Appraisal of Cassava Starch as Coagulant Aid in the Alum Coagulation of Congo Red from Aqua System

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Abstract

Cassava starch (CS) was evaluated as coagulant aid in the alum coagulation of an acid dye, Congo red (CR), from aqua system. The use of CS, as coagulant aid reduced the value of the optimum alum dose, required for coagulation of CR, by 50%. The abilities of alum and CS were assessed, separately, on the coagulation of varying concentrations of CR contaminated water by method of continuous variation of the alum and CS dosages. Alum coagulated the CR while the CS performed poorly. Varying dosages of the CS were combined with half the optimum alum dose, for each concentration, and reduction in the aqua CR concentration was observed. The percentage of CR removed was appreciable at all the pH studied and the amount of CR removed increased with increase in the flocculation time. The kinetics of the flocculation process was studied by fitting the data obtained to a kinetic model and the flocculation rate constant increased with increase in the initial CR concentration.

Keywords: Cassava starch; Alum; Coagulant-aid; Congo red; Coagulation kinetics; Acid dye; Bioflocculant; Flocculation

1. Introduction

Treatment of water and wastewater involves a number of unit processes whose success depends on the quality of water source, process economy and regulatory guidelines or standards. The economy of the unit processes, required to achieve the desired quality and quantity of water, depends amongst other things on the cost and availability of requisite chemicals. The conventional chemicals used for water treatment are synthetic organic and inorganic chemicals. Aside the high cost, which made them unaffordable in some regions of the world, many of the chemicals have also been reported to impact grievous health risks. Premised on this, water treatment professionals are shifting attention to the use of materials of biological origin in the water and wastewater treatment unit processes.
In coagulation and flocculation, for example, the use of the conventional coagulants (i.e., the hydrolyzing metal salt based on Al and Fe and synthetic polyelectrolytes) are being discouraged while the use of biocoagulants and bioflocculants are been encouraged. The materials of biological origin that have been used in coagulation and flocculation processes include *Moringa oleifera* (Ndabigengesere and Narasiah, Olsen 1987; Jahn, 1988), Nirmali (Tripathy et al., 1976), Okra (Al-Samawi and Shokrala, 1996), *Cactus latifera* and *Prosopis julifora* (Diaz et al., 1999), tannin from valonia (Ozacar and Sengil, 2000; 2003), apricot, peach kernel and beans (Jah, 2001), maize (Ragiwanshi et al., 2002), extract of plantain peel ash (Oladoja and Aliu, 2008), snail shell (Oladoja and Aliu, 2009 and 2011) and tannin (Oladoja et al., 2011).

In the present studies, the ability of cassava starch (CS) to act as coagulant aid in the decolouration of an anionic dye (Congo red) contaminated water, using alum as the primary coagulant, shall be studied. Starch is a simple food commodity which has been studied for non-food applications for many years (Whistler et al., 1984). Starch is a polysaccharide originated from plants as renewable resources. With an increasing awareness of environmental problems in recent years, versatile applications has been found for starch in many areas such as flocculants, adhesives, biodegradable plastics and drug delivery system. Due to their availability and cost, modified starches have also been used in many non-food applications. Cationic starches and starch phosphate esters have been used as adhesives and coatings in papermaking, as flocculant in water and as sizers in textiles (Shey et al., 2006).

Starch itself may be used as flocculant (Aigian et al., 2004). However, its flocculation efficiency is low, possibly due to the poor cationic charge density. As a flocculant, starch is generally modified in other to obtain products of good flocculation efficiency. Modification of starch produces starch of good flocculation properties but some of the properties that make it attractive as a natural material (e.g. biodegradability, non-toxicity) are lost via this process. Furthermore, chemical modification, often, introduces persistent chemicals that are not eco-friendly into the environment. Consequent upon this, the present studies aimed at the use of unmodified starch, obtained from cassava, as coagulant aid in the alum coagulation of anionic dye, congo red (CR), from aqua system. In order to achieve this, the optimum alum dose for CR coagulation shall be determined by method of continuous variation of the alum dose. The ability of starch to act as a coagulant shall also be studied. The ability of starch to act as coagulant aid in the coagulation of CR dye molecules shall be studied by combining different dosages of starch with a fixed alum dosage (i.e. 50% of the optimum alum dose). The process operating variables (pH and flocculation time) shall be optimized by method of continuous variation and the coagulation-flocculation kinetics shall be evaluated.

2. Materials and Methods

Starch Preparation and Characterization
Cassava (*Manihot utilissima*) starch was obtained from a cassava starch processing plant (Matna Foods, Ogbese, Ondo State) in Nigeria. The CS was used as obtained from the factory, without further purification.

The CS powder was characterized thus: The apparent amylose (AAM) content (%) was determined by colorimetric iodine assay index method (Juliano, 1985). The moisture, protein, lipid, and ash content were determined following the AACC (2000) procedure and the phosphorus content was
determined using the AOAC (1995) method. The bulk density was determined by the method of Wang and Kinsella (1976) while the starch dispersibility was determined by the method of Kulkarni et al., (1991).

**Dye Preparation and quantification**
The dye used in the present studies, CR (C.I. 2212), chemical formula \( \text{C}_{32}\text{H}_{22}\text{N}_{6}\text{Na}_{2}\text{O} \lambda_{\text{max}} = 500 \text{nm} \) was accurately weighted and dissolved in distilled-deionised water to prepare the stock solution (1000mg/l). Different working solutions were prepared from the stock solution by serial dilution. The CR concentrations in the aqua medium were quantified by the determination of the absorbance at the characteristic wavelength using a double beam UV/Visible spectrophotometer. Standard solution of the dye was taken and the absorbance was determined at different wavelengths to obtain a plot of absorbance versus wavelength. The wavelength corresponding to the maximum absorbance \( \lambda_{\text{max}} \), as determined from this plot, was noted and the wavelength was used for the preparation of the calibration curve, used for the quantification of residual dye concentration in the present studies.

**Coagulation Experiment**
The conventional jar test procedure with a six unit multiple stirrer system was used. Alum, the primary coagulant was added to the samples of the synthetic CR contaminated water and rapid mixing was performed at 200rpm for 2min. A flocculation time of 20min was allowed and then 30min settling time. When alum was used alone, as the primary coagulant, different concentrations \((10–200\text{mg/l})\) of the CR solutions were prepared and varying dosages of the alum, ranging from \(100\text{mg/1} – 600\text{mg/l}\) were added.

When CS was used as a coagulant aid, the CS was added after the rapid mixing and the other procedures were followed accordingly. In this experiment, different dosages of the CS \((0.5–3\text{g})\) was used as a primary coagulant in the removal of different concentrations \((10–200\text{mg/l})\) of CR. The effect of alum/CS combination was studied at fixed alum concentration \((50\%\text{ of the optimum alum dose})\) and varying CS dosages \((0.5–3\text{g/l})\).

Optimization of the coagulation process was performed by method of continuous variations of two reaction conditions viz: pH \((3, 4, 5, 6)\), and flocculation time \((5, 10, 20, 30, 60, 90, 120)\).

### 3. Results and Discussion

**CS Characterization**
The physicochemical characteristics of the CS are presented in Table 1. The pH of the CS is close to neutral (6.56), which made it suitable for application in water treatment, since the pH of natural water is neutral. The value of the bulk density of the CS \((0.54\text{g/mL})\), which is a measure of the degree of coarseness of starch sample, is moderate. This shows that the particles of the CS are moderately smooth. Dispersibility is a measure of reconstitution of starch flour in water. The higher the dispersibility, the better the flour reconstitutes in water (Kulkarni et al., 1991). The value of dispersibility of the CS \((85.02)\) is very high which showed that it reconstitutes in water very easily. The lipid content in CS was within the range reported for most tuber and root starches \((0.1-1.14\%)\) (Hoover, 2001), but the protein content was lower than that reported (Elevina, et al., 2005).
Table 1 Physicochemical Characteristics of CS

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.5±0.03</td>
</tr>
<tr>
<td>Bulk density</td>
<td>0.54±0.04</td>
</tr>
<tr>
<td>Dispersibility</td>
<td>85.02±0.07</td>
</tr>
<tr>
<td>Moisture</td>
<td>8.07±0.30</td>
</tr>
<tr>
<td>Protein</td>
<td>0.10±0.40</td>
</tr>
<tr>
<td>Lipid</td>
<td>0.10±0.20</td>
</tr>
<tr>
<td>Ash</td>
<td>0.20±0.01</td>
</tr>
<tr>
<td>Amylose</td>
<td>22.00±0.21</td>
</tr>
<tr>
<td>Amylopectin</td>
<td>78.00±0.30</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.007±0.30</td>
</tr>
</tbody>
</table>

Determination of the optimum alum dose

The ability of alum to coagulate the CR dye molecules from the aqua system was studied by the addition of different dosages of alum (100, 200, 300, 400, 500 and 600 mg/l) to the CR solution. Different initial concentrations of CR contaminated aqua system were prepared. The results obtained from the different studies (Fig I) showed the coagulating ability of alum for this dye. The percentage of CR removal increased with increase in the alum dosage. At low CR concentration (10 and 25 mg/l), the percentage of the dye removed at low alum dosage was very high (>80%) whereas when the CR concentration was increased from 50 – 200 mg/l, the percentage of CR removed was relatively low at low alum dosage. Although the percentage of CR removed at low alum dosage was low in high CR concentration, it is noteworthy that the amount (in mg/L) was higher than that of low CR concentration.

Fig. 1. Results of the determination of the optimum alum dose for the coagulation of CR from aqueous solution
At low CR concentration, the variation in the percentage of CR removed as the alum dosage was increased was negligible. Hence, it could be concluded that the optimum alum dose was attained at low alum dosage. At high CR concentration, the magnitude of the percentage of CR removed increased as the alum dose was increased (Fig 1).

CR (1-naphthalenesulphonic acid, 3,3- (4,4- biphenylenebis (azo) bis (4-amino-) disodium salt) is a benzidine based anionic diazo dye. This dye metabolizes to benzidine, a known human carcinogens. Owing to the structural stability, CR is difficult to biodegrade. In the aqueous solution, the acid dye is first dissolved and the sulphonlic group of the acid dye (CR-SO\textsubscript{3}Na) is dissociated and converted to anionic dye ions viz:

\[
\text{CR-SO}_3^\text{Na} \rightarrow \text{CR-SO}_3^- \text{Na}^+
\]

Alum (the coagulant used) is a hydrolyzing metal salt based on aluminum. It has a high cationic charge (Al\textsuperscript{3+}) which makes them effective colloidal destabilization. Since the CR molecule is anionic in nature and the coagulant used (alum) is cationic, an interaction between the two species is expected and this interaction produced an insoluble aluminium salt. The interaction between these two species could be represented thus:

\[3\text{CR-SO}_3^- + \text{Al}^{3+} \rightarrow \text{Al}[\text{CR-SO}_3]_3\]  
(Insoluble aluminium salt)

The insoluble aluminium salt initially forms micro flocs (coagulation) which gradually grow to become macro flocs (flocculation). Over time, the macro flocs get settled and clear water is produced

**Determination of optimum starch dose**

The ability of starch to act as primary coagulant in the coagulation of CR dye molecule from aqueous solution was studied by varying the dosage of starch added to the different concentrations of CR dye solution (10, 25, 50, 100 and 200 mg/l). The results obtained from the experiment showed the poor coagulating ability of starch in CR dye molecule coagulation. The highest percentage of CR (66%) was removed from the 200 mg/l CR dye solution while for the other CR dye concentrations used (10 – 100 mg/l), the percentage removed was lower than 50%. The ability of starch to remove the CR dye molecule was poorer at lower CR concentrations (Fig 2).
Starch contains an abundance of hydroxyl groups. Each anhydroglucose unit contains two secondary hydroxyls and a large majority contains primary hydroxyls. Considering the nature of hydroxyl functional group on starch, non-ionizing, an interaction between the CR dye molecule (anionic) and the functional group could be poor. The results obtained from the present studies showed a possible interaction, though poor, between the CR dye molecule and the starch molecule. Despite the poor ionization potential of the functional group on starch, it is assumed that the ionization of the OH group on the starch molecule could occur in different forms, which is pH dependent. This makes the starch molecule to be susceptible to different forms of reactions. The different possible forms of ionization of the functional group are presented below:

i) **Dissociation:**  
$$\text{ROH} \rightarrow \text{RO}^- + \text{H}^+$$

ii) **Accept a proton:**  
$$\text{ROH}^- + \text{H}^+ \rightarrow \text{ROH}_2^+$$

Since the different ionic forms are pH dependent and the present studies were conducted at the natural pH of the CR dye (pH 6.7) it is possible that few of the OH groups accepted protons from the aqua medium. This confers positive charges on the surface of the starch molecule and made electrostatic attraction possible between the CR dye molecule and the CS molecule.

**The use of starch as coagulant aid**

The inorganic salt, aluminium sulphate (alum) is one of the most widely used coagulants in conventional water and wastewater treatment. However, since high concentration in water may
have human health implications, a reduction in the quantity used is required. In order to assess the ability of CS to act as coagulant aid in the alum coagulation of CR dye molecule, half of the quantity of the optimum alum dose obtained from the different coagulation experiments was used as the primary coagulant and varying dosages of the CS was used as coagulant aid. The alum/CS combination was used in the treatment of different concentrations of CR dye molecules.

The results obtained from the different studies are presented in Fig 3. The results showed that the magnitude of CR dye molecule abstracted from the aqueous solution was very high for all the concentrations studied. This is evident in the value of percentage CR removed in each case. When this combination was used in the treatment of CR dye solution containing 10 mg/l, the value of percentage CR dye molecule removed was greater than 96%, even at the lowest starch dose (0.5 gm/L). The percentage of CR removed increased with increase in starch dose from 0.5g/L to 2.5g/L (at 0.5g intervals).

![Fig. 3. Results of the determination of the optimum alum/starch dose for the removal of CR from aqueous solution](image)

An increase in the starch dose from 2.5g/L witnessed a reduction in the value of percentage CR removed from 98.32 to 96.00. This same trend was observed in all the concentrations studied. The efficiency of the alum/starch combination increased with increase in concentration of the CR dye molecule. For concentrations of 100 and 200 mg/l, the values of the percentage of CR dye molecule removed were greater than 99%.

**Effect of pH**

The effects of pH on the removal of CR from aqua system were studied between the pH value of 3-6, at three different initial CR concentrations and at the optimum alum/starch combination ratio. It was observed that the removal of CR from solution was favored at acidic pH. The values of the percentage CR dye removed was greater than 99% at all the pH of interest and all the concentrations (50, 100 and 200 mg/l) studied. Mall et al., (2005) reported that pH affects the
structural stability of CR and therefore its colour intensity and that the colour of CR dye solution is stable at pH around 7. Furthermore, maximum colour removal was obtained at pH 3 to 13. It was concluded that the colour removal due to pH change alone may be due to the structural changes being effected in the molecules (Mall et al., 2005). When the experiment was conducted at the natural pH of the CR (pH 6.7), the values of the percentage CR removed was not less than 99% in almost all the concentrations studied. Hence we can infer that pH has no negative effects on the removal of CR dye molecule from solution and that the possible structural change, occasioned by the change in pH did not affect the interaction between the dye molecule and alum-starch complex used for the coagulation.

**Effect of settling time**

The coagulation-flocculation process is made up of three distinct stages. The first step involves the addition of coagulant/coagulant aid which is followed by rapid and high intensity stirring of the mixture. The slow stirring of the suspensions obtained from the fast stirring, is the second stage. At the last stage, an end is put to the stirring and the floc is allowed to settle. In the coagulation-flocculation process, the settling speed of the sludge is very important since this parameter influences the design of the water and wastewater treatment plant. The present studies aimed at investigating the effect of time on the settling of the macro flocs formed for this process. This effect was monitored at 5, 10, 20, 30, 60 and 120 minutes. The results obtained are presented in Fig 4.

![Graph](image.png)

**Fig. 4.** Results of the effect of time on flocculation
It was observed that the sedimentation of the macro floc from this process was very fast and at 10 minutes, the residual dye concentration in the suspension was less than 1%. The settling profiles of the flocs formed from this experiment do not display any significant difference in sludge characteristics with change in the initial dye concentration.

**Flocculation kinetics**

In order to understand the kinetics of the coagulation-flocculation of CR dye molecule using alum as the primary coagulant and starch as the coagulant aid, the time concentration profile of the process was analyzed by using the following equation proposed by Pan et al., 2006.

\[
Q_t = Q_0[1 - \exp(kt^{1/2})]
\]

The removal rate \( R_t \) (mg/l/min) can therefore be described as follow:

\[
R_t = \frac{dQ_t}{dt} = -0.5Q_0kt^{-1/2}\exp(kt^{1/2})
\]

Where \( Q_t \) (mg/l), is the amount of CR dye molecule removed at time \( t \), \( Q_0 \) is the initial concentration of CR dye molecule (mg/l), \( k \) is the flocculation rate constant.

The data obtained from the analysis of the values obtained from the flocculation kinetics studies are presented in Table 2. The flocculation rate constant increased with increase in the initial CR concentration. The values of the \( Q_0 \) (i.e. the initial concentration of the CR), obtained from the plot, was close to the actual initial concentration of the CR.

The optimization procedure requires an error function to be defined in order to be able to evaluate the fit of the equation to the experimental data. Unlike the linear analysis, different forms of equation would affect \( r^2 \), significantly, and impact the final determination, where non-linear chi-square analysis would be a method of avoiding such errors. In this study, linear coefficient of determination and nonlinear Chi-square were used. The results obtained when the \( r^2 \) was used (Table 2) showed a poor fitting of the equation to the experimental data.

**Table 2** Flocculation kinetics parameters

<table>
<thead>
<tr>
<th>Initial CR concentration (mg/L)</th>
<th>K(mg/L/min)</th>
<th>( Q_0 )</th>
<th>( r^2 )</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>4.8639</td>
<td>47.01</td>
<td>0.294</td>
<td>0.1902</td>
</tr>
<tr>
<td>100</td>
<td>5.1413</td>
<td>94.98</td>
<td>0.300</td>
<td>0.2520</td>
</tr>
<tr>
<td>200</td>
<td>5.458</td>
<td>192.5</td>
<td>0.300</td>
<td>0.2813</td>
</tr>
</tbody>
</table>

The analysis of the same experimental data with Chi square test statistics (\( \chi^2 \)) revealed that the value of the \( \chi^2 \) were small which showed that the equation was suitable for the description of the flocculation kinetics of this system. Similar contradictory results in the use of error analysis for the determination of the best fit of equations have been reported by Mall et al., 2005, Wong et al., 2004. Consequent upon the ability of this equation to describe the flocculation process, the values of the parameters obtained from the fittings of the equation (1) to the experimental data were fitted into
equation (2) to predict the removal rate, \( R_t \) (mg/L/min) at each time. The results obtained from these fittings are presented in Table 2. The results presented in Table 2 showed that the removal rate reduced with increase in time for all the initial concentration studied.

**Table 3** The removal rate constants, \( R_t \) (mg/L/min) for the coagulation of CR using alum/starch combination

<table>
<thead>
<tr>
<th>( t^{1/2} )</th>
<th>200mg/L</th>
<th>100mg/L</th>
<th>50mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.24</td>
<td>1.2 x 10^{-3}</td>
<td>11 x 10^{-3}</td>
<td>9.5 x 10^{-4}</td>
</tr>
<tr>
<td>3.16</td>
<td>5.4 x 10^{-6}</td>
<td>6.8 x 10^{-6}</td>
<td>7.6 x 10^{-6}</td>
</tr>
<tr>
<td>4.47</td>
<td>3.0 x 10^{-9}</td>
<td>5.0 x 10^{-9}</td>
<td>9.3 x 10^{-9}</td>
</tr>
<tr>
<td>5.48</td>
<td>9.8 x 10^{-12}</td>
<td>2.6 x 10^{-11}</td>
<td>5.6 x 10^{-11}</td>
</tr>
<tr>
<td>7.75</td>
<td>2.9 x 10^{-17}</td>
<td>1.6 x 10^{-16}</td>
<td>6.3 x 10^{-16}</td>
</tr>
<tr>
<td>10.95</td>
<td>5.3 x 10^{-25}</td>
<td>7.9 x 10^{-24}</td>
<td>7.7 x 10^{-23}</td>
</tr>
</tbody>
</table>

In order to further assess the ability of the flocculation kinetics equation proposed by Pan (2006) to correlate with experimental data, the theoretical plots of the \( Q_t \) versus \( t^{1/2} \) are shown with the experimental data for the flocculation of CR by Alum/Starch combination in Fig. 5.

![Fig. 5. Fitting of the kinetic experimental data to the predicted values](image)

**4. Conclusion**

CS acts effectively as coagulant aid in the alum coagulation of CR from aqueous solution. The effect of pH on the removal of CR was not noticeable but the percentage of CR removed was appreciable at
all the pH studied. The amount of CR removed increased with increase in the flocculation time. The linearities of the plots of the flocculation kinetic were very poor but the non-linear chi-square test ($\chi^2$) results was good and showed a good fit of the experimental data to the theoretical data.

References


