analysis revealed that the BOD and COD of the sludge liquor were high, as well as the levels of solids concentration, nitrogen, phosphorus and total bacterial counts. These showed that sludge from the brewery have high pollution potentials and therefore, needed treatment before disposal or reuse. The sludges were treated by integrated biological and chemical methods. Percentage solids reduction achieved were in the range of 21.4 - 27% total solid (TS), 27 - 32% suspended solids (SS) and 32 - 48% volatile solids (VS) for integrated aerobic/chemical treatment and 24.3 - 27.2% TS, 30.3 - 33% SS and 34.4 - 36% VS for anaerobic/chemical treatment. BOD and COD reductions were in the range of 97 - 98 and 97.3 - 98.2%, respectively for aerobic/chemical treatment and 97.7 - 97.9 and 98 - 98.3%, respectively for anaerobic/chemical treatment. Phosphorus, ammonia and nitrate nitrogen were found to be substantially reduced in this sludge thus preventing the eutrophication of water bodies, up to 57 - 85.2% NH_3 and 31.7 - 61.9% NO_3. Reduction was achieved using aerobic/chemical treatment while the anaerobic/chemical method achieved a reduction of up 100% NO_3.

Key words**:** Brewery sludge, Pollution, Chemical treatment, Biological techniques, Eutrophication.

Introduction

In the recent times, efforts have been geared towards the treatment of domestic and industrial wastewaters while sludges associated with them are merely dumped untreated into the environment. Many of the steps, taken to treat wastewaters results in the concentration of pollutants into a sludge (Priestly 1991), sludge can therefore, become unstable, putrescible and pathogenic. Thus sludges must be treated before disposal or reuse in order to alleviate pollution problems and create a good and healthy environment.

Sludge treatment processes can be categorized essentially into two generic types, one based on biological and the other on chemical techniques.

In biological systems of treatment, treatment principles involve oxidation of all biodegradable organics by bacterial action. Complex biodegradable substances are broken down into less complex ones to produce cleaner and clearer effluent. However, non biodegradable substances pass unaffected. In cases where there are heavy toxic metals or toxic substances in any wastewater or sludge to be treated, the lives of the bacteria to effect biodegradation of the waste may be killed and so little or no treatment occurs in the wastewater. Additionally, nitrates and phosphate present in any wastewater or sludge are not well reduced by any biological method; these substances are known to cause the problem of eutrophication in water bodies (Ademoroti 1996a). Nitrate has been found to increase in trickling filtration and surface aerated activated sludge treatment in tropical countries (Ademoroti 1983). Nitrate has also been found to increase in wastewater sludge treated by aerobic digestion due to nitrification (Asia 2000). Nitrate in water is known to cause the disease called methemoglobinemia in infants. Furthermore, reduction of metals is limited and toxicants are not reduced. All these are the demerits of biological methods of treatment.

Chemical method of treatment is to some extent applied to the treatment of sludge but it has many shortfalls as well. The quantity of sludge resulting after treatment is always sizeable especially when lime is used, and only a small quantity of ammonia is removed. In some studies conducted in Nigeria, only 5 - 8% ammonia was removed when alum and iron (III) chloride salts were used in wastewater treatment (Ademoroti 1982). This reduction is insignificant when 2-3 mg/l ammonia is known to have lethal effect on fish.

In this work, wastewater sludge from the brewery industry was characterized and treated by the integration of the biological and the chemical methods (aerobic/chemical and anaerobic/chemical methods). This was to ensure proper and effective treatment. This was considered adequate to produce a superior effluent and sludge to those of either method in isolation so that what is lacking in the biological methods is obtainable in the chemical method and vice versa.

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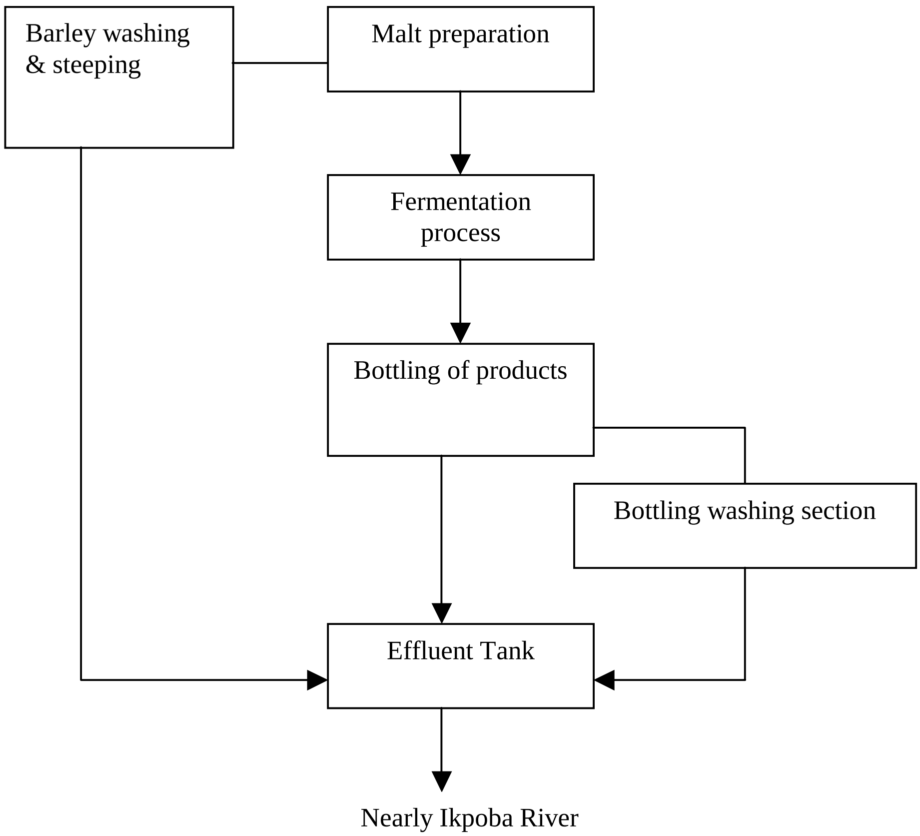

Fig 1. Wastewater flowchart of a brewery in Benin city, Nigeria.

Materials and Methods

Industrial sludges used. The wastewater containing the sludge was obtained from a brewery factory located at Benin City. The factory is a large one and produces about 7.4 x 10^4 litres of bottled product daily. The main products of the factory are crystal classic beer and crystal malt. The amount of wastewater generated daily was about 1.9 x 10^3 litres.

The various sources of the wastewater in the factory were from malt preparation fermentation processes and bottling of beer products. The waste sludge arising from malt-house was formed during barley washing and steeping. During steeping process, water soluble substances such as polysaccharides (capable of undergoing ready hydrolysis), saccharose, glucose, pectin, mineral salt and albuminous compounds (fibrin and legumin) from the husks diffused into the water. The color produced was yellowish - brown and the wastewater displayed a tendency toward putrefaction. All the effluent from the brewing plant, fermentation and storage cellars, bottling and bottle-washing plants and equipment washing process were passed into an effluent tank from where it was channeled through a pipe into a nearby river. Wastewater flow chart of the brewery is as shown in Fig 1.

Sampling of sludges. Composite samples of the sludges were obtained from the primary sedimentation tanks of the factory. Seven plastic bowls of 1 litre capacity were used to take samples manually over 12 h while sampling period at 2 h intervals started at 07. 00 and ended at 19.00. This time (period) was found to be the peak (optimum) period for work and sampling was most convenient during this period.

Composite samples were collected once a week for seven weeks and analyzed. Where analysis could not be carried out immediately, samples were preserved in a refrigerator maintained at 4°C. At this temperature, biodegradation is inhibited. Each week the day for sample collection was different from that of the preceding week. This was done so that the total exercise might account for the cyclic and intermittent variations occurring at the work site.

Sample preparation. Sludge was sampled as described under sampling. Four litres of the sludge was put into a plastic container as illustrated in Fig 2.

The sludge was allowed to sediment for one hour in order to separate the liquor from the settled sludge. The sludge liquor was used for analysis for the following parameters: pH, temperature, conductivity, specific gravity, turbidity, DO, BOD_5,

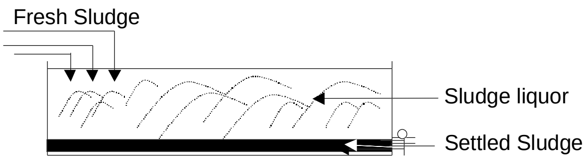

Fig 2. Schematic diagram of sludge sedimentation.

COD, total alkalinity, hydrogen carbonate alkalinity, ammonia nitrogen, nitrate nitrogen, organic nitrogen, chloride, sulphate, alkyl benzene sulphonate (ABS) and total bacteria count.

Settled sludge samples were used for settleable solids, percentage moisture, volatile solids, total solids, ash, total nitrogen, phosphorus, potassium, oil and grease, iron, calcium, magnesium, manganese, copper, cadmium, chromium, lead and zinc.

Methods of analysis. All samples were analyzed as described in the Standard Methods for the Examination of Water and Wastewater (APHA 1985) and Standard Methods for water and effluents analysis (Ademoroti 1996b). Where analysis was not immediately possible, they were preserved to inhibit biodegradation as described in Ademoroti (1996b).

All the reagents used for the analysis were of analytical grade and obtained from BDH Chemicals Limited, Poole, England.

Integrated biological/chemical treatment procedure. The sludge samples were treated first using the biological systems (aerobic and anaerobic) as described below but without dewatering and disinfection, the resultant sludges were then treated by the chemical method.

The flow charts for the integrated biological/chemical treatment are shown in Fig 3a and 3b.

Aerobic treatment procedure. Two litres of sludge were placed in a 4 litre plastic container which serves as the digester (Fig 3c).

Natural air in an open environment serves as the aeration system. 5 ml of phosphate solution was added as buffer, 1 ml each of magnesium sulphate, calcium chloride, and iron (III) chloride solutions were added as nutrient for bacterial population in the sludge. 1 ml of 50% hydrogen peroxide was also added to keep dissolved sulphide below 0.6 mg/l and eliminate odor. The plastic container was covered with loose plastic cap to allow air to enter. The sludge was stirred at an interval of 6 h and was allowed to digest for 45 days (Asia 2000), after which the digestion was deemed to have been completed as pH had stabilised. The sludges were then analysed to determine compositional changes and treated with calcium oxochloride until residual chlorine was between 0.2 and 0.7 mg/l (Henry and Heinke 1989). This was to ensure maximum level of bacteria kill before dewatering. Dewatering was sand bed by filtration using Teflon as the filter medium. The wet sludge was pasteurized for 30 min at 100°C and then sun dried for three days.

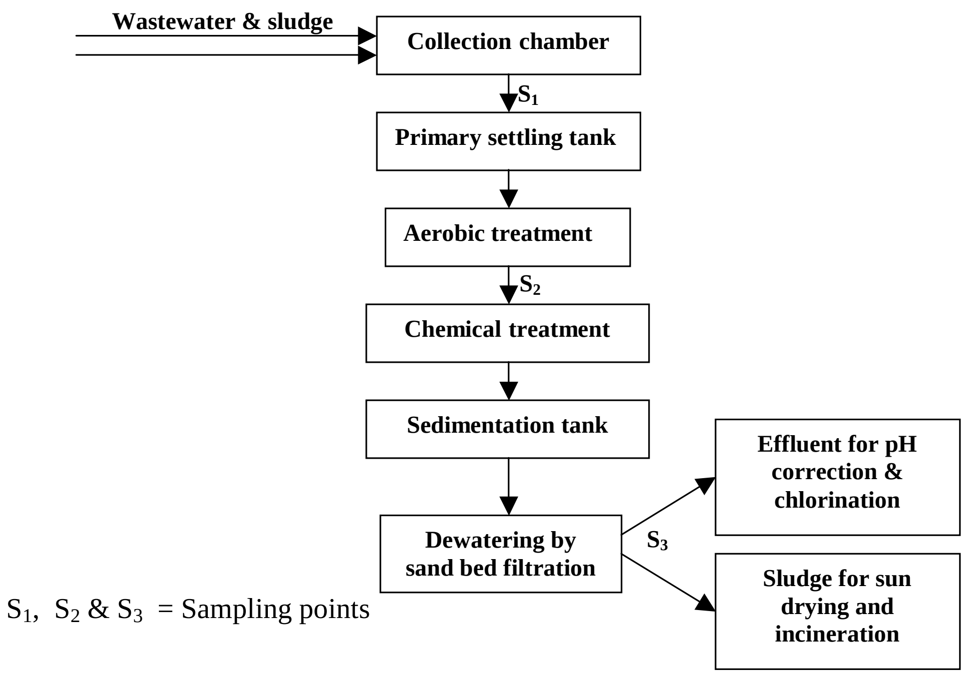

Fig 3a. Flowchart for integrated aerobic and chemical treatment of Brewery sludge.

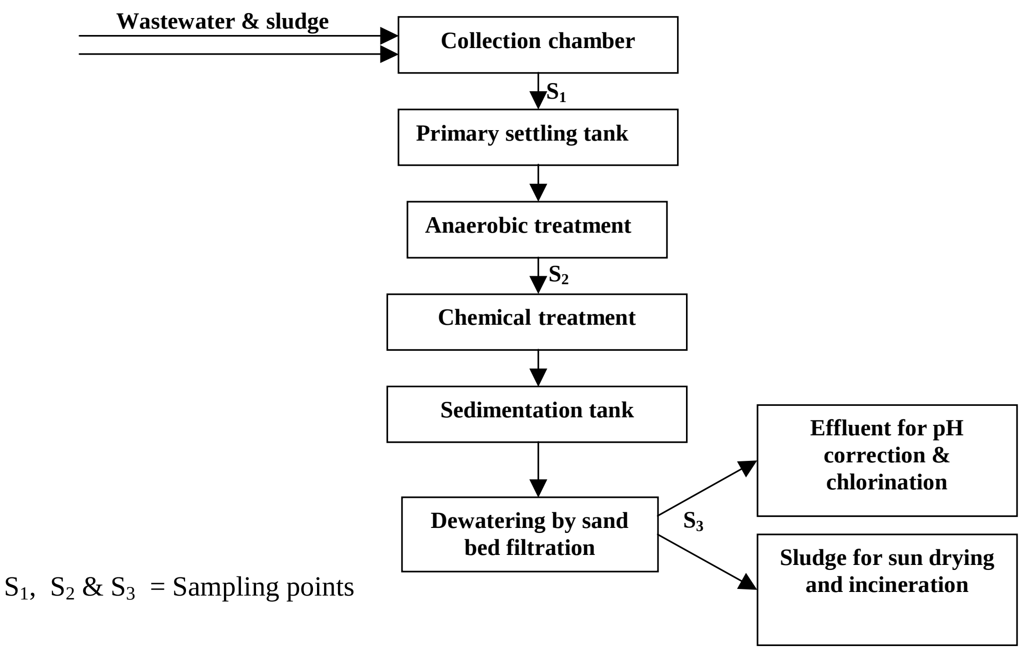

Fig 3b. Flowchart for integrated anaerobic and chemical treatment of Brewery sludge.

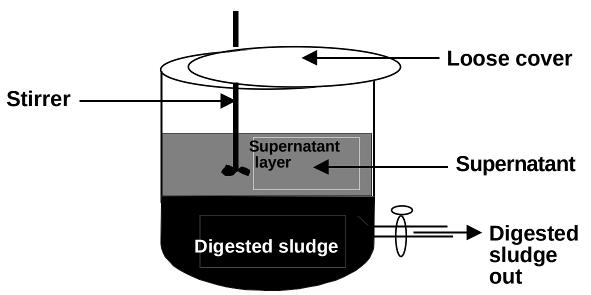

Fig 3c. Laboratory apparatus for conducting aerobic digestion studies.

Anaerobic treatment procedure. Two litres of sludge was placed in a closed digester as shown in Fig 3d.

The digester was incubated at mesophilic temperature (35±2°C) and supplemented with 5 ml of phosphate solution as buffer, 1 ml each of magnesium sulphate, calcium chloride and iron (III) chloride solutions as nutrients for the bacterial population in the sludge. Sodium hydrogen carbonate was added at concentration of 9g/1 to maintain the digestion at the optimum pH of 6.0 - 8.0 for anaerobic system (Dinsdale *et al* 1996). Also alkalinity in the sludge was maintained at 2 - 5 g/1 by the addition of sodium hydrogen - carbonate (Hawkes *et al* 1994). Sodium hydrogen - carbonate directly added hydrogen - carbonate alkalinity; it does not react with carbon (IV) oxide produced during digestion. The addition of sodium hydrogen - carbonate was to prevent pH increasing beyond 8.3 (Andrew 1975) and to increase digester efficiency (Barber 1978).

A control digester was set up containing 2 litres of de-ionized water instead of sludge but with all nutrients added. The mesophilic temperature (35±2°C) was maintained and at a detention time of 25 days (Long 1990). After 25 days digestion was deemed to have been completed, and samples of well mixed digester contents were obtained for analysis.

The sludge was dewatered using a sand bed and disinfected by adding calcium oxodichloride ($CaOCl_2$) until residual chlorine was found to be between 0.2 and 0.7 mg/1 (Henry and Heinke 1989). The wet sludge was pasteurized for 30 min at 100°C, then sun dried for 3 days using a sludge drying bed and incinerated.

Coagulation studies. 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.

(a) Coagulation/flocculation with alum and iron (III) chloride. Two sets of sludge samples were coagulated each with 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5 g/l commercial alum, $Al_2(S0_4)_3.14H_2O$ an iron (III) chloride, $FeCl_3$ in a mixer as shown in Fig 3e.

Sand-bed filtration was carried out using Teflon to trap the sludge solids. The sludge liquor was analysed for COD and percentage COD reductions were calculated. The highest point on a plot of % COD reductions versus coagulant doses gave the optimum coagulants doses for alum and iron (III) chloride, respectively.

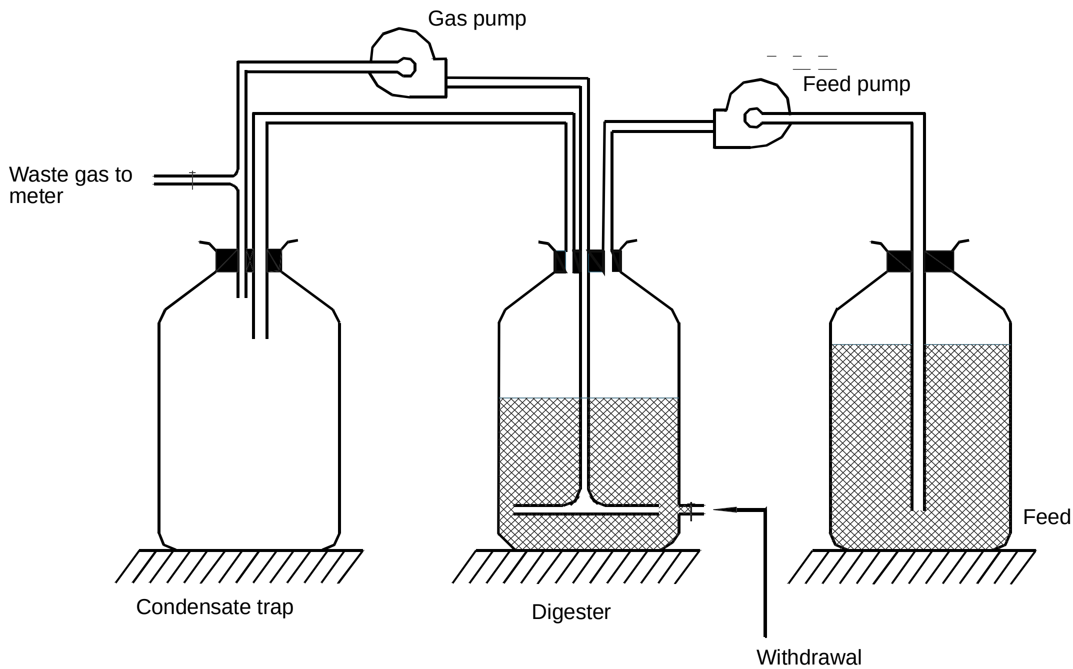

Fig 3d. Laboratory bench scale anaerobic digestion studies.

(b) Coagulation/flocculation with lime. $Ca(OH)_2$. A set of sludge samples were coagulated with 7.5, 9.5, 11.5, 13.5, 15.5, 17.5, 19.5, 21.5, 23.5 and 25.5 g/l lime in a mixer (Fig 3a) and filtered by means of sand bed and Teflon. The sludge liquor was analysed for COD. The highest points on a plot of % COD reductions versus dosages in g/l were taken as the optimum doses for lime.

(c) Coagulation/flocculation with polyacrylamide (a polyelectrolyte). A set of sludge samples were flocculated with 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 mg/l polyacrylamide partially hydrolysed with soda. They were filtered through a sand bed and Teflon cloth to trap the floc and analysed for COD. Optimum doses for polyacrylamide were determined from the plot of %COD reductions versus doses in mg/l in similar manner as in (a) and (b) above.

Chemical treatment procedure. Four sets of sludge samples were treated each with the optimum doses of alum, iron (III)

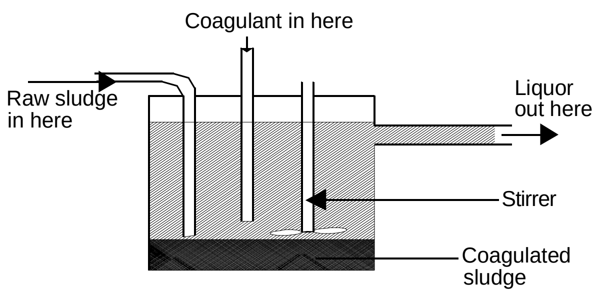

Fig 3e. Mixer for coagulation and flocculation.

chloride, lime and polyacrylamide. A Teflon cloth placed on a sand bed was used as the filter medium. The sludges were analysed for any chemical changes after treatment and disinfected with chlorine.

Optimum doses for the coagulants/flocculant were determined from the plot of percentage COD reductions against coagulants doses (Fig 4a-d).

For alum treatment of brewery sludge, optimum dosage was 4 g/l at a pH of 4.8. While iron (III) chloride, lime and polyelectrolyte gave optimum dosages of 3.5 g/l at a pH of 4.6, 15.5 g/l at a pH of 11.4 and 400 mg/l at a pH of 4.6 respectively (Asia 2002a; 2003).

Results and Discussion

The pH values for fresh brewery sludge range between 5.2 and 9.5 with the mean values at 7.5 showing it to be weakly alkaline. The specific gravity of 1.03 shows that it is slightly denser than water. Its mean moisture content was 95%. This indicated that the solids in fresh brewery sludge amounted to 5%. The total, settleable and the volatile solids were 8.4 g/kg, 2.15 g/kg and 6.45 g/kg, respectively Tables 1 and 2.

The BOD and COD values of the fresh sludge liquor were very high. The bacteria counts were also very high. These indicated strong pollution potentials and therefore called for treatment before reuse or disposal.

Fig 5a depicts the results of the amount of solids for inte-

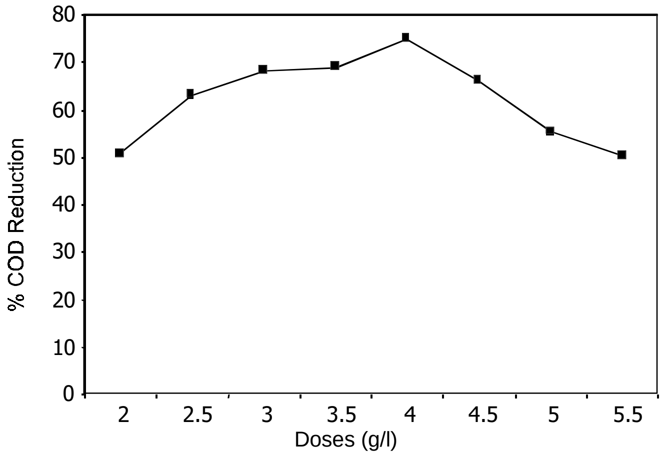

Fig 4a. Alum treatment of brewery sludge.

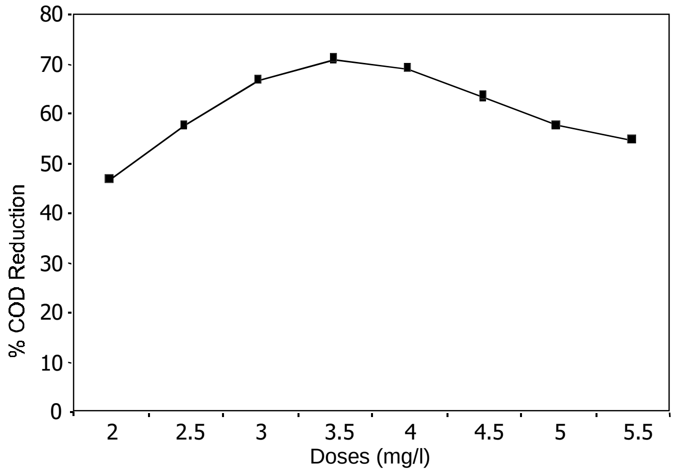

Fig 4b. Iron (III) chloride treatment of brewery sludge.

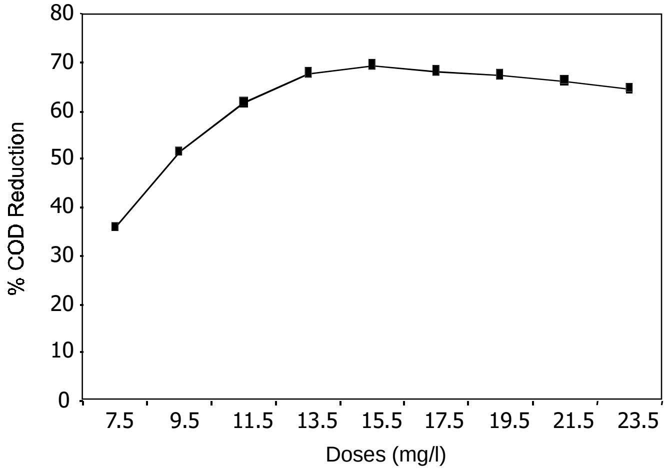

Fig 4c. Lime treatment of brewery sludge.

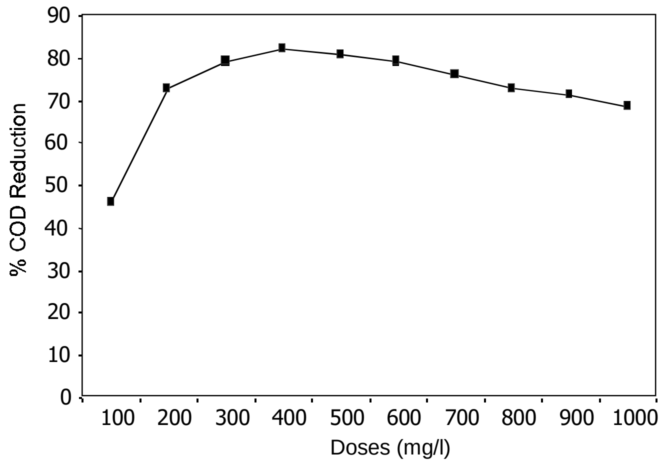

Fig 4d. Polyelectrolyte treatment of brewery sludge.

Fig 4a-d. Results of the optimum coagulants/flocculant dose determination.

grated biological and chemically treated brewery sludge. From the results, it was found that the combined aerobic/chemically treated brewery sludge had solids reductions in the range of 21.4 - 27% total solids, 27 - 32% suspended solids and 32 - 48% volatile solids. The anaerobic/chemical method gave a solid reduction better or comparable to the combined aerobic/chemical method. Solids reduction for the combined anaerobic/chemical method ranges from 24.3 - 27.2% total solids, 30.3 - 33% SS and 34.4 - 36% VS. Lime treated biological sludge achieved the least percentage solids reduction. Percentage solids reduction achieved for combined aerobic/chemical treatment of sludge was not as high as either the aerobic or the anaerobic method alone, and so, if reduction in sludge quantity is intended, either of the biological methods is more promising than the combined aerobic/chemical method.

Oxygen demand. The results of the oxygen-demand concentrations of raw and treated sludge are depicted in Fig 5b. From the results, it was found that the combined biological and chemical treatment methods proved more efficient than either of the biological methods.

BOD and COD reductions were in the range of 97-98 and 97.3 - 98.2%, respectively for aerobic/chemical treatment and 97.7 - 97.9 and 98 - 98.3%, respectively for anaerobic/chemical treatment.

Nitrogen concentrations. Nitrogen concentrations in the combined aerobic/chemical treated sludge depicted in Fig 5c show that there were considerable reductions in the nitrogen content of treated sludge. The highest reductions were noticed in lime treated aerobic 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 is converted to nitrate, while more ammonia was further reduced by the chemical treatment processes. Total nitrogen was also found to reduce for all

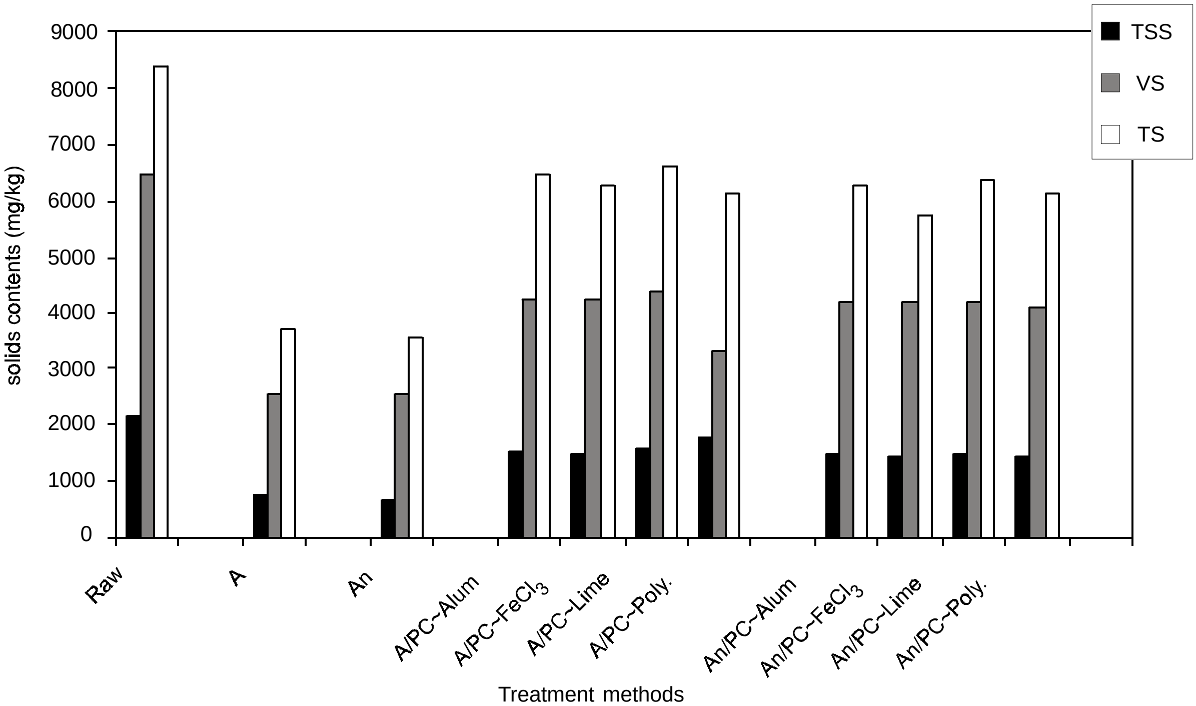

Fig 5a. Results of the solids content of brewery sludge.

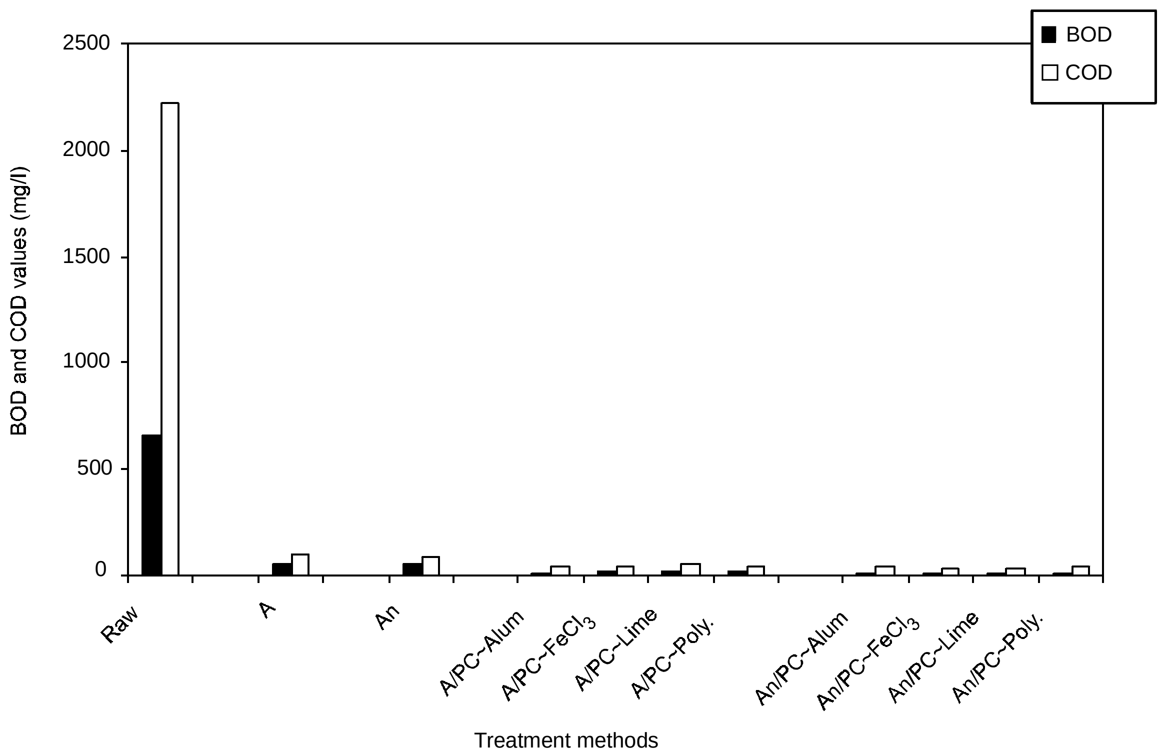

Fig 5b. Results of the BOD and COD of brewery sludge.

sludge treated by the combined aerobic/chemical method. Reductions were in the range of 59.1- 84.5%. The highest reductions were also found with the lime treated aerobic sludges. This study revealed that lime is a better coagulant if nitrogen removal is the focus of treatment from aerobically digested sludge.

The results of the combined anaerobic/chemically treated sludge revealed that ammonia nitrogen concentrations in-

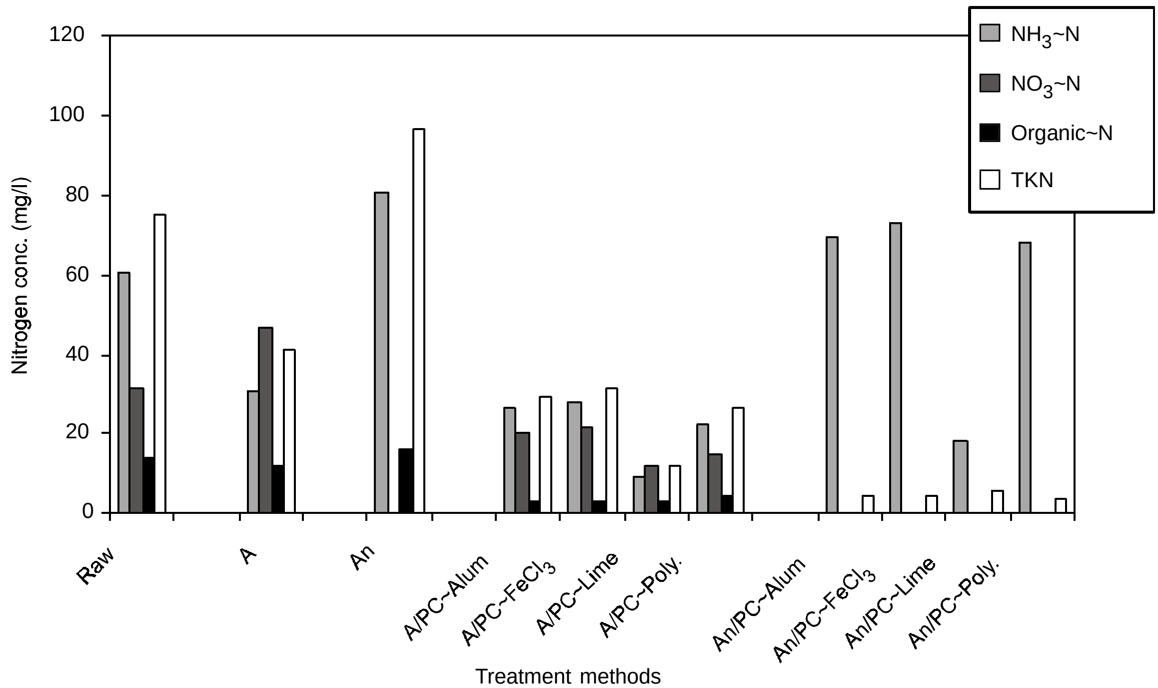

Fig 5c. Results of Nitrogens concentration in brewery sludge.

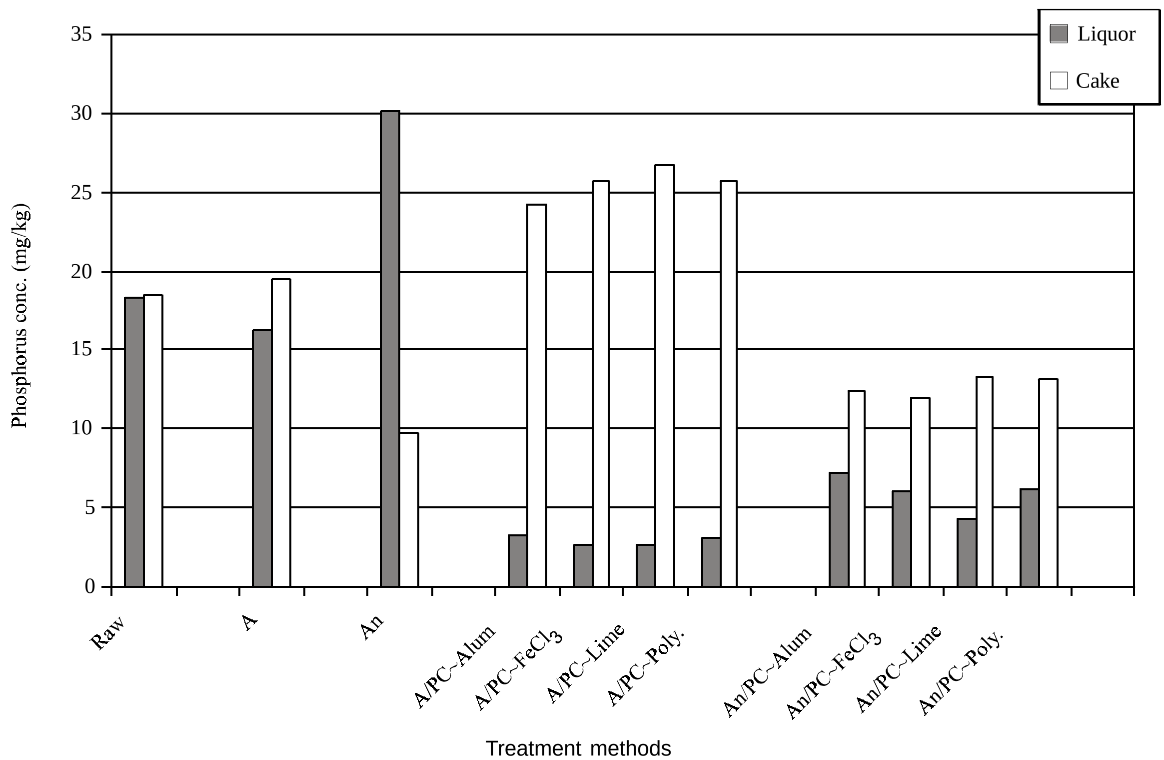

Fig 5d. Results of Phosphorus concentration in brewery sludge.

creases considerably with other coagulants and reduces for lime treated anaerobic sludge. Nitrate nitrogen was found to reduce to zero for almost all sludges treated by this method. Organic nitrogen was also found to reduce in concentration, due to its conversion to ammonia in the anaerobic digester. This is probably why ammonia nitrogen was found to increase for combined anaerobic/chemical method. Except for lime treated anaerobic sludge, the total nitrogen obtained by this

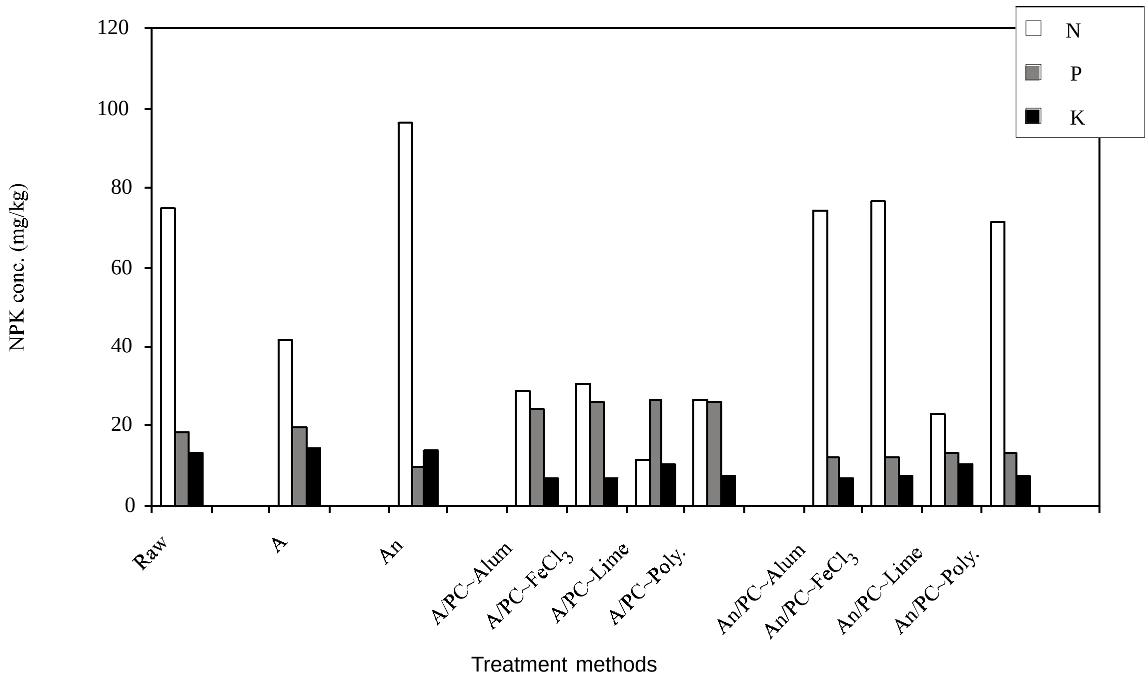

Fig 5e. Results of NPK concentration in brewery sludge.

A	=	Aerobic treatment only
An	=	Anaerobic treatment only
A/PC-Alum	=	Integrated method using aerobic and alum treatment
A/PC/$FeCl_3$	=	Integrated method using aerobic and iron (III) chloride treatment
A/PC-Lime	=	Integrated method using aerobic and lime treatment
A/PC-Poly	=	Integrated method using aerobic and polyelectrolyte treatment
An/PC-Alum	=	Integrated method using anaerobic and alum treatment
An/PC/$FeCl_3$	=	Integrated method using anaerobic and iron (III) chloride treatment
An/PC-Lime	=	Integrated method using anaerobic and lime treatment
An/PC-Poly	=	Integrated method using anaerobic and polyelectrolyte treatment
TSS	=	Total suspended solid
VS	=	Volatile solid
TS	=	Total solid
NH_3~N	=	Ammonia nitrogen
NO_3~N	=	Nitrate nitrogen
Organin~N	=	Organic nitrogen
TKN	=	Total Kjeldahl nitrogen

method was either a little higher or lower than that in the raw sludge depending on the concentration of ammonia nitrogen reached after anaerobic digestion. This study revealed that the combined anaerobic/chemical method offers the best option for nitrate removal from sludges.

Phosphorus. The results of phosphorus concentrations are shown in Fig 5d. The results revealed that the combined anaerobic/chemical method can be used to reduce phosphorous both in the sludge cake and in the liquor, and so this method offers a good alternative if complete disposal of sludge is intended. This is so because the basic nutrients in sludge, nitrates and phosphates are best removed by the combined anaerobic/chemical method.

NPK values. It has been reported that anaerobic treatment alone raises the fertilizer value of brewery sludge (Asia and Ademoroti 2002b). The results in this study however show that brewery sludge treated by the combined anaerobic/chemical method has a reduced fertilizer value as measured by the percentage of NPK concentrations (Fig 5e). Therefore, if improvement in fertilizer value of sludge is one of the objectives of treatment, this method may not be used, as a better method such as the anaerobic biological system can ensure such improvement.

For all sludge treated by the various methods, biological and the combined biological/chemical, alkylbenzene sulphonate in the effluents was adsorbed by powder activated carbon (PAC). PAC is also known to adsorb phenol and phenolic compounds, organic toxicants and odors, hence, the processed liquid would not contain these substances in significant amounts (Ademoroti 1988). Thus, the quality of the effluent left was detergent free and comparable to World Health Organisation standard (WHO 1971) for potable water. This means that, the final effluent obtained could be recycled or discharged into the environment without fear of pollution.

Table 1
Characteristics of fresh sludge liquor from the brewery

Sludge liquor characteristic	Unit	Range of value	Mean
pH	-	5.20 - 9.50	7.50
Temperature	˚C	28.00 - 32.10	29.50
Conductive	Scm^{-1}	140.00 - 152.00	144.00
Specific gravity	-	1.01 - 1.04	1.03
Turbidity	NTU	1000.00-1050.00	1025.00
DO	mg/l	1.80 - 2.80	2.40
BOD_5	mg/l	390.00 - 850.00	660.00
COD	mg/l	1450.00-2930.00	2220.00
Total alkalinity	mg/l	520.00 - 690.50	640.00
Hyd. carbonate alkalinity	mg/l	43.20 - 57.80	52.00
Ammonia nitrogen	mg/l	37.10 - 94.10	61.00
Nitrate nitrogen	mg/l	21.60 - 41.50	31.20
Organic nitrogen	mg/l	16.00 - 53.10	34.55
Chloride	mg/l	3.10 - 5.20	4.10
Sulphate	mg/l	1.00 - 3.40	2.70
ABS	mg/l	18.20 - 30.10	25.00
Total bacteria count	/100ml	3.50 - $4.70x10^8$	$4.10x10^8$

Table 2
Characteristics of fresh settled sludge from the brewery

Settled sludge characteristics	Unit	Range of values	Mean
Settleable solids	mg/kg	1982.00-2410.00	2145.00
Moisture	%	93.00 - 97.00	95.00
Volatile solids	mg/kg	5824.00-6900.00	6450.00
Total solids	mg/kg	7800.00-8600.00	8400.00
Ash	%	19.80 - 25.30	23.20
Total nitrogen	mg/kg	57.00 - 101.20	75.00
Phosphorus	mg/kg	16.20 - 22.10	18.40
Potassium	mg/kg	10.00 - 17.50	13.50
Oil and grease	mg/kg	3.70 - 8.40	5.20
Iron	mg/kg	0.15 - 0.22	0.19
Calcium	mg/kg	25.00 - 34.00	28.00
Magnesium	mg/kg	20.20 - 27.00	26.00
Manganese	mg/kg	0.01 - 0.02	0.01
Copper	mg/kg	0.10 - 0.15	0.12
Cadmium	mg/kg	Nil	Nil
Chromium	mg/kg	Nil	Nil
Lead	mg/kg	0.10 - 0.15	0.12
Zinc	mg/kg	2.00 - 6.00	4.20

Conclusion

The present study revealed that integrated biological/chemical methods are efficient methods in the treatment of brewery sludge. While the aerobic biological system converts almost all ammonia present in the sludge to nitrates, the chemical method removes the nitrates from the solution by denitrification. Also, the anaerobic/chemical method converts the entire nitrate to molecular nitrogen by nitrification and ensures substantial reduction of phosphorus thus preventing eutrophication of the discharge water body.

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