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Electrochemical treatment of a Kenyan tea factory wastewater

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Chemomi tea factory discharges large quantities of wastewater with high levels of colour, chemical oxygen demand (COD) and biochemical oxygen demand (BOD). In this factory, constructed wetlands have been introduced for biological treatment of wastewater. However, the system has been ineffective in the removal of colour, COD, BOD and heavy metals to acceptable standards. Electrochemical method that utilizes two sacrificial steel electrodes was utilized in the treatment of tea effluent and the process conditions used were; 24 volts, 5mm inter – electrode spacing and surface area to volume ratio of 18.2 m²/m³. Wastewater samples were collected from four sites; SP 1, SP 2, SP 3 and SP 4, in the constructed wetland treatment cells and analyzed for pH, colour, electrical conductivity, COD, BOD and selected heavy metals (Zn, Cd, Pb, Cu, Cr and Co). Electrochemical method reduced COD, BOD and electrical conductivity of the raw effluent, SP 1 by 91.3%, 84.0% and 31.5%, respectively. The treated effluent, SP 4 quality, was also improved through the reduction of COD, BOD and electrical conductivity by 96.6%, 42.4%, and 20.9% respectively. Except iron that had a 67% reduction, electrochemical treatment had a 100% reduction in Zn, Cd and Pb. However Cu, Cr and Co, were not detected. These results indicate that electrochemical treatment of tea effluent is efficient in the reduction of colour, COD, BOD and selected heavy metals (Zn, Cd and Pb).

Key words: Tea wastewater, electrochemical, colour, heavy metals.

Introduction

Chemomi tea factory (CTF) was established in the 1950's and produces several tea grades for the export market. Since then, the factory has expanded its production over the years to meet the demand in export and now produces 6,600 tonnes per annum. This has led to doubling in water usage during the factory cleaning procedures, hence large volumes of effluent wastewater is discharged daily (from 10m³ to 20m³). At present the biological wastewater treatment facility is unable to remove colour from the tea effluent and this has been a major issue in the whole tea industry that is in Kenya.

The River Yala into which a number of industries including tea, sugar and chemical industries discharge their effluents, which consequently drain into Lake Victoria that has been highly polluted in Kenya (Etiégni *et al.*, 2007). For liquid effluents, the removal of COD, BOD, and suspended solids can be successfully removed by primary treatment followed by biological treatment (Springer, 1995). However, colour is difficult and expensive to remove (Ahonen, 2001; Arudel, 2000). High colour levels in the wastewater change the aesthetic quality and reduce light penetration of the receiving waters and this potentially affects benthic plant growth and habitat. Effluent colour is also used as an indicator in quantitative terms of pollution strength (Mahida, 1981).

The effluents that emanate from the tea factory have varying contents of lignin such as theaflavins (Fig. 1), a product of black tea manufacture, responsible for colour.



Fig 1: Formation of theaflavins from simple catechins (Robertson, 1983).

There are several methods of removing chloro-lignin organic materials such as adsorption, coagulation, ultraviolet irradiation and membrane based technology such as ultra filtration (Archibald and Arcand, 1995; Hilleke, 1991). Advanced oxidation processes were found to remove 99% COD in a polyester and acetate fiber dying effluent (Azbar *et al.*, 2004). Electrochemical treatment combined with wood ash leachate (ELCAS) was tested and proved effective in Kraft and paper mill colour reduction. However, over electrical polarization within electrodes, which causes excess voltage remains the biggest impediment in this method (Orori *et al.*, 2005; Etiégni *et al.*, 2007).

Materials and Methods

Sample collection and analysis

Four sampling sites were established along the constructed wetlands of Chemomi tea factory in Nandi South District as shown in Fig. 2. These were: discharge from gravel bed hyponomics (SP1), discharge of surface cell 1 (SP2), discharge of surface cell 2 (SP3) and discharge of the surface cell 3 (SP4). The samples were transported to the laboratory using insulated icebox and were then preserved below 4 ^oC to avoid any biological degradation before analysis (Arudel, 2000). Four sets of water samples were obtained, one set for colour removal, another for metal determination, the third one for BOD and lastly COD measurements. The portion for metal analysis was treated by addition of a 2ml nitric acid to 500ml effluent. The acidification prevents loss of trace metals by adsorption into the walls of polyethylene container.



Fig. 2: Sampling points in Chemomi constructed wetland system, SP1 – SP4

Electrochemical measurements were carried out by measuring 500ml effluent sample in a 600 ml beaker. Two steel electrodes were connected and the operating conditions were; a potential of 24volts, 5mm electrode spacing and surface area of electrodes to effluent volume ratio of 18.2 m^2/m^3 (Maghanga, 2008). Electrochemical reaction was carried out until separation took place. After colour removal for each sample, the electrodes were rinsed with 8% sulphuric acid to avoid fouling. The clarified samples were divided, stored in polypropylene bottles and pre-treated based on the subsequent analysis (APHA, 1992).

For each sample, the parameters measured were; pH, colour, conductivity, BOD, COD, Fe, Cu, Zn, Pb, Cr and Co. pH was measured by a digital PH meter (HANNA 211, Italy) while electrical conductivity was determined by a digital probe conductivity meter (HANNA EC 215, Italy). Colour of the samples was determined by the Pt-Co standard method using the DR 2010 dataloging spectrophotometer (HACH, U.S.A). BOD was determined by the standard 5-day BOD incubation method while COD was determined by the open reflux titrimetric method. Fe, Cu, Zn Pb, Cr and Co were determined by a computer interfaced Varian atomic absorption spectrophotometer method, (AAS) (WHO, 2006, Csuros, 2006). Data obtained was analyzed using SAS and Excel spreadsheets data packages.

Results and Discussion

The physico-chemical characteristics of wastewater used is shown in Table1. The wastewater had high colour levels, COD and BOD levels above recommended limits by the Kenya Government (GOK, 1991). The dissolved oxygen decreased as the effluent moved from one treatment cell to another. The intensity of colour in the effluent varied from one sampling point to another in the constructed wetland as shown in Figure 3. Colour intensity increased as the effluent moved down the treatment system, which was attributed to formation of organic compounds as a result of oxidation that took place when the effluent cascaded from SP1 to SP4.

Parameter	SP1	SP2	SP3	SP4
P ^H	6.72	6.69	6.51	6.49
Colour, Pt-Co colour units	2004	2265	7370	9210
Electrical conductivity, Ec, µS/cm	317	298	201	134
Dissolved oxygen, mg/L	2.37	1.51	1.05	0.84
COD, mg/L	607.0	628.0	427.0	293.0
BOD, mg/L	193.4	184.8	103.0	42.0

Table 1: Characteristics of tea wastewater used

Dissolved oxygen was taken up from the effluent and there was a net reduction of 64.6% (from 2.37 mg/L at SP1 to 0.84 mg/L) at discharge point in SP4. This reduction is probably due to formation of theaflavins from catechins, a process that requires the presence of oxygen (Robertson, 1983). Theaflavins compounds absorb at a higher wavelength as compared to catechins, hence appear as reddish - brown pigments. SP1 had the highest colour index and the intensity increased down the treatment system as shown in Table 1. Electrochemical treatment reduced colour by 100% to zero colour units. Previous studies have shown that removing colour from SP4 required higher power consumption as compared to SP1 though the time taken for complete colour removal was not significantly different (Maghanga, 2008).



Fig. 3: BOD levels of raw and clarified effluent

BOD levels varied from one treatment point to another as seen in Fig.3. Electrochemical treatment led to a reduction in BOD at all sampling points with the highest reduction of 84% at SP1 and 42% at SP4. In the electrochemical decolourization, distillery effluent recorded a 98.1% reduction (Manisankar *et al.*, 2003) while cigarette industry had 84% reduction (Bejankiwar, 2002). BOD levels were influenced by the colour intensity, hence the higher the intensity of colour the higher the BOD (APHA, 1992). The discharge of SP4 had a BOD value higher than

the maximum accepted level (KBS, 1996). Electrochemical colour removal had a better final BOD than what CTF is discharging currently at 42.0mg/L. However, BOD of clarified effluent, SP4, lied within the accepted limits of drinking water (KBS, 1996). The percentage reductions in BOD by electrochemical method are similar to the 80% obtained by Ahonen (Ahonen, 2001).

Chemical oxygen demand varied from SP1 – SP4 as shown in Table 1. The highest COD was in SP1 while SP4 had the least, indicating that, the constructed wetland is effective in the reduction of COD but not to acceptable discharge levels to the water course (GOK, 1993). Clarified effluent had a COD reduction from SP1 to SP4, indicating that electrochemical treatment further reduced their levels (Fig. 5). The highest COD value of 628 mg/L was recorded in SP2, and reduced downstream to the discharge point at SP4. This could be attributed to the high organic matter levels in solution since most solid wastes had settled at the sedimentation tank in SP1.



Fig. 4: COD levels of raw and clarified effluent

From Fig. 4, the average reduction of COD in all treatment cells varied between 87.2 to 96.6%. The highest reduction of 96.6% was achieved in the treated effluent at SP4 while the lowest was 87.2% at SP2. The highest reduction could be attributed to the action of the waterweeds, which were removing N and P as well as oxygenating the effluent in the ponds. At the discharge point of the constructed wetlands, SP4, the COD was 293 mg/L; however, the COD of electrochemically clarified effluent was 10 mg/L. This value was within the acceptable drinking water limits of 50 mg/L (KEBS, 1996). Electrochemical decolourization has been effective in the reduction of COD of other effluents. Reduction of COD in some industrial wastewaters has been reported as; cigarette industry, 56% (Bejankiwar, 2002), distillery effluent, 92% (Manisankar *et al.*, 2003), while saline dyestuff wastewater recorded 87% reduction (Zhang *et al.*, 2003).

Electrical conductivity of raw and treated effluent decreased from SP1 to SP4 as seen in Fig.5. SP1 had a higher conductivity than SP4 in raw and clarified effluents. The constructed wetlands system is hence effective in the reduction of conductivity in all the treatment cells. The water plants introduced in the constructed wetland system at SP1 takes up nutrients in the

wastewater hence reducing their concentration in the treated effluent. Azolla has found its way to these cells and feeds on phosphates while introducing nitrates back to the water. The introduced nitrates are in turn taken up by water lettuce. Electrochemical treatment reduced conductivity levels at SP1, SP2, SP3 and SP4 by 31.5%, 24.8%, 23.4% and 20.9% respectively. The higher conductivity reduction in SP1 was possible due to a higher concentration of nutrients and metal ions as well as a higher coagulation rate. Electrocoagulation led to a reduction in conductivity along all the treatment cells.



Fig. 5: Electrical conductivity, $(\mu S/cm)$ of raw and clarified effluent

Heavy metal concentrations in raw and clarified effluents are shown in Fig. 6. Levels of Zn, Cd, Pb and Fe in raw effluent varied from one treatment cell to another; however, Cu, Cr and Co were not detected in all samples. The presence of Zn could be attributed to the ZnO foliar sprayed to tea during the cold weather to break dormancy, while Cd and Pb are impurities present at low concentrations in the ZnO formulation. Although copper sprays are commonly applied together with Zn, Cu was not detected. This could be attributed to the copper being complexed in the tea oxidation enzyme, polyphenol oxidase (PPO), which is a copper based enzyme that is used in the oxidation of green tea catechins to form black tea pigments, mainly theaflavins and thearubigins (Robertson, 1983). Electrochemical treatment achieved a 100% reduction in Zn, Cd and Pb while Fe was reduced by 67%. Iron is naturally present in the water system, however, during electrolysis, dissolution of iron electrode leads to the final effluent containing iron in solution since not all of it is precipitated with the colour molecules (Maghanga, 2008).



Fig. 6: Heavy metals in raw (CL) and clarified effluent (EC)

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