Anthropogenic activities resulting in accelerated pollution and eutrophication of rivers and streams are an increasing concern worldwide and the natural rubber industry is not exempted. The processing of field latex into rubber sheets generates large volumes of aqueous effluents approximately 25 m$^3$ for a metric ton of dry rubber sheet produced. Present in this rubber wastewater are uncoagulated rubber particles, organic matter, nutrients (nitrates, phosphates, ammonium formate) and proteins (hevein). These pollutant charges lead to pollution and ecological imbalance in the receiving water bodies. Some rubber factories make use of a rubber trap as a treatment method to recover the uncoagulated rubber particles in the wastewater before it is sent into the environment. However, this method has been proven to be ineffective since auto-flocculation of the rubber particles in the wastewater is very slow. On the other hand, others use primary coagulants and flocculants to treat rubber wastewater. Nevertheless, the technology is not mastered and the rubber takes several weeks to flocculate. Thus, most of the water enters receiving water bodies with high amounts of uncoagulated rubber particles. Previous work on the recovery of rubber from rubber factory wastewaters with cationic polyelectrolytes showed an efficiency of about 98 per cent. The testing of rubber recovered with polyelectrolytes showed that it had the same properties as that of natural rubber coagulated normally (with

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formic acid) and therefore, the recovered rubber could be valourised. Rubber factory wastewater treatment with polyacrylamide partially hydrolysed with soda\(^5\), showed that in addition to removing suspended solids, physicochemical methods may be used to achieve a considerable reduction in biological oxygen demand (BOD) and chemical oxygen demand (COD) with a >89% removal of both. Thus, coagulation and flocculation may be a good alternative for rubber recovery from wastewater prior to biological treatment. Hence, our point of interest in this work will be the determination of optimum parameters (polymer demand, pH and clarification time (mins)) to recover rubber and clarify latex wastewaters.

**EXPERIMENTAL**

**Chemicals and Raw Materials**

Polymer stock solutions were prepared with reverse osmosis filtered water where the pH was adjusted with 1M HCl and 1M NaOH (Riedel de Haën, Germany). Commercial grade formic acid (85%) diluted to 2% was used to adjust the pH of synthetic rubber latex wastewaters to the required value. Field latex was obtained from the CDC central rubber factory located in Tiko, southwest region of Cameroon. Polyelectrolyte stock solutions were prepared at 0.1% w/v according to manufacturer’s specifications Floeger (France) for FO 8650 and Ultrafloc (South Africa) for U 5000. Material characteristics are described in Tables 1, 2 and 3 respectively.

**Synthetic Rubber Wastewater Preparation**

Total solids content (TSC) of the field latex was determined by oven drying method as the percentage ratio of the mass of the dried residue to the field latex sample volume. The dry rubber content (DRC) on its part was calculated as the product of the TSC and a factor of 0.92, representing theoretical 5% non-rubbers and other impurities in field latex (CDC Rubber Manual).

\[
TSC \ (w/v) = \frac{mass \ of \ dry \ sample \ (g)}{volume \ of \ sample \ (L)} \quad \ldots \ 1
\]

\[
DRC \ (w/v) = TSC \ (g/L) * 0.92 \quad \ldots \ 2
\]

The results of this experiment are shown in Table 2.

Variation of the rubber concentration in the wastewater was done by dilution of the field latex with reverse osmosis filtered water using an appropriate dilution factor while pH adjustment was done with 0.2% formic acid. The turbidity and pH of the prepared wastewater samples were measured with the help of a RATIO/XR Turbidimeter (HACH Company, USA) and a pH Meter (Consort C863) respectively whilst the final rubber concentration was done by the oven drying method. The results of this experiment are shown in Table 3.

**Preparation of Polyelectrolytes**

Polyelectrolyte stock solutions were prepared according to manufacturer’s specifications Floeger (France) for FO 8650 and Ultrafloc (South Africa) for U 5000 both stated at 0.1% w/v. The stock solutions were renewed every three days. Dissolution of the polymers was carried out in reverse osmosis filtered water adjusted to pH 7.

**Jar Test Procedure**

This study was done in two parts and at room temperature of 24 ± 2ºC.
Influence of Rubber Concentration on Polymer Demand, Amount of Rubber Recovered, and Residual Turbidity.

Coagulation/flocculation studies were performed by jar test (Bioblock Scientific with 6 agitation paddles and an agitation speed that ranges from 0 – 260 rpm). The objective of this study was to determine the optimum dose of polymer that would cause effective flocculation of the rubber particles. Synthetic rubber latex wastewater prepared at varied rubber concentrations (0.5, 1.0, 2.0, 4.0, 6.0, 8.0 g/L) at pH 6 was treated separately with varied concentrations of FO 8650 and U 5000 by jar test (fast agitation: 200 rpm for 2 min; slow agitation: 60 rpm for 60 min (clarification time); flotation time: 60 min). At the end of flotation, the residual turbidity of the clarified effluent was measured and floating flocs were recovered by skimming whilst flocs stuck onto the paddles were scraped off. The recovered rubber was oven-dried for 4 h at 105°C and then weighed. The efficiency of recovery (%) was then calculated.

<table>
<thead>
<tr>
<th>Code</th>
<th>Nature of flocculant</th>
<th>Molecular weight *10^6 (g/mol)</th>
<th>Ionicity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FO 8650</td>
<td>Cationic polyacrylamide (CPAM)</td>
<td>11</td>
<td>78</td>
</tr>
<tr>
<td>FLOEGER (France)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U 5000</td>
<td>Cationic polyacrylamide (CPAM)</td>
<td>0.05-0.06</td>
<td>78</td>
</tr>
<tr>
<td>ULTRAFLOC (South Africa)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(*) multiplication sign

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Average values</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
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</tr>
<tr>
<td>Total solids content (TSC)</td>
<td>350 g/L</td>
</tr>
<tr>
<td>Dry rubber content (DRC)</td>
<td>322 g/L</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Wastewater rubber concentration (g/L)</th>
<th>Turbidity (NTU)</th>
<th>pH</th>
<th>Conductivity (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>2151</td>
<td>6</td>
<td>0.55</td>
</tr>
<tr>
<td>1</td>
<td>4804</td>
<td>6;7;8</td>
<td>0.55</td>
</tr>
<tr>
<td>2</td>
<td>9549</td>
<td>6</td>
<td>0.96</td>
</tr>
<tr>
<td>4</td>
<td>14793</td>
<td>6</td>
<td>1.33</td>
</tr>
<tr>
<td>6</td>
<td>20340</td>
<td>6</td>
<td>2.61</td>
</tr>
<tr>
<td>8</td>
<td>43700</td>
<td>6</td>
<td>3.05</td>
</tr>
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</table>
as the percentage ratio of the amount of rubber recovered from the sample after treatment to that present in the sample before treatment.

**Influence of Wastewater Initial pH on Polymer Demand and Flocculation Kinetics.** Synthetic rubber latex wastewater prepared at a rubber concentration of 1.0 g/L at pH 6, 7 and 8 was treated separately with varied concentrations of FO 8650 and U 5000 by jar test (fast agitation: 200 rpm for 2 min; slow agitation: 60 rpm for 60 min (clarification time); floatation time: 60 min). At the end of floatation, floating floccs were recovered by skimming whilst floccs stuck onto the paddles were scraped off. The recovered rubber was oven-dried for 4 h at 105ºC and then weighed. The polymer concentration that gave the highest recovery of rubber at each given pH was noted and used to perform flocculation kinetics. Next, synthetic rubber factory wastewater prepared at a rubber concentration of 1.0 g/L at pH 6, 7 and 8 was flocculated with the predetermined optimum polymer doses of FO 8650 and U 5000 (fast agitation: 200 rpm for 2 min; slow agitation: 60 rpm for 0; 10; 20; 40; 60; 80 min; floatation time: 60 min). At the end of each slow agitation time, the agitation was stopped and after floatation, the floating floccs were recovered by skimming whilst floccs stuck onto the paddles were scraped off. The recovered rubber was oven-dried for 4 h at 105ºC and then weighed. The efficiency of recovery (%) was then calculated as the percentage ratio of the amount of rubber recovered from the sample after treatment to that present in the sample before treatment.

**RESULTS AND DISCUSSION**

**Influence of Rubber Concentration**

This study was carried out to investigate the influence of latex wastewater rubber concentration on polymer demand (critical flocculation concentration), amount of rubber recovered, and residual turbidity.

**Influence of Rubber Concentration on the Critical Flocculation Concentration**

*Figure 1* shows the effect of rubber concentration on the critical flocculation concentration of two polyelectrolytes, at pH 6. From *Figure 1*, it was observed that the critical flocculation concentration increased with increasing rubber concentration, for both polymers. Attachment of polymer chains to particles occurs at a rate that depends primarily on their concentrations, broadly according to Smoluchowski kinetics. As the rubber particle concentration is increased, the optimum polymer dosage will generally increase proportionally. Treatment with U 5000 uses lesser polymer than FO 8650. This suggests that the action of U 5000 being a short chain polymer would be largely by charge neutralisation while FO 8650 being a long chain polymer would be largely by bridging. Polyelectrolytes of high charge density are more effective, simply because, for a given dosage, they deliver more charge to the particle surface and since high charge density polymers tend to adsorb in a rather flat configuration, there is little opportunity for bridging interactions. Thus, quite low molecular weight high charge density polyelectrolyte, such as U 5000, is quite an effective flocculant. Further evidence such as performing floc aggregation kinetics could be used to affirm the principal mechanism of action of the polymers. The difference in the critical flocculation concentration for both polyelectrolytes is small at lower rubber concentration and more important at higher rubber concentrations. This may be associated with problems of polymer dispersion in suspension and diffusion to the surface of rubber particles whereby it is difficult for high molecular weight polymers...
to rapidly disperse and diffuse in concentrated suspensions. In Figure 1 there is a range of rubber concentrations (2.0-4.0 g/L) for which there was no apparent change in the critical flocculation concentration. It would be technologically advantageous to work in this range, where, the combine action effect of charge neutralisation and bridging of both polymers is just sufficient to cause effective flocculation of the rubber particles. This observation strongly suggests that the same amount of polymer could be used to treat wastewater of a concentration between 2.0-4.0 g/L. Similar results of increase in optimal dose of flocculant with increases in suspension concentration have been reported in literature\textsuperscript{7,8}. The polymer demand per gram of rubber was obtained by dividing the critical flocculation concentration by the corresponding rubber concentration. The effect of rubber concentration on the polymer demand per gram of rubber is shown in Figure 2.

In Figure 2, it was observed that the polymer demand per gram of rubber decreased sharply with increasing rubber concentration up to 4.0 g/L and tends to rise slowly above this concentration. This observation is supported by Smoluchowski kinetics which states that flocculation is a second order reaction and therefore increase in rubber concentration will increase inter-particle collision frequency which greatly improves flocculation performance and decrease polymer demand\textsuperscript{9}. Also, the trend suggest bridging flocculation to be partly involved with both polymers because if the mechanism of flocculation was solely by charge neutralisation, then we expected the polymer demand per gram of rubber to increase with increasing rubber concentration. We affirm that charge neutralisation is the dominant mechanism of flocculation above a rubber concentration of 4.0 g/L. When high charge density polyelectrolytes adsorb on negative surfaces with a fairly low density of charged sites, there exist a possibility of

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**Figure 1.** Effect of rubber concentration on the polymer critical flocculation concentration at pH 6, $T = 24 \pm 2^\circ C$, $RC = 1.0$ g/L, $CT$ 60 min, $FT$ 60 min for U 5000 (●), FO 8650 (△).
electrostatic patch mechanism. In this situation therefore, re-flocculation after flocc breakage occurs more readily in the case of electrostatic patch than bridging. Thus, the polymer demand for U 5000 is lower compared to that of FO 8650 as shown in Figure 2. In conclusion we could suggest that economically it would be advantageous to work at rubber concentrations above 4.0 g/L.

Influence of Rubber Concentration on the Amount of Recovered Rubber

In Figure 3, it is prominent that there is no marked difference in the recovered rubber for both polymers with increase in rubber concentration as the amount of recovered rubber is statistically the same at 5% error. However, there is a dip in the recovered rubber for both polymers at concentration of 6.0 g/L which is linked to a problem of floc consistency and recovery and not to flocculation efficiency. Hence, the flocculation performance and the amount of rubber recovered using the optimum polymer demand is not affected by the wastewater rubber concentration in the range tested. Therefore, in every suspension concentration, there exists an optimum dose of polymer that would cause effective flocculation of the dispersed particles.

Influence of Rubber Concentration on the Residual Turbidity of Clarified Wastewater

Figure 4 shows the effect of rubber concentration on the residual turbidity of clarified wastewater after an hour of flotation at pH 6. From Figure 4, it is apparent that the residual turbidity of wastewater varies with rubber concentration. Turbidity is related to recovered rubber in the sense that it decreases generally with increase in recovered rubber. However, turbidity does not only depend on suspension concentration, it also depends on particle size. So microfloccs of different sizes
Figure 3. Effect of rubber concentration on the amount of rubber recovered after 60 min, at pH 6, 
$T = 24 \pm 2^\circ C$, $RC = 1.0 \text{ g/L}$, FT 60 min for U 5000 (●), FO 8650 (△).

Figure 4. Effect of rubber concentration on the residual turbidity at 60 min, pH 6, $T = 24 \pm 2^\circ C$, 
$RC = 1.0 \text{ g/L}$, FT 60 min for U 5000 (●), FO 8650 (△).
that find themselves in the residual effluent would diffract light differently. In this case we expect turbidity values to be non-consistent despite the optimum flocculation efficiency. U 5000 gave a better floc consistency and recovery compared to FO 8650 and as a result its residual turbidity was also relatively low. It is however important to note that a global residual turbidity value of ≤12 NTU was recorded in both treatment cases after 60 min of floatation, thus, the resulting wastewater is clarified in every case and can be sent directly into the environment. There is a possibility of using this clarified wastewater as soil supplement by controlled spread to agricultural soils as a fertilizing agent\textsuperscript{11}. The clarified wastewater could possibly be recycled after further treatment.

**Influence of Wastewater Initial pH**

This study was carried out to investigate the influence of wastewater initial pH on polymer demand (critical flocculation concentration) and flocculation kinetics. This experiment was run as a separate batch from the previous. Hence, slight variations in the polymer demand (<20%) could occur due to variation in the surface characteristics of the rubber particles in suspension as a result of the adsorbed layer of proteins and phospholipids.

**Influence of pH on the Critical Flocculation Concentration**

*Figure 5* shows the influence of pH on the critical flocculation concentration of two cationic polymers, U 5000 and FO 8650 at a rubber concentration of 1.0 g/L. It was observed that polymer demand is dependent on pH and increases with increasing pH. Similar results of increase in polymer demand with pH have been reported in literature\textsuperscript{12}. The increase in polymer demand with pH is because the negative zeta potential of natural rubber latex increases (increase of negative charge) with

\[ \text{pH} \]

\[ 5 \quad 6 \quad 7 \quad 8 \quad 9 \]

Critical flocculation concentration (mg/g rubber)

\[ 0 \quad 2 \quad 4 \quad 6 \quad 8 \quad 10 \quad 12 \]

*Figure 5. Effect of pH on polymer critical flocculation concentration at 60 min, } T = 24 \pm 2^\circ\text{C}, \text{ RC} = 1.0 \text{ g/L, FT 60 min for U 5000 (○), FO 8650 (△).}
the increase in pH, thereby increasing the polymer demand. The increase in polymer demand with pH for FO 8650 is more drastic than that for U 5000. Moving from pH 6 to pH 8, there were about 53% and 178% increase in polymer demand in the case of U 5000 and FO 8650 respectively.

Influence of pH on Flocculation Kinetics of Rubber Latex Wastewater

Figures 6(a) and (b) show a graph of rubber recovered with time at different pH values for treatment with U 5000 and FO 8650 polymers, respectively, at 1.0 g/L rubber concentration. It was observed that there is a general increase in the rubber recovered with time for both polymers tested irrespective of pH and in addition, polymer flocculation is very rapid and tends to stabilise at about 60 minutes. At 60 min of floatation, the rubber recovered for U 5000 polymer was 94.37%, 97.50% and 98.75% at pH 6, 7 and 8 respectively, while FO 8650 polymer recorded 96.25%, 96.87% and 98.75% at pH 6, 7 and 8 respectively. These values are statistically the same at 5% error.

Therefore, it indicates clearly that flocculation performance of polymers is independent of pH at the optimum polymer demand.

CONCLUSION

Physicochemical flocculation with cationic polyelectrolytes namely U 5000 and FO 8650 gave excellent clarification and recovery of rubber from latex wastewater. At room temperature, pH 6 and clarification time of 60 min, there was an increase in the critical flocculation concentration (mg/L) with increase in rubber concentration (g/L) for both polyelectrolytes. However, the polymer demand (mg/g rubber or g/g rubber) decreased with increase in rubber concentration for low suspension concentrations. The amount of recovered rubber was independent on the rubber concentration at the optimum polymer dose. Generally, in the treatment of rubber latex wastewater, we could attain a 98% recovery of rubber and residual turbidity ≤12 NTU. At room temperature, rubber concentration of 1.0 g/L and clarification time of 60 min, the critical flocculation concentration increased with
increasing pH for both polymers. However, rubber recovery was still kept at its maximum. Hence, polymer demand is pH dependent but the flocculation performance of polymers at the optimum polymer concentration is independent of pH.

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REFERENCES


