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Column Treatment of Brewery Wastewater Using Clay Fortified with Stone-Pebbles

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Abstract. The study aimed at providing a low-cost treatment for brewery wastewater, which was achieved by mixing clay with stone-pebbles to improve the low permeability of water through clay beds. The combination (clay/stone-pebbles) was used in columns for the treatment of brewery wastewater . The crystal chemistry of the clay samples was studied using X-ray diffractometer. Three principal clay minerals (kaolin, illite and smectite) were detected in the samples. Atomic absorption spectrophotometer was used to study the geochemistry of the clay samples. The results of the geochemical studies showed that all the samples were hydrated aluminosilicates. Performance efficiency studies were conducted to determine the best combination ratio of clay to stone-pebbles, which showed that combination ratio 3:1 (clay/stone-pebbles, w/w) performed better. The flow-rate studies showed that brewery wastewater had longer residence time in non-fortified clay than in fortified clay. The flow-rate of the wastewater in the percolating media varied from one medium to another. Two modes of treatment (batch and continuous) were used. The effluent passed through the continuous treatment mode had better quality characteristics as compared with the effluent passed through the batch treatment mode. The effect of repeated use of the fortified column on the performance efficiency was also studied. The pH, total solids, and the chemical oxygen demand (COD) of the effluent was monitored over time. The results of the COD monitored over time were analysed using breakthrough curves. The different columns were found to have different bed volumes at both the break-through and exhaustion points.

Keywords: fortified clay column, batch treatment, continuous treatment, brewery wastewater, breakthrough curve, exhaustion point, bed volume

Introduction

The wastewater from brewery differs from most of the other industrial wastewaters because large fractions of the pollutant therein are biodegradable and relatively less toxic. A typical brewery wastewater flows intermittently. It has a high biochemical oxygen demand (BOD), total solids (TS) and chemical oxygen demand (COD). Although it contains less toxic substances, the high BOD, TS and COD render its discharge into natural water bodies, without treatment, undesirable. It increases the organic load of the water body, thereby causing oxygen sag, thus creating a hostile environment for the aquatic life and an imbalance in the ecosystem.

In order to overcome these problems, breweries have used conventional treatment methods, specifically biological, to improve the quality characteristics of their wastewater for safe disposal and reuse. Examples of biological treatment methods used in breweries are activated sludge, fixed-film system, and aerobic and facultative ponds. Beside the various limitations, which are peculiar to the different biological methods of wastewater treatment, the operational characteristics of conventional methods of treatment have been found to be unattainable in the developing countries.

Several studies have been carried out on the application of non-conventional, low-cost sorbents for the removal of pollutants in batch and column treatments (Saeed *et al*., 2005a; 2005b; Waranusantigul *et al*., 2003; Saeed *et al* ., 2002; Nigam *et al*., 2000; Low *et al*., 1995; Namasivayam and Yamuna, 1995; McKay *et al*., 1984).

The use of clays in water industries has been principally in the area of water clarification and impedance (McLenz and King, 1955; Nordell, 1951). Recently, the use of clays and other natural microporous materials (e.g., zeolite and sepiolite) for the treatment of water and wastewaters have been reported by several workers (Brigatti *et al*., 1996a; 1996b; Mondale *et al*., 1995; Passaglia and Miselli, 1994). The performance of these materials, in this regard, has been attributed to the ability to adsorb and exchange many cations and hence restrict their mobility and bioavailability. The use of different clay minerals as sorbents for the removal of pollutants in batch adsorption have been reported by many workers (Wu *et al*., 1999; Laird and Flemming, 1999; Viraraghavan and Kapoor, 1994; Sharma

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*Author for correspondence; E-mail: bioladoja@yahoo.com *et al.*, 1990; Cadena *et al.*, 1990). These reports showed that clays can compete with known commercial sorbents, such as activated carbon, but its low permeability to water has continued to restrict its application as percolator in fixed-bed columns. Bailey *et al.* (1999) suggested the use of artificial support for use in columns containing clays to improve on the low permeability to water.

The present study aimed at investigating the use of clay fortified with stone-pebbles to function as percolator in a column for the treatment of brewery wastewater.

Materials and Methods

The fortified clay stone-pebbles percolator. Clay samples were collected from five different clay deposits in Nigeria, namely, Auchi, Bauchi, Benin-City, Ozanagogo and Ubuluuku, respectively, coded as AU, BA, BC, OZ and UB. In order to fortify the clay against low permeability to water, erosion smoothened stone-pebbles that had withstood environmental weathering were collected from a northern area of Edo State, southwestern Nigeria. The collected stone-pebbles (average dia of 2.0 cm) were washed under running tap water to remove attached dirt and then rinsed with distilled water.

Wastewater sample and sampling technique. The wastewater was collected from a brewery located in Benin-City, Edo State, Nigeria. The factory produces beer and malt drink as their main products. The various sources of the wastewater in the factory were from malt preparation, fermentation processes, and bottling of beer products. The wastewater had a yellowish brown colour and displayed a tendency towards putrefaction. Wastewater samples were collected in plastic containers at hourly intervals for 12 h, starting at 7.00 am and ending at 7.00 pm. The flow rate of each sample was measured with a flow meter. At the end of the sampling period, a single composite sample was made by mixing together the 12 separate hourly-collected samples, using volume of each proportional to their respective flow rates. The pH determinations were done and the dissolved oxygen was fixed as recommended by the standard methods (Ademoroti, 1996a; 1996b; APHA, 1985).

Analytical procedures. The crystal chemistry of the clay samples was studied using X-ray diffractometer (DIANO 2100*E) with a copper anticathode (ë= 1.54 Å). Computer software XSPEX version 5.41 was used for the interpretation of the diffractograms obtained. The geochemistry of the samples was studied by digestion in a polypropylene bottles using a mixture of analytical grade conc. HF, HCl and H_2ClO_4. The elemental analysis of the digested solution was carried out using atomic absorption spectrophotometer (AAS). All the wastewater samples were analysed for turbidity, total solids (TS), dissolved solids (DS), suspended solids (SS), dissolved oxygen (DO), chemical oxygen demand (COD), biochemical oxygen demand (BOD), total kjeldahl nitrogen (TKN), ammonium nitrogen (NH^+_4-N), nitrate-nitrogen (NO_3-N), and total bacterial count in accordance with APHA (1985) and standard methods for water and effluent analysis (Ademoroti, 1996b).

Performance efficiency determination. Attempt was made to determine the best combination ratio of clay to stone-pebbles to produce optimum water purification. Different combination ratios (w/w) based on a constant weight of one kilogram (1Kg) to the clay/stone-pebbles mixtures were made. The different ratios were mixed together and carefully packed into plastic columns of length 30 cm and 7.5 cm dia. For quick analysis, COD was selected to assess the degree of purification since low COD values are indices of purification (Ademoroti, 1980).The percentage COD reduction was calculated for each clay and stone-pebbles combination ratios and the one that gave the best COD reduction was selected for further detailed studies.

Flow rate studies. The residence time of the wastewater in each percolating medium was determined. Through each of both the fortified clay, coloumn (1:3, stone-pebbles/soil-clay) and non-fortified soil-clay column, 500 ml distilled water was passed. The time taken to collect 100 ml from each medium was noted. The mean value of triplicate determinations was taken as the flow time (t). The flow rate (Q), expressed as the volume of liquid (V, ml) passing through per unit time (t, sec), was determined using the following formula:

$$Q = V/t$$

Wastewater treatment procedure. Each clay type (AU, BA, BC, OZ, UB) was mixed with stone-pebbles in the ratio 3:1 in accordance with the preliminary performance efficiency determinations. The packed column was flushed several times with distilled water until clear effluent was obtained, which was then used for the wastewater treatment. In order to assess the efficiency of the columns, two modes of treatment, viz., batch and continuous treatment, were used for the treatment of brewery wastewater.

Batch treatment (BTM) determinations. A single fortified clay column was prepared and loaded with a litre of the brewery wastewater. The wastewater was allowed to pass through the column by gravity flow. The treated effluent was collected and analysed for various water characteristics as mentioned in analytical procedures.

Continuous treatment (CTM) determinations. Two percolating media columns were prepared and connected in series to act as multiple columns. The treatment of the wastewater was carried out by allowing its continuous flow from one column to the other. The treated wastewater was collected at the end of the second column. The effluent collected was analysed for water characteristics as was done for BTM. Wastewater was passed continuously through the CTM percolating medium. A known volume of the treated effluent was collected at regular intervals and each collected sample was analysed for COD, pH and TS.

Results and Discussion

Clay characterization. The results of the crystal chemistry as studied with X-ray diffractometer is shown in Table 1. The results of the geochemical studies are presented in Table 2. The prominence of silica (SiO_2), alumina (Al_2O_3) and structural water (H_3O^+) in all the clay samples studied showed that they were all hydrated aluminosilicates.

Performance efficiency studies. The results of the combination ratios that gave noteworthy results are presented in Table 3. It was observed from the computation of the percentage reductions of the obtained COD values that the clay/stone-pebbles ratio (3:1) gave the highest COD reductions (78. 15 % - 95.98%) for all the clay samples studied. The combination ratio of 1:3 gave the least percentage COD reductions (69.41% - 83.92%). This revealed that the higher the ratio of clay to stone-pebbles in the combination ratios studied, the higher the treatment efficiency of the system.

Flow rate for the passage of brewery wastewater. The flow rates of columns containing the fortified clay combination ratio (3:1; clay : stone-pebbles) were compared with those containing only clays as non-fortified columns. The results obtained for the flow of 100 ml are presented in Table 4. The rate of flow of wastewater was in the order of UB > AU > OZ > BA > BC. The UB clay had the highest flow rate and consequently the least residence time, while BC had the least flow rate and the longest residence time. In the soil-clay columns that were not fortified with stone-pebbles, the flow rate was generally lower than that obtained with fortified soil-clay columns. An overview of the flow rate studies showed that the residence time of wastewater in the percolation media had a direct relationship with the mineralogical assemblage of the clays in the different columns.

Wastewater treatment studies. The quality characteristics of both the treated and untreated brewery wastewater using the two treatment methods (BTM and CTM) are shown in Tables 5 and 6. The quality characteristics of effluents from the different fortified columns were observed to be improved. The ability of the fortified clay to treat the wastewater varied from one clay type to another. Variation in the crystal chemistry of the different clay samples may have contributed to the differences observed. An appraisal of the results obtained from BTM showed that the raw brewery wastewater had a pH of 6.41, which increased (7.30-7.80) when it was passed through the different columns. The increase in pH may have resulted from the leaching of some exchangeable cations, such as Na, K, Ca, Mg into the effluent as a result of exchange of these metals with some cationic pollutants present in the wastewater. These cations leached into the wastewater and formed metal hydroxides.

More than 95% of the total solids (TS) present in the wastewater were removed when the brewery wastewater was passed through different columns. The highest value of TS reduction was observed in columns containing BA and BC clays, which was noted to be 97.32% and 97.37 %, respectively. However, clays AU and UB showed lower reductions, which were 95.78% and 95.67%, respectively. The ability of these clay columns to reduce the amount of TS in the effluent may be attributed to the large surface area and platy morphology of clay minerals. These characteristics render them to be closely packed and allow them to serve as the primary barrier to solids movement in the influent.

The reduction of the COD values of effluents from the different columns ranged between 88.83% and 93.51%. The highest COD reduction was obtained in effluents passed through BA (93.51%) and BC (93.40%), while the lowest was noted in effluents passed through UB (88.83%) and AU (89.20%). The COD reduction of effluent passed through OZ was 91.63%. BOD reductions of 93.16, 94.06, 92.56, 95.47, and 95.89 (%) were obtained for AU, OZ, UB, BC and BA, respectively. A comparison of some of the results obtained from this study with results obtained from similar studies using different

Table1. Mineralogical analysis of clay samples showing percentages of different clay minerals present

Clay mineral	Clay source*				
	BA	BC	AU	OZ	UB
Kaolinite	34.46	27.68	12.00	66.0	14.0
Montmorillomite (smectite)	nil	7.55	nil	nil	nil
Illite	10.62	16.43	0.50	6.50	nil
Mixed layer	11.72	8.48	nil	nil	nil
Quartz	43.20	39.86	86.50	24.0	85.0
Dolomite	nil	nil	nil	nil	nil
Hematite	nil	nil	nil	2.50	nil

* sources of clay samples collected from different places in Nigeria: BA=Bauchi; BC=Benin-City; AU= Auchi; OZ=Ozanangogo; UB=Ubuluuku

percolators showed that the performance of fortified clay columns for brewery wastewater treatment was high. For example, about 80% COD removal was recorded when Reed-beds were used in the treatment of industrial waste in Britain (Adcock *et al.,* 1999). A natural process for the treatment of wastewater in Japan known as Shimanto-gawa system has been reported by Matsumoto (1998) to have a 91.86% and 81. 20% removal of BOD and COD, respectively. Netpraditt *et al.* (2004) also reported 67-78% reduction of COD when they evaluated the use of metal hydroxide sludge for reactive dye adsorption in a column experiment. The high level of COD and BOD reductions by fortified clay columns could be attributed to the different forms (i.e., anionic and cationic) in which the pollutants contained in the wastewater may be present. These pollutants can be exchanged for the loosely held ions on the clay structure and adsorbed onto the clay structure to make up for the excess or deficit charge due to isomorphic substitution, which is more on smectite than any other clay mineral.

The total nitrogen (TKN) removed from the influent, by the different fortified soil clay columns, was greater than 75%, ranging between 75.38 % - 83.33% for the effluent passed through AU and BA clays, respectively. The ammonium nitrogen (NH_4^+-N) removal was above 90% in all cases. Nitrate-nitrogen (NO_3^- -N) showed the least reduction (about 50%) in the effluent passed through all the percolating media. This could have resulted from the anionic nature of the NO_3^- -N, which is expected to be repelled by the clay surface if the negative charge on clay surface is to be considered. Mortland (1970) offered an explanation on the occasional uptake of negatively charged compounds by clay surfaces, who was of the opinion that the hydroxyl groups (OH^-) on clays are attached to Si and Al and are liable to either dissociate as illustrated below:

$$\text{-Si, Al-OH} = (\text{Si, Al})^+ + OH^-$$

or accept a proton as follows:

$$\text{-Si, Al-OH} + H^+ = (\text{Si, Al}) - OH_2^+$$

giving rise to positively charged clays which take part in anion exchange reactions.

The total bacteria removed from all the effluents were above 90%. The ability of the fortified clays in this regard could be attributed to the fact that bacteria behave like charged particles and so could be adsorbed on the clay surface. It has been reported that due to the functionality of certain chemical materials comprising bacterial cell wall, bacteria exhibit surface charge similar to colloids (Ademoroti, 1996a).

Table 2. Mineralogical analysis of clay samples showing percentages of the different metal oxides

Metal oxides	Clay source**				
	OZ	UB	BC	BA	AU
SiO_2	54.44	73.10	50.11	56.08	72.29
Al_2O_3	25.21	13.62	17.00	23.01	7.80
Fe_2O_3	3.66	2.02	1.42	2.02	2.80
MgO	0.40	0.18	5.78	0.98	0.20
CaO	0.30	0.31	6.01	1.43	0.28
Na_2O	1.38	1.01	1.61	1.64	1.01
K_2O	1.78	0.41	1.84	3.31	0.94
TiO_2	0.08	0.03	0.21	0.41	0.31
P_2O_5	0.08	0.02	0.01	0.01	0.04
MnO	0.002	0.01	0.001	0.003	0.003
$^*H_2O^+$	12.20	8.30	15.01	13.14	13.14

* H_2O^+ = structural water; ** refer Table 1 for abbrevations corresponding to the clay sources

Table 3. Chemical oxygen demand (COD) values* obtained for raw and treated wastewater when passed through different clay: stone-pebble ratios

clay:stone-pebble ratio	Wastewater treated on passing through clays of different sources**				
	AU	BA	BC	OZ	UB
1:1	119.20	42.80	40.00	92.00	121.87
2:1	98.20	40.00	36,80	73.60	110.40
3:1	92.00	20.00	18.40	55.20	100.00
1:2	124.60	60.00	55.20	11.40	140.00
3:2	110.40	40.00	36.80	83.10	121.87
1:3	138.10	80.00	73.60	128.80	140.00
2:3	124.60	60.00	49.20	92.00	138.42

* COD of the raw wastewater was 457.60; **refer Table 1 for abbreviations corresponding to the clay sources

Table 4. Mean flow rates of brewery wastewater when passed through non-fortified and fortified clays by different sources (clay: stone-pebble ratio 1:3)

Clay*	Mean flow rate (cm^3/s)	
	Non –fortified clay	Fortified clay
BA	5.36×10^{-3}	8.03×10^{-3}
BC	5.14×10^{-3}	7.4×10^{-3}
AU	0.013	0.021
OZ	0.011	0.014
UB	0.017	0.026

* refer Table 1 for abbreviations corresponding to the clay sources

Table 5. Treatment of brewery wastewater using clay* fortified with stone-pebbles in the batch treatment mode

Parameters	Raw sample	Effect on different parameters on treatment using clay fortified with stone-pebbles				
		AU	OZ	UB	BA	BC
pH	6.41	7.40	7.30	7.30	7.80	7.60
Turbidity (NTU)	150.0	1.1	1.1	1.1	1.1	1.1
Total solids (mg/1)	280.0	10.600	11.830	12.120	7.500	6.800
Dissolved solids (mg/1)	92.5	9.930	11.010	11.100	6.780	5.030
Suspended solids (mg/1)	187.5	0.670	0.820	1.020	0.720	0.770
Dissolved oxygen (mg/1)	0.81	4.55	4.35	4.28	4.60	4.70
Chemical oxygen demand (mg/1)	728.8	61.00	78.70	81.40	48.10	42.30
Biochemical oxygen demand (mg/1)	360.0	21.40	24.61	26.80	16.30	14.80
Total kjeldhal nitrogen (mg/1)	18.6	4.30	4.58	4.80	3.16	3.10
Ammonium nitrogen (mg/1)	11.4	1.74	1.78	1.92	1.11	1.02
Nitrate nitrogen (mg/1)	3.2	1.22	1.71	1.81	1.42	1.48
Bacterial lead (count/100 ml)	3.8×10^7	3.0×10^6	3.4×10^6	3.8×10^6	2.3×10^6	1.5×10^6

* refer Table 1 for abbreviations corresponding to the clay sources

Table 6. Treatment of brewery wastewater using clay* fortified with stone-pebbles in continuous treatment mode

Parameter	Raw sample	Effect on different parameters on treatment using clay fortified with stone-pebbles				
		AU	OZ	UB	BA	BC
pH	6.41	7.50	7.50	7.40	8.10	8.10
Turbidity (NTU)	150.00	ND	ND	ND	ND	ND
Total solids (mg/l)	280.00	3.810	5.240	5.170	2.120	2.120
Dissolved solids (mg/l)	92.50	3.810	5.240	5.170	2.120	2.120
Suspended solids (mg/l)	187.30	ND	ND	ND	ND	ND
Dissolved oxygen (mg/l)	0.81	7.70	7.40	7.40	8.30	8.30
Chemical oxygen demand (mg/l)	728.80	16.80	19.41	21.42	11.10	10.30
Biochemical oxygen demand (mg/l)	360.00	9.41	11.40	13.10	6.92	6.70
Total kjeldhal nitrogen (mg/l)	18.60	0.21	0.51	0.84	0.13	0.12
Ammonium nitrogen (mg/l)	11.40	0.11	0.33	0.67	0.08	0.08
Nitrate nitrogen (mg/l)	3.20	0.62	0.86	0.87	0.72	0.78
Bacterial load (count/100 ml)	3.8×10^7	1.8×10^6	2.0×10^6	2.8×10^6	9.8×10^5	9.2×10^5

* refer Table 1 for abbreviations corresponding to the clay sources

An appraisal of the results obtained from the CTM showed that an improvement in the quality characteristics of water and wastewater could be achieved by passage through more than one percolating media connected in series. An overview of the results obtained from the use of CTM showed that over 90% reduction was achievable in all the parameters monitored. This was unattained in some of the parameters monitored using the BTM.

Effect of repeated use on performance efficiency. The results of the breakthrough curves used to analyse the observations on the COD determinations carried out on untreated and treated brewery wastewater samples collected at intervals is presented in Fig. 1. The COD was selected as a pollution indicator in this study because of the contributions of other pollution characteristics to COD values in wastewater.

In order to evaluate the performance of an active carbon column, breakthrough curve and bed volume (BV) are usually employed (Chen and Wang, 2000). The breakthrough point is chosen arbitrarily at some low value C_b (breakthrough concentration) for the effluent concentration (C_x), closely approaching C_o (initial concentration of sorbate), when the sorbent is

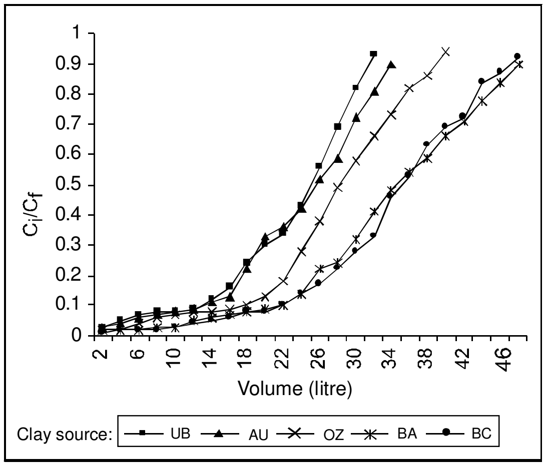

Fig. 1. Breakthrough curve analysis of COD of brewery wastewater; refer Table 1 for abbreviations corresponding to the clay sources; c_i/c_f = influent sorbate concentration/effluent sorbate concentration.

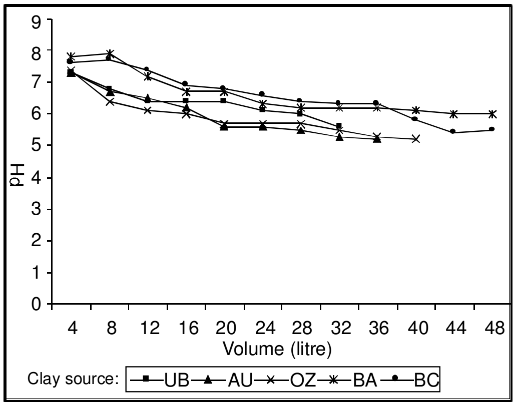

Fig. 2. The effect of repeated use of fortified clay columns on the effluent pH; refer Table 1 for abbrevations corresponding to the clay sources.

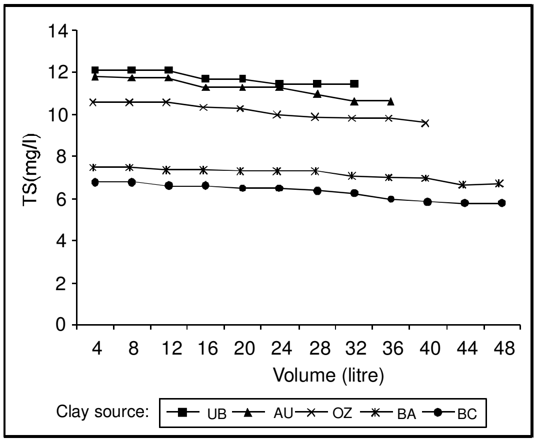

Fig. 3. The effect of repeated use of fortified clay columns on the effluent total solids (TS); refer Table 1 for abbreviations corresponding to the clay sources.

considered to be essentially exhausted (Gupta *et al.*, 2000). The desired breakthrough point (C_b) in the present study was determined at 10% of the influent COD, which was 0.1 C_i/C_f, where C_i is the influent sorbate concentration and C_f is the effluent sorbate concentration, while the exhaustion point was fixed at 90% (i.e., 0.9 C_i/C_f). The bed volume was determined as the volume of metal waste stream treated divided by the volume of sorbent used (Chen and Wang, 2004).

The bed volumes at breakthrough point for the respective fortified clay columns, UB, AU, OZ, BA and BC were: 8.17, 8.80, 11.32, 13.83 and 13.83. The difference in the bed volume at the breakthrough point may have resulted from the variation in the crystal chemistry of the different clays (Table 1). The bed volumes of fortified clay columns used, at exhaustion points, were: 20.11(UB), 21.37(AU), 24.51(OZ), 29.54 (BA), and 30.11(BC).

The pH of the brewery wastewater used in this study was 6.41, but when the pH of the effluent was monitored with time, the pH values of the effluents at the point of exhaustion ranged between 7.30 and 5.20. An increase in the value of the pH was noticed at the inception of the study, which was followed by a decrease in the value of pH with repeated use (Fig. 2). The possible cause of the initial increase was explained in the section on water treatment studies. The subsequent drop in the pH value was considered to have resulted from the production of aerobic and anaerobic digestion of biodegradable constituents of the wastewater. The products of aerobic digestion that way have caused the lowering of the pH of the effluents were CO_2 and H^+. In the case of anaerobic system, the fall in pH may have resulted from the volatile acids released into the effluents.

The total solids in each effluent were observed to reduce over time until it became stable (Fig.3). The stone-pebbles used to fortify the clay also served as an inert surface for microbial attachment and growth as obtained in trickling filter (a conventional biological method of sewage treatment). The attached microorganisms helped both in the aerobic and anaerobic digestion of the biodegradable fractions of the solids, which accounted for the reduction in the value of total solids over time.

Conclusion

The crystal chemistry of the different clay samples in this study revealed the presence of three major clay minerals (i.e. kaolinite, illite and smectite). Quartz was present as a non - clay mineral in all the clay samples. Hematite (an oxide) was present as an impurity in clay from Ozanagogo (OZ), while dolomite (a carbonate) was present as an impurity in clay from Bauchi (BC). The geochemical studies showed the prominence of SiO_2, Al_2O_3 and structural water (H_2O^+) in all the samples, which indicated that they were all hydrated aluminosilicates. The performance efficiency studies showed that the best combination ratio for optimum COD reduction was 3:1 ratio (clay : stone-pebbles, w/w). The flow rate studies showed that the different fortified clay columns had different flow rates for the passage of wastewater. The flow rates of the fortified columns were higher than the flow rates of non-fortified columns for each clay type. The two modes of treatment used showed that the effluent from the continuous treatment method (CTM) had better quality characteristics than those from the batch treatment method (BTM). The repeated use of the different fortified columns, using CTM, showed that the bed volume at both the breakthrough and the exhaustion points of fortified columns containing a higher percentage of kaolinite were lower than that of fortified columns containing other minerals. The pH of the effluent from the column was basic at the inception of the study, which later became acidic over time. The total solids (TS) values decreased over time.

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