Electro-coagulation treatment efficiency of graphite, iron and aluminum electrodes using alum and wood ash electrolytes on a Kraft pulp and paper mill effluent

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ABSTRACT

Specific power consumption and reduction of BOD, COD, TS, pH, and chemical elements were used to determine the treatment efficiency of Fe, graphite and Al electrodes with alum and wood ash as supporting electrolytes on the effluent from a Kraft pulp and paper mill in Kenya. Five sampling points were selected along mill’s effluent treatment system: primary settling tank (SP1), first aerated lagoon (SP2), second aerated lagoon (SP3), stabilization pond (SP4), and at discharge point (SP5). Operating costs were also compared between treatments. Graphite electrodes combined with alum showed the lowest power consumption (0.5 to 3.9 mWh/m³), followed by Al and Fe. All the electrodes reduced color from a maximum of 3,200 H to the minimum local standard of 15 H. However Al electrode with alum was the most effective method for BOD and COD reduction by over 60% and 58.8% respectively and generated less sludge at all sampling points. The cost of treatment was lowest with graphite electrode (US$0.006 to 0.0008 per m³ of effluent), but highest with Al electrodes combined with wood ash (US$31.74 to 8.34 per m³). Further study is required for the effectiveness of increasing the concentration of wood ash leachate at higher concentration and current density.

Key words | aluminum, electro-coagulation, graphite, iron, Kraft mill, wastewater

INTRODUCTION

Historically, pulp and paper mills, the world over, have been discharging a wide range of liquid and solid wastes into waterways. These effluents can cause varying and considerable damage to receiving waters if not properly treated because of their high biochemical oxygen demand (BOD), chemical oxygen demand (COD), phenolic aromatic or/and chlorinated compounds, suspended solids, fatty acids, tannins, lignin and its derivatives. They can also lead to changes in the aesthetic quality of receiving waters, reduced sun light penetration and potentially negatively affect benthic plant growth and habitat because of their high color levels (Nestman 1985; Muna 2001). The brownish color of a mill effluent is mainly attributed to products of lignin polymerization formed during pulping and bleaching operations (Luner et al. 1970). These chromophoric groups are mainly quinonic types with conjugated double bonds originating from pulping processes (Luner et al. 1970; Frostell et al. 1994).

Most pulp and paper mill wastewaters are usually detoxified by conventional methods such as biological oxidation, adsorption, flotation, coagulation, UV photodecomposition and electrochemistry (Panizo et al. 2000; Gürs et al. 2002; Pérez et al. 2002). However many of these systems remain largely ineffective for color removal. Several physical and chemical processes for effluent treatment in pulp and paper mill effluents have been extensively studied (Wang et al. 2001). They include rapid filtration through
soil, membrane-based technology such as ultrafiltration, ion-exchange, activated sludge, lime precipitation and sorption on activated carbon (Clark et al. 1994; Diez et al. 1999; Thompson et al. 2001; Mänttäri & Nyström 2007). These technologies can reduce pollution load including effluent color to acceptable levels, but most are quite expensive and very few are in common practice. Electrochemical technology alone or in combination with other methods offers an ideal tool for addressing the pulp and paper mill effluent problem because the main compound used is electron, which is clean and usually requires no additional reagent (Verench et al. 2001; Ügurlu 2005). During electro-coagulation, the coagulant is generated in situ by electrolytic oxidation of an anode of appropriate material. Charged ionic species are removed from wastewater by allowing ions to react with oppositely charged ions, or with floci of metallic hydroxides generated within the effluent (Mollah et al. 2001). The electrode material impacts markedly on the performance of the electro-coagulation reactor because the anode material usually determines the cation introduced into solution. Several researchers have studied the choice of electrode material with a variety of theories as to the preference of a particular material.

In 2006, Kenya enacted new environmental laws that make it difficult for many local industries to meet new effluent discharge standards. The effluent treatment system at PanPaper, a local Kraft pulp and paper mill, has remained largely ineffective in reducing its effluent characteristics that include a color index of 3,263 at the point of discharge into the near-by river Nzoia, a level clearly unacceptable according to the new environmental regulations. In this paper we evaluate and compare the performance of electro-coagulation method on the mill’s effluent using three different types of electrode materials.

**STUDY AREA**

The study was conducted on effluent from Kenya’s Pan African Paper Mill (PPM), one the two largest pulp and paper mills in East Africa. The mill has an annual production capacity of 120,000 tonnes of paper. The pulp is obtained through Kraft process of a mixture of Pinus patula, Cupressus lusitanica and Eucalyptus saligna and stone grinding process of Pinus patula. Pulp bleaching is accomplished by CEHH or CEHP sequences depending on the quality and brightness of the paper required. The mill products include newsprint, writing and packaging papers for local and export markets in East and Central Africa and some parts of Asia. These paper grades are produced on four flat open wire Fourdrinier machines, with one or multiple head boxes, running at a maximum speed of 300 m/min. The mill discharges on average a combined effluent of 35,000 m$^3$ per day (up from an initial design flow of 25,000 m$^3$/day) of pitch brown colored wastewater with an initial and final average color index of 1,868 H to 3,263 H respectively (Orori et al. 2005). The factory effluent goes through a treatment process that includes two clarifiers, followed by two aerated lagoons and two facultative lagoons. This treatment system has over the years proved grossly inadequate to treat mill’s effluent to acceptable national standards. The low level of effluent quality has become a major concern because the mill discharges its effluent into River Nzoia that flows into Lake Victoria, the World’s second largest fresh water lake, with a fragile ecosystem. More than thirty million people depend on Lake Victoria for their livelihood.

**MATERIALS AND METHODS**

Samples of waste water were collected at five sampling points (SP1, SP2, SP3, SP4, SP5) for 3 months and transported for storage in a cold environment at 4°C to avoid any biological deterioration. Several parameters including color, pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total solids (TS), and selected inorganic elements were determined according to TAPPI standard procedures (Tappi Test Methods 1992). Electro-coagulation experiments were carried out in a bi-polar batch reactor using three types of electrodes that included graphite, iron and aluminum with alum and wood ash as supporting electrolytes (Figure 1). Only the outer electrodes were connected to a DC power source. The active surface area of the three different set of sacrificial electrodes was kept uniform at 50 m$^2$/m$^3$ of wastewater. The distance between the electrodes was kept constant at 5 mm. Each experimental set up consisted of three parallel electrode plates separated by a non-conducting material. For each run, a sample of 100 ml waste water was placed...
into a beaker with a magnetic stirrer and the electrodes immersed to a given depth into the effluent sample to achieve surface area coverage of 30 m²/m³ of waste water and current density of 0.1 A m⁻². Different alum (Al₂SO₄·18H₂O) 40.1 M and wood ash leachate were dosed separately for each experimental run. Wood ash leachate was prepared by mixing 200 g of wood ash with one liter of effluent and stirred for 24 hours. The aluminum electrodes used in this experiment were prepared from a commercial anodized electroplated rolled aluminum, 0.5 mm thick. The samples were cut into 3.5 × 5 cm² pieces and were etched in a solution containing 35 g chromic VI oxide and 20 ml H₃PO₄ (85%) per liter at 80°C for 7 min to ensure electrical conductivity (Mwamburi & Wäckelgård 2000).

The disappearance of the effluent color was chosen as the reaction end point (below 15°H). Electrodes were rinsed in a bath of 5% sulphuric acid after every run to avoid fouling. For each run, the time required for complete color removal was measured and the specific power consumption (mWh/m³) calculated. After color removal, settleable solids were determined using a modified Imhoff cone under quiescent conditions. Elemental analysis of the raw and treated pulp and paper mill effluent was carried out for quality assessment using Atomic Absorption Spectroscopy (AAS). Data were analyzed using Statistical Package for Social Scientists (SPSS Version 12.1). Analysis of variance and means separation by Least Significance Difference (LSD) and Duncan’s test were performed to separate means among different treatments.

RESULTS AND DISCUSSION

The mill’s raw and treated effluent characteristics compared with local discharge effluent standards are listed in Table 1. Some of the mill’s treated effluent characteristics such as BOD, COD and color were found to be above the required discharge standards. However, treated effluent characteristics such as pH, alkalinity, temperature and turbidity were within the allowable limits.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Raw effluent</th>
<th>Treated after last stabilization lagoon</th>
<th>Effluent discharge standards¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.5</td>
<td>7.2</td>
<td>6.5–8.5 (non marine)</td>
</tr>
<tr>
<td>Alkalinity (mg/l)</td>
<td>338.4</td>
<td>79.15</td>
<td>–</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>39.0</td>
<td>20.2</td>
<td>&lt;30.0</td>
</tr>
<tr>
<td>TS (mg/l)</td>
<td>980.7</td>
<td>457.5</td>
<td>30.0</td>
</tr>
<tr>
<td>TDS (mg/l)</td>
<td>689.6</td>
<td>324.5</td>
<td>1,200.0</td>
</tr>
<tr>
<td>TSS (mg/l)</td>
<td>291.5</td>
<td>133.0</td>
<td>30.0</td>
</tr>
<tr>
<td>Colour (°H)</td>
<td>1,867.71</td>
<td>3,263.3</td>
<td>15.0</td>
</tr>
<tr>
<td>BOD₅ (mg/l)</td>
<td>182.50</td>
<td>62.8</td>
<td>30.0</td>
</tr>
<tr>
<td>COD (mg/l)</td>
<td>591.54</td>
<td>296.7</td>
<td>50.0</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>133.1</td>
<td>331.3</td>
<td>–</td>
</tr>
<tr>
<td>Conductivity (µS cm⁻¹)</td>
<td>2,109.3</td>
<td>841.3</td>
<td>–</td>
</tr>
</tbody>
</table>

¹Source: Kenya Gazette Supplement No. 68, 29th September 2006, Legal Notice No. 120.
Specific energy consumption for Fe, graphite and Al electrodes each combined with alum at different sampling points are shown in Figures 1–3. Figure 4 shows the variation of specific energy consumption for Al electrodes combined with wood as supporting electrolyte at different sampling points (SP1, SP2, SP3, SP4 and SP5).

Most electrodes decolorized the PPM effluent to 15°H with varying levels of energy consumption. The decolorization can be linked to the cathodic electrogenerated H₂O₂ which might partly have helped degrade chromophoric compounds by chemical oxidation pathway leading to the stripping-off of organic pollutants (Alvarez-Gallbergos & Pletcher 1999).

There was a significant decrease ($p \leq 0.05$) in energy with increasing dosage of the two electrolytes for all electrode types tested and the reduction had similar trend with alum and wood ash leachate as shown in Figures 1–4. Low alum dosages were required compared to higher dosage of wood ash leachate to reach the same level of treatment (final color of treated effluent). The possible reason may that the low dosage of wood ash leachate yielded low counter-ions such as Cu²⁺, Al³⁺, Fe²⁺ compared to alum which produced large amounts of counter ions of Al³⁺. Figure 4 shows that Al electrodes when combined with wood ash had the highest specific energy consumption at different ash dosages at all sampling points.

Graphite electrodes gave the best specific energy consumption with low alum dosage at sampling point one (SP1). This was followed by Al and finally Fe electrodes at SP1. However, specific energy consumption for Fe electrodes combined with alum decreased at a higher rate (slope = 2.58) from SP1 to sampling five (SP5). For graphite electrodes combined with alum the rate of specific energy consumption reduction was significantly lower (Slope = 0.40), and recorded the lowest specific energy consumption at all sampling points. Based on energy consumption alone graphite electrodes can be considered as the best. However previous investigators have found graphite to be unstable, ineffective but inexpensive (Chen 2004).

Preliminary investigations in this study had shown that graphite electrodes alone had low ability to cause substantial floc formation leading to effluent coagulation. When graphite electrodes were combined with wood ash there
was no appreciable color changes. This may be ascribed
to the lack of release of chemical elements from the
graphite electrodes that could have assisted the electro-
coagulation process.

Al electrodes combined with wood ash leachate showed
higher specific energy consumption compared with iron
electrodes as reported by Orori et al. (2005). This may be
probably due to the higher electrode surface coverage
of 80 m²/m³ as compared to 30 m²/m³ used in this study
and the ability of the electrodes to release their respective
oxides. It could also be that the experiment of aluminum
combined with wood ash leachate was run after the
aluminum electrodes had undergone passivation, one of
the potential drawbacks of Al electrodes. The same negative
exponential trends were recorded when aluminum was
combined with wood ash. Increasing the wood ash dosage
reduced specific energy consumption. It is therefore likely
that an increase in wood ash leachate concentration above
200 g per liter of wastewater used in the study may give
further positive results in terms of specific energy
consumption reduction. Chemical analysis of wood ash
had previously shown the presence of several chemical
elements in the form of their corresponding oxides when
dissolved in water (Etiegni & Campbell 1991). It is believed
these chemical elements assist the flow not only of electrical
current because of the increase in the solution’s electrical
conductivity but also facilitate the rate of coagulation by
reducing the zeta potential of colloidal and other polluting
materials dispersed in the pulp and paper mill effluent.

**Treatment effect on biochemical oxygen demand**

Effect of effluent treatment using iron, graphite and
aluminum electrodes combined with different doses of the
alum and wood ash as supporting electrolytes on BOD is
shown in Figure 5. Initially BODs (174.5 – 58.7 mg/l) at SP1,
SP2, SP3, SP4 and SP5 were all above the required national
discharge standards of 30 mg/l. No method, even in
combination with supporting electrolytes reduced BOD to
within the allowable limits at sampling points SP1 and SP2.
However at SP3, higher doses of supporting electrolytes
helped both graphite and iron electrodes reduce BOD
to within allowable limits. The reduction in BOD was over
60%. The highest BOD reduction was recorded with
aluminum electrodes combined with alum (65.3%
to 81.2%). Graphite combined with alum reduced BOD by
between 61.6% and 78.2%, while Fe combined with alum
resulted in a BOD reduction of between 60.9% and 79.0%.
At SP4 and SP5, all the 3 electrodes and supporting
electrolytes reduced BOD to levels below the maximum
allowable limits. Al electrodes combined with wood ash
decreased BOD between 62.3% and 79.8%; much higher
results than those obtained by Orori et al. (2005). At all
sampling points, Al electrodes proved the most effective for
BOD removal followed by Fe and then graphite but their
efficiency was not significantly different \( p \leq 0.05 \).

**Treatment effect on chemical oxygen demand**

Figure 6 shows the effect of effluent treatment using iron,
graphite and aluminum electrodes at different dosage of
alum and wood ash leachate on COD. The initial COD ranged between 581.6 to 284.6 mg/l along the sampling points. The discharged COD level to river Nzoia stood at 284.6 mg/l, well above the national discharge standard of 50 mg/l.

Al combined with wood ash yielded the lowest reduction in COD (58.8–71.9%), whereas aluminium combined with alum reduced COD by between 81.7% and 88.3% at all sampling points. Graphite and iron combined with alum reduced BOD between 80.2% and 88.1%. None of the electrodes achieved the required discharge standards at SP1 to SP3. However higher doses of supporting electrolytes helped the three electrodes reduce COD to within allowable limits but their efficiency was not significantly different ($p \leq 0.05$) (Figure 7).

Treatment effect on total solids (TS) and settleable sludge levels produced

Figure 8 shows the effect of effluent treatment using Fe, graphite and Al electrodes using different dosage of the alum and wood ash as supporting electrolytes on TS. From Table 1, we can see that initial TS had decreased from 980.7 to 457.5 mg/l prior to effluent discharge into the river, well above Kenya’s National Effluent Standards of 30 mg/l. All electrodes and coagulant combinations reduced TS by over 99%. All combinations of electrodes and electrolytes met the discharge requirements for TS. The amount of sludge produced by all effluent treatment methods is shown in Figure 9. All methods generated settleable sludge levels between 64.6 to 116.7 mg/l. Lowest of sludge level was produced by iron Fe combined with alum and Al combined with alum. The highest sludge amount was produced by Fe and Al combined with wood ash leachate. The result
obtained was this study was within the range reported by Kurt et al. (2008) for a number of electrocoagulation treatment methods of domestic wastewater. The amount of sludge produced is a factor that could negatively impact on the implementation of most of these methods.

Treatment effect on pH

The effect of alum and wood ash leachate on the effluent treatment using Fe, graphite and Al electrodes on the pH is shown in Figure 10. The initial pH at the mill’s effluent ranged from 6.9 to 8.5, which are well within the required discharge standards. All electrodes combined with alum reduced the pH to between 10.4 and 6.7 at all sampling points with different alum dosages. Alum has been known to depress pH of treated water or waste water especially when applied in large quantities. There was a significant difference between the final treated pH of Al, Fe and graphite electrodes combined with alum at all sampling points. The pH of Al combined with wood ash treated

<table>
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<th>Chemical elements before and after treatment using various electrodes and coagulant combination at selected sampling points</th>
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<td>**</td>
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<tr>
<td>National standard limits</td>
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<td>Initial</td>
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<td>IRA8</td>
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<td>GRA8</td>
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<tr>
<td>ALS2</td>
</tr>
<tr>
<td>ALS8</td>
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<tr>
<td>Wood ash leachate</td>
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The effluent increased to 7.5 and 9.6 at all sampling points, probably because wood ash contains large quantities of alkaline earth metals that shifted the pH towards the alkaline range. There was a significance difference \((p \leq 0.05)\) in pH between wood ash and all the alum combinations at all sampling points.

**Treatment effect on chemical elements**

Table 2 shows chemical elements before and after treatment by various electrodes combined with supporting electrolytes. The effluent samples used in this experiment were obtained from SP1, SP3 and SP5. Elements found to be below the detectable level were referred to by minus sign (\(-\)). Those that were not determined at all were marked by asterisk sign (\(*\)). Generally Cr, Zn and Cd were present in the treated effluents with all the electrodes and electrolyte combinations at all sampling points. Fe and Co were not detected except when Al electrodes were combined with wood ash at some selected sampling points. Cu was detected in some treatments such as graphite and Fe electrodes combined with alum at SP1 and SP5. The levels of these elements were below the maximum national discharge limits. Analysis of wood ash leachate used in this study indicated that there was initially a high level of certain metals as shown in Table 2. This is probably the reason why a disproportionately high level of the same elements was recorded in the treated effluent, when the supporting electrolyte was from wood ash. During electro-coagulation, \(\text{Al}^{3+}\), \(\text{Fe}^{2+}\) and \(\text{OH}^-\) ions generated at the electrode surfaces react in the bulk waste water to form aluminum hydroxide, Ferric oxides depending on the electrode metal in use. The hydroxide flocs act as adsorbents and/or traps for metal ions and other pollutants leading to their elimination from the solution. Simultaneously, when Al electrodes were used, the hydroxyl ions, produced at the cathode further contributed to depression of the solution pH, especially in the presence of alum used as supporting electrolyte. This can help explain why the final pH of the effluent treated by Al electrode combined with alum was surprisingly low.

**Operational cost efficiency of the methods**

Operational costs per year were calculated based on the amount of supporting electrolyte used and electric power consumed by various electrodes. Mass loss of the electrodes over time can increase the operating cost. But in this instance, no detectable level of electrode mass loss was recorded because of the short time of the experiment and was therefore considered negligible. No monetary value was attached to wood ash since it is available as a waste material at the mill. As indicated in Table 3 Al combined with wood ash had the highest overall operational costs at all sampling points with all the wood
ash leachate. The operation cost ranged between US$3,466,043 and 1,022,404 because of high energy consumption. Graphite had the highest initial operating cost when combined with alum at SP1 (US$62,091.7), but the lowest when effluent from SP5 was treated (US$9,649.2). There was no significant difference \((p < 0.05)\) in operating cost per year between Fe and Al electrodes combined with alum at all sampling points. But the difference became significant \((p < 0.05)\) with an increase in the alum dosage at all sampling points. Based on operating cost, it would be less expensive by 50% compared to conventional method to treat the mill effluent at SP5 with Graphite electrode combined with alum.

**CONCLUSIONS AND RECOMMENDATION**

This study has shown that graphite electrode combined with alum had the lowest operating cost in terms of energy consumption, hence it was the most efficient followed by Al and Fe combined with alum. Al combined with wood ash was the least efficient in operation cost per year, but with increase in ash concentration the total operational cost may be lower than that of graphite combined with alum. The study also showed that all the electrodes and supporting electrolyte had almost the same reduction in COD, BOD and TS of over 58.0, 60, and 99% respectively. Only the final TS was below the discharge standards for all the methods. BOD and COD of the treated effluent could be lowered to within the required national discharge standards only when the effluent samples were collected from SP4 and SP5 and with an increase in alum or wood ash leachate concentrations. The most efficient method in terms of percent reduction of effluent physico-chemical parameters was AI combined with alum. The concentrations of metal tested for all the electrodes and electrolytes combinations were within the required discharge standards and did not require further reduction. Because the combination of Al electrodes with wood ash leachate yielded unusually higher electric power consumption, it was recommended that further study be carried out at higher wood ash leachate concentrations. It was also recommended that a study be carried out on current density and electrode separation distance to make these methods more economical.

**REFERENCES**


