

A COMPARATIVE STUDY OF COPPER, ZINC AND ALUMINIUM AS ELECTRODES IN THE PREPARATION OF STARCH-BASED POLYELECTROLYTE

ABSTRACT

Alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) has been the coagulant mostly used in the water treatment process. Alum imported into the country gets stuck at the port because of the congestion of the port. When alum is used to coagulate water, it depresses the pH of the water, thus, requiring a pH booster. Because of the high dependence on alum, alternative coagulants produced with local raw materials will be of great advantage. A starch-based polyelectrolyte was prepared by dispersing 3 g of cassava starch and 10 g of heaping teaspoon of high-test granular calcium hypochlorite (commercially available as HTH) in 100 ml distilled water; making it up to a litre solution with hot distilled water (temperature $80^\circ\text{C} - 100^\circ\text{C}$) and electrolysing by means of stabilized power supply using aluminium rods as electrodes to produce polyelectrolyte A. Copper rods and zinc rods were similarly used to polyelectrolyte B and polyelectrolyte C respectively. To test the effect(s) and interaction of the charging variables, i.e. separating distance, power supply and time of charging, a three-factor experiment (2^3 factorial design) was carried out. The variables were operated at High Level (+) and Low Level (-). The analysis indicates that the power of charging has the most significant effect on the coagulation characteristics of the starch-based polyelectrolyte. Polyelectrolytes A and C were tested with raw water drawn from Opa dam and were found to be effective water coagulants. Polyelectrolyte B on the other hand, adds to the turbidity of the raw water with which it was tested. Polyelectrolyte A was found to be as effective as Alum at natural water condition (pH 7) causing better than 88% turbidity removal with the dosage of 65 mg/l.

Keywords: Comparative, Starch-based polyelectrolyte, alum, coagulant, surface water treatment.

1. INTRODUCTION

Water which is absolutely pure is not found in nature, every water vapour condensing in the air contains solid and dissolved gases. As condensed waterfalls it sweeps up other material from the air and becomes contaminated on reaching the ground, running over the surface and percolating through the various strata of the soil [1]. These contaminants may be removed by passage through the soil as a result of filtration and exchange and adsorption reactions; some may be removed from the surface water by sedimentation and biological activity; others may be removed by the specifically engineered process in water treatment plants. New impurities are introduced by dissolution and exchange reactions in the soil, others by the accumulation of decomposition and reactions with the materials of the distribution system [2]. In order to provide a potable water supply, raw water from the source has to be treated. The source may be a river, reservoir, well or natural lake. Each of these sources has its own peculiar impurities and means of

42 removing them. A large portion of the suspended particles in water is sufficiently small that their removal
43 in the sedimentation tank is impossible at a reasonable surface overflow rate [3]. Coagulation is also
44 called chemically assisted sedimentation; it is the process of causing the finely divided particles in water
45 to cluster together and form larger particles (flocs) and later settle before passing the water to the filter [4].
46 The four major mechanisms of coagulation are double-layer compression, adsorption and charge
47 neutralisation, enmeshment in a precipitate and adsorption by polymers, and inter-particle bridging. The
48 understanding of the four processes is necessary for understanding the phenomena of coagulation [5].
49 The coagulation unit is essential in the removal of impurities and alum (aluminium sulphate) is the most
50 common coagulating agent. There is a need for the local substitute due to the rapid increase in the
51 number of water treatment plants and the constantly increasing cost of alum. Cationic starches have long
52 been used to flocculate negatively charged particles from aqueous suspension. Safi *et al.* [6] reported the
53 preparation of 2-aminoethyl ether derivatives of starch which readily flocculated aqueous suspensions of
54 negative colloids. Salim *et al.*[7] reported the use of high molecular weight polyamines, polyalkylamines
55 and polyacrylonitriles as flocculating materials. Cationic quaternary ammonium starch ether which was
56 found to be an excellent flocculant for materials in an aqueous system [8].
57 Though these starches are effective flocculating agents for aqueous suspension of negatively charged
58 inorganic and organic particle. Their precise modes of operation were not precisely understood. Sirin [9]
59 was able to give a simple explanation, the simple ionic attraction between the product formed and the
60 colloidal particles leading to the production flocculants – particle aggregates large enough to settle from
61 the suspension; the polyelectrolyte, according to his discovery also form bridge structure that leads to
62 precipitation. Tenney *et al.* [10] explained that many of the suspended particles in raw water are too small
63 to settle out by themselves in a separation by sedimentation process. The benefit of adding polymer is
64 derived from the agglomeration of these individual particles into larger clumps or flocs allowing them to
65 settle and be removed. The list of synthetic polymers which have been successfully applied to the
66 treatment of water.

67

68 2. MATERIALS AND METHODS

69 Locally purchased cassava was peeled and washed. They were then crushed, with a cassava grater
 70 machine (it's a machine which makes shreds of cassava), then oaked for some time in the water after
 71 which they were sieved. The filtrate was allowed to settle for some hours and the settled starch was
 72 separated from the water by careful decantation of the topwater. The residue was then air-dried,
 73 grounded and stored in a desiccator to prevent the adsorption of water vapour from the atmosphere. The
 74 material obtained from this process was then used in the preparation of the starch-based polyelectrolyte.

75 **2.1. Preparation of Starch-based Polyelectrolyte**

76
 77 Tablets of calcium hypochlorite ($\text{Ca}(\text{OCl})_2$), commercially available as HTH, were ground and stored in a
 78 desiccator [11]. Three gram of starch and 10 g of hypochlorite were made into a well-mixed slurry with
 79 100 ml distilled water in a one-litre beaker. Hot distilled water ($70^\circ\text{C} - 100^\circ\text{C}$) was added to the slurry,
 80 making it up to a litre solution with continuous stirring. The resulting solution was electrolysed on a
 81 stabilized power supply with aluminium rods, copper rods and zinc rods as electrodes one after the other,
 82 to produce polyelectrolytes A, B and C respectively. The solution was gently stirred in each case
 83 throughout the process of charging. The variables i.e. power, P, separating distance, D and time of
 84 charging, T; were tested at the high level (+) and low level (-) for each of the electrodes to generate a 2^3
 85 factorial runs for each of the electrodes (Tables 1 and 2).

86

87 **Table 1: Electrolysing Variables Values at High and Low Levels**

Variable	High Level (+)	Low Level (-)
Power product of voltage and current (watts)	400	100
Separating distance (mm)	150	50
Time of charging (min)	60	30

88

89

90

91 **Table 2: Factorial Design Table**

Run	1	2	3	4	5	6	7	8
Power, P (Watts)	-	+	-	+	-	+	-	+

Separating Distance, D (mm)	-	-	+	+	-	-	+	+
Time, T (mins)	-	-	-	-	+	+	+	+

92

93 2.2. Coagulation of Water Samples

94 Raw water from the university dam, Opa Dam, was collected and used in testing the effectiveness of the
 95 starch-based polyelectrolyte as a coagulant under neutral condition i.e. natural water, pH 7.

96 Treatment in each case consisted of dosing varying amount of the prepared polyelectrolyte into the water,
 97 mixing rapidly for 60 seconds and then slowly for 10 minutes in a jar test stirrer. The water was then
 98 allowed to settle for 30 minutes. Coagulation effectiveness was determined by measuring the turbidity of
 99 the water sample before and after treatment using a Hach's Model 2100A turbidimeter.

100

101

102 3. RESULTS AND DISCUSSION

103 Preliminary coagulation test carried out with the starch-based polyelectrolyte as coagulant revealed the
 104 following: the ratio of hypochlorite to starch must not be less than 3; the polyelectrolyte can be stored at
 105 room temperature for more than 12 days without materially losing its effectiveness as a coagulant; a
 106 better turbidity removal can be achieved if the settling time is increased; and when water at natural pH
 107 and temperature was used to make the slurry to a litre solution without stirring, the turbidity removal is
 108 relatively low compared with when hot distilled water is used with continuous agitation [12].

109 3.1. Comparing the Effectiveness of the Polyelectrolytes

110 Varying amounts, in millilitres, of the polyelectrolytes, were used to treat litres of raw water sample
 111 (turbidity, 28 NTU). Table 3 shows the conversion from millilitre to milligrams per litre; the conversion is on
 112 the basis that 1 mg/l of the solution prepared as indicated in the preceding contain 3 mg/l of starch and 10
 113 mg/l of hypochlorite and that when 1 ml is dosed into a litre of water sample, the dosage is 3 mg/l
 114 expressed in term of combination of hypochlorite and starch (i.e. in terms of polyelectrolytes itself).

115 **Table 3: Expression of Polyelectrolyte (ml) in terms of Dosage (mg/l)**

The volume of coagulant per litre (ml)	Polyelectrolyte expressed as		
	Starch (mg/l)	Hypochlorite (mg/l)	Polyelectrolyte (mg/l)
0	0	0	0
2.5	7.5	25.0	32.5
5.0	15.0	50.0	65.0
7.5	22.5	75.0	97.5
10.0	30.0	100.0	130.0
12.5	62.5	125.0	187.5
15.0	75.0	150.0	225.0

116

117 Table 4 shows the relative performance of varying dosages of polyelectrolytes A, B and C under neutral
 118 condition. The performance of polyelectrolyte A is generally better than those of B and C at neutral pH.
 119 Polyelectrolyte B, on the other hand, increases the turbidity of the water with which it was tested. The
 120 percentage of turbidity removals were computed based on Table 4 for polyelectrolytes A, B and C for
 121 each experimental run. Table 5 shows that polyelectrolyte A at pH 7 performs generally better than
 122 polyelectrolytes B and C.

123

124

125

126

127

128

129

130

131

132 **Table 4: Relative effects of varying dosages of polyelectrolytes A, B and C on turbidity**
 133 **removal and pH of treated water samples**

Dosage	Polyelectrolyte C	Polyelectrolyte B	Polyelectrolyte A
--------	-------------------	-------------------	-------------------

(mg/l)	Final turbidity (NTU)	Final pH	Final turbidity (NTU)	Final pH	Final turbidity (NTU)	Final pH
0						
15	13.2	7.8	42.2	7.6	6.2	7.7
32.5	11.6	7.7	43.4	7.6	4.8	7.7
65	9.8	7.6	44.0	7.5	3.8	7.5
97.5	10.0	7.4	44.0	7.4	4.2	7.4
130	12.4	7.3	44.7	7.4	5.6	7.4

134

135 Table 5: Summary of Percentage Turbidity Removal of Polyelectrolytes A, B and C

Dosage (mg/l)	Percentage Turbidity Removal		
	Polyelectrolyte A	Polyelectrolyte B	Polyelectrolyte C
130	63.52	-18.26	45.48
97.5	70.39	-17.8	50.15
65	74.8	-16.44	52.68
32.5	70.48	-14.46	49.08
15	59.75	-12.95	43.84

136

137

138

139

140

141 3.2. Main Effect and Interaction of Charging Variables by Factorial Analysis

142 The main and interaction effect(s) were used to determine the level of influence the factors had on one
 143 another and how the influence was occurring (Uduman *et al.*, 2010). Table 6 shows a summary of these

144 results. It can be seen that power had the most significant main effect on the coagulation characteristics
 145 of the starch-based polyelectrolyte while the highest level of interaction effect was observed between the
 146 separating distance and the time of charging.

147

148 **Table 5: Summary of main effect and interaction effect of the charging variables**

Effect	Polyelectrolyte A	Polyelectrolyte B	Polyelectrolyte C
Mean	74.75	27.98	52.63
P	19.0	-21.07	17.25
D	-0.5	8.43	1.25
PD	0	2.17	-1.75
T	1.0	5.97	1.25
PT	-3.5	-3.68	4.25
DT	-7.0	1.98	-8.75
PDT	2.5	-12.03	-0.75

149
 150

151 **4. CONCLUSION**

152 Based on the results, the following conclusions could be drawn: when 3 g of cassava starch and 10 g of
 153 calcium hypochlorite are dispersed in hot distilled water and charged, the resulting product, starch-based
 154 polyelectrolyte, is effective in coagulating raw water. A dosage of 65 mg/l of polyelectrolytes A and C
 155 results in 88% and 69% turbidity removal respectively. The same dosage of polyelectrolyte results in
 156 7.5% turbidity addition.

157 Polyelectrolyte A performs generally as well as an alum but does not depress the pH as alum does. This
 158 means that the starch-based polyelectrolyte needs little or no lime to aid it in the reduction of potable
 159 water at the neutral pH range. The solution is stable at room temperature.it neither spoils nor loses its
 160 coagulation effectiveness for at least 12 days. Power supplied during the charging process has the most
 161 significant effect on the coagulation characteristics of the starch-based polyelectrolyte while the highest
 162 level of interaction effect is between separating distance and time of charging.

163 **REFERENCES**

- 164 [1] Gerde J. A., Yao, L. X., Lio, J. Y., Wen, Z. Y. & Wang, T. (2014). Microalgae flocculation:
165 Impact of flocculant type, algae species and cell concentration. *Algal Research-Biomass*
166 *Biofuels and Bioproducts* **3**, 30-35.
167
- 168 [2] Ellis, A.E., Stanley, I.U., Abiola, O. and Ogedengbe, M.O. (1981). "Preparation of cationic
169 starches as flocculants for water." *Water Resources*. Vol. 16, pp. 1433 – 1435.
170
- 171 [3] Granados, M. R., Acien, F. G., Gomez, C., Fernandez-Sevilla, J. M. & Grima, E. M. (2012).
172 Evaluation of flocculants for the recovery of freshwater microalgae. *Bioresource Technology*
173 **118**, 102-110.
174
- 175 [4] Lee, A. K., Lewis, D. M. & Ashman, P. J. (2014). Microbial flocculation, a potentially low-
176 cost harvesting technique for marine microalgae for the production of biodiesel. *Journal of*
177 *Applied Phycology* **21**, 559-567.
178
- 179 [5] Rashid N., Rehman, S. U. & Han, J. I. (2013). Rapid harvesting of freshwater microalgae using
180 chitosan. *Process Biochemistry* **48**, 1107-1110.
181
- 182 [6] Safi C., Zebib, B., Merah, O., Pontalier, P. Y. & Vaca-Garcia, C. (2014). Morphology,
183 composition, production, processing and applications of *Chlorella vulgaris*: A review.
184 *Renewable & Sustainable Energy Reviews* **35**, 265-278.
185
- 186 [7] Salim S., Bosma, R., Vermue, M. H. & Wijffels, R. H. (2011). Harvesting of microalgae by
187 bioflocculation. *Journal of Applied Phycology* **23**, 849-855.
188
- 189 [8] Sanchez J. F., Fernandez, J. M., Acien, F. G., Rueda, A., Perez-Parra, J. & Molina, E. (2008).
190 Influence of culture conditions on the productivity and lutein content of the new strain
191 *Scenedesmus almeriensis*. *Process Biochemistry* **43**, 398-405.
192
- 193 [9] Sirin, S. (2012). Harvesting the microalgae *Phaeodactylum tricornutum* with polyaluminum
194 chloride, aluminium sulphate, chitosan and alkalinity-induced flocculation. *Journal of Applied*
195 *Phycology* **24**, 1067-1080.
196
- 197 [10] Tenney M. W., Echelber, Wf, Schuessl, Rg & Pavoni, J. L. (1969). Algal flocculation with
198 synthetic organic polyelectrolytes. *Applied Microbiology* **18**, 965-&.
199
- 200 [11] Uduman N., Bourniquel, V., Danquah, M. K. & Hoadley, A. F. A. (2011). A parametric study
201 of electrocoagulation as a recovery process of marine microalgae for biodiesel production.
202 *Chemical Engineering Journal* **174**, 249-257.
203
- 204 [12] Vandamme D., Foubert, I., Fraeye, I., Meesschaert, B. & Muylaert, K. (2012). Flocculation
205 of *Chlorella vulgaris* induced by high pH: Role of magnesium and calcium and practical
206 implications. *Bioresource Technology* **105**, 114-119.
207