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FLOCCULATION CHARACTERISTICS OF POLYACRYLAMIDE-SODIUM CARBOXYL METHYL CELLULOSE GRAFT COPOLYMER

Kevin I Idehen

Petroleum Processing Department, Petroleum Training Institute, PMB 20 Effurun, Delta State, Nigeria

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Preparation of polyacrylamide- sodium carboxyl methylcellulose graft having a percentage graft on level of 527.21% and graft polyacrylamide chains of 1.22×10^5 viscosity average molecular weight is described. A comparative water treatment study with particular emphasis on the flocculation potentials of the graft copolymer with aluminium sulphate, ferric sulphate and polyacrylamide using Warri River water sample is reported. The graft copolymer was not only found to exhibit relatively good flocculation characteristics but was significantly found not to impact treated water with any polymer residue. When used with aluminium sulphate in the ratio of 4:1, the turbidity of test water improved from 43.4 NTU to as low as 0.008 NTU.

Key words: Graft copolymer, Flocculation characteristics, Polyacrylamide, Water turbidity, Water treatment, Polymer residue, Sodium carboxy methylcellulose.

Introduction

Water for domestic and industrial uses are drawn from several sources which include rivers, lakes and wells. The quality of source water can be broadly ascertained by parameters such as level of suspended solids, dissolved solids and microbial population, which directly or indirectly accounts for the turbidity, odor and taste in water. The turbidity of water is very important in producing products destined for human consumption and in several manufacturing uses. Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through the sample. Thus, turbidity in water can be caused by harmful organisms, particles that feed them or particles that can shield them from disinfections processes. These include suspended mater such as clay, silt, finely divided organic and inorganic matter, soluble colored organic compounds, plankton and other microscopic organisms.

Water turbidity is treated conventionally by the use of coagulation and flocculation chemicals or reagents, such as, aluminium salts and iron salts prior to filtration. More recently aminated starch and high molecular weight polyamines have been employed in place of the inorganic coagulants (Black and Vilaret 1969). A major drawback of the latter is that they alter the pH value of treated water and at low pH values metal ions or their soluble complexes pass through the pores of the filters readily only to form insoluble species in storage reservoirs and distribution lines (Nojiri 1980). Although organic flocculants are not known to significantly affect the pH value of treated water they however have the tendency of impacting treated water with trace amounts of their organic composition (Crummett and Hemmel 1963). With the foregoing problems in mind this paper reports on the preparation of polyacrylamide-carboxyl methyl cellulose graft copolymer and a comparative study of the flocculation properties of the graft copolymer with conventional chemicals such as aluminium sulphate, ferric sulphate and polyacrylamide using composite water sample from a popular river in the crude oil rich Niger Delta area of Nigeria.

Experimental

Materials and carboxymethylation. Acryl amide monomer from Cambrian Chemicals was purified by recrystallization from chloroform. Ceric ammonium nitrate from BDH Ltd. was used without further purification. Holocellulose from *Terminalis superba* (white afara) wood meal was obtained as described previously (Okieimen and Idehen 1988). The cellulose was carboxymethlated using the standard solvent method with monochloroacetate/ sodium hydroxide in an isopropanol/ water mixture reported by Heinze *et al* (1994).

Graft copolymerization. Graft copolymerization of acrylamide onto carboxymethyl cellulose was carry out at 29^{0}C using a semi-contineous polymerization procedure. 1.0g of carbonylmethyl cellulose was dissolved in 50ml of aqueous medium and initiated with 5ml of 10.00mmoles l^{-1} of ceric ammonium nitrate solution for 15min.

After the initiation, 15ml of the initiator and 20ml of 40mmoles l^{-1} of monomer were introduced in a drop wise manner simultaneously into the reaction flask with stirring continuously for 1 h. The polymerization was stopped by addition of 1 ml of 2% (wt v^{-1}) quinol solution in acetone to the reaction mixture. The product was poured into a large excess of methanol, filtered and the residue air dried and weighed.

The ungrafted polyacrylamide homopolymer was removed by soxhlet extraction with morpholine (Tetrahydro-1, 4-oxazine) (Idehen 1998). The graft copolymer was then air-dried and reweighed. The measured weighed increase divided by the weight of carboxymethyl cellulose substrate and then multiplied by 100 was reported as the percent graft level.

Isolation of polyacrylamide grafted chains and molecular weight determination. The grafted polymer was isolated from the substrate by the method of Ogiwara Kubota (1967) and purified by solution in distilled water and precipitation with methanol. The molecular weight of the isolated polymer was determined by measuring the intrinsic viscosity in IM aqueous solution of $NaNO_3$ at 30°C using the relationship (Suen *et al* 1958).

$$[\eta] = 3.73 \times 10^{4}\ Mv^{-0.66}$$

The number of grafted polyacrylamide chains was reported as the ratio of percent graft level and molecular weight expressed in mmoles $100g^{-1}$ of substrate.

Characterization. The graft copolymer of acrylamide and carboxyl methyl cellulose using ceric ion initiator and the same graft copolymerization procedure have been characterized and reported earlier by my co-workers, (Ogbeifun 1995; Okieimen and Ogbeifun 1996) who used infrared (IR) spectroscopy, Fourier transform spectrophotometer and nitrogen content using elemental analysis.

Determination of flocculation properties of the graft polymer. Composite water sample collected from Warri River was analyzed for selected parameters in accordance with ASTM and APHA procedures in (1985).

Results and Discussion

The Holocellulose used (Idehen 1998) had a degree of polymerization (DP) of 287 and was carboxymethylated to a degree of substitution (DS) of 0.438.

The prepared graft copolymer was found to have a percent graft-on level of 527.21%, isolated polyacrylamide chains of 1.22×10^{5} average molecular weight and calculated to contain 33.15 mmoles of grafted polyacrylamide chain $100g^{-1}$ of carbonylmethyl cellulose backbone reported by Okieimen and Idehen (1988).

The physicochemical properties of River water sample used for the flocculation experiments and the World Health Organization (WHO) standards for portable water are presented in Table1, while Table 2 shows the physicochemical properties of the River water after treatment with various concentrations of aluminium sulphate solution.

The results showed that increase in the concentration of aluminium sulphate solution resulted in decrease of the treated water pH value below the WHO permissible level of pH 6.5 for portable water even at relatively low concentration of 10ppm (Fig 1).

The turbidity of test water after aluminium sulphate treatment ranged from 7.39 NTU for 10ppm solution to 0.13 NTU for 5000ppm solution, confirming the good coagulation/

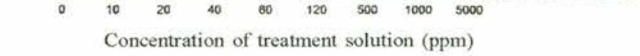

Fig 1. Effect of treatment solution concentrations on the pH value of Warri River Water.

Table 1

Physicochemical properties of Warri River water sample and (WHO) standards for portable water

Parameters	Value	Max. Permissible level	Desirable level
PH at 28°C	6.70	6.5 - 9.2	7.0 – 8.0
Turbidity (NTU)	43.4	10	Nil
Total Dissolved Solid (TDS) ppm	217.8	500	200
Total Suspended Solid (TSS) ppm	40.0	25.0	5.0
Bicarbonate content (mg L^{-1})	61.0	300 – 500	60 – 120
Sulphate content (mg L^{-1})	77.92	250	50
Nitrate content (mg L^{-1})	1.18	45	10
Chloride content (mg L^{-1})	88.75	250	25

* Analysis was carried out after filtration of water sample through Whatman No.1 filter paper.

flocculation properties of aluminium sulphate solution even at relatively low concentration.

The total dissolved solid (TDS) results in Table 2 showed that the use of aluminium sulphate solution above 20-40 ppm may not be desirable, since higher aluminium sulphate concentrations resulted in total dissolved solid values above that of the untreated water (217.8mg l^{-1}). As expected the level of sulphate anions in the water sample after treatment increased as the concentration of treatment solution was increased. There were no marked effects on the chloride and nitrate contents of treated water at all concentration of aluminium sulphate considered.

The effect of ferric sulphate solution treatment is shown in Table 3. The results showed that as with aluminium sulphate that the pH of treated water decrease with ferric sulphate concentration. The turbidity results as shown in Table 3, indicated that ferric sulphate is not an effective flocculation/coagulation agent when compared with aluminium sulphate, it can be seen from the result that as much as 500ppm ferric sulphate solution is required to change test water turbidity to within allowable level for portable water. The use of 10ppm ferric sulphate solution improved test water turbidity by only 13.69% as compared to a significant 83.12% improvement by aluminium sulphate at the same concentration. The use of ferric suphate above concentration of 80ppm resulted in marked increase in the levels of total dissolved solid as compared to untreated River water. The sulphate content of the treated water as expected increased with the concentration of ferric sulphate solution. While the levels of bicarbonate nitrate and chloride were virtually unaffected by ferric sulphate treatment.

The effects of treatment with polyacrylamide and polyacrylamide-carboxymethyl cellulose (PAAM -g- CMC) graft copolymer solutions are shown in Tables 4 and 5 respectively.

The pH results show that unlike the inorganic water treatment agents, polyacrylamide and PAAM -g- CMC graft polymer solutions changes the pH value of test water towards the

Table 2

Physicochemical characteristics of Warri River water after treatment with aluminium sulphate solution

Aluminium sulphate Conc. (ppm)	pH	Turbidity NTU	TDS (mg L^{-1})	HCO_3^- (mg L^{-1})	SO_4^{-2} (mg L^{-1})	NO_3^- (mg L^{-1})	Cl^- (mg L^{-1})
0	6.82	43.27	217.8	61.0	77.9	1.18	88.70
10	6.4ß	7.30	215.3	80.25	78.40	1.18	88.75
20	6.41	3.84	219.4	60.25	78.31	1.20	88.75
40	6.38	2.33	219.7	60.25	80.50	1.25	88.75
80	6.35	0.23	220.4	60.25	82.50	1.25	88.75
120	6.20	0.20	251.6	60.25	82.75	1.24	88.75
500	5.96	0.17	263.3	60.25	98.47	1.27	88.75
1000	5.63	0.16	312.8	60.25	106.15	1.30	88.75
5000	4.21	0.13	370.0	60.25	127.00	1.28	88.75

Table 3

Effect of treatment with ferric sulphate solution on the physicochemical characteristics of Warri River water

Ferric sulphate Conc. (ppm)	pH	Turbidity NTU	TDS (mg L^{-1})	HCO_3^- (mg L^{-1})	SO_4^{-2} (mg L^{-1})	NO_3^- (mg L^{-1})	Cl^- (mg L^{-1})
0	6.82	43.27	217.8	61.0	77.9	1.18	88.70
10	6.74	37.46	218.0	80.25	79.15	1.18	88.75
20	6.76	31.23	217.8	60.25	76.98	1.20	88.75
40	6.62	28.80	220.1	60.25	80.78	1.25	88.75
80	6.54	28.35	220.6	60.25	81.0	1.25	88.75
120	5.94	20.56	244.7	60.25	80.02	1.24	88.75
500	4.87	3.62	256.3	60.25	113.20	1.27	88.75
1000	4.25	1.24	300.0	60.25	134.47	1.30	88.75
5000	4.10	1.09	399.5	60.25	127.69	1.28	88.75

Table 4

Effect of treatment with polyacrylamide solutions on the physicochemical characteristics of Warri River water.

Polyacrylamide[a] Conc. (ppm)	pH	Turbidity NTU	TDS (mg L^{-1})	HCO_3^- (mg L^{-1})	SO_4^{-2} (mg L^{-1})	NO_3^- (mg L^{-1})	Cl^- (mg L^{-1})
0	6.82	43.27	217.8	61.0	77.9	1.18	ND
10	6.85	41.20	217.4	80.25	77.77	1.18	0.27
20	6.88	40.17	217.0	60.25	80.71	1.18	0.43
40	7.03	38.15	217.7	60.25	79.50	1.20	0.49
80	7.07	37.84	217.9	60.25	84.25	1.19	1.32
120	7.10	29.08	217.9	60.25	59.10	1.18	4.51
500	7.12	17.25	217.8	60.25	64.58	1.20	3.94
1000	7.12	11.74	217.9	60.25	60.42	1.20	4.68
5000	7.12	10.83	217.6	60.25	59.70	1.20	4.56

A, polyacrylamide used Mv of 2.58 x 10^6; ND, not-detected.

Table 5

Effect of treatment with polyacrylamide – carboxymethyl cellulose graft copolymer solution on the physicochemical characteristics of Warri River water

PAAM-g-CMC Conc.(ppm)	pH	Turbidity NTU	TDS (mg L^{-1})	HCO_3^- (mg L^{-1})	SO_4^{-2} (mg L^{-1})	NO_3^- (mg L^{-1})	Cl^- (mg L^{-1})	PAAM (mg L^{-1})
0	6.82	43.27	217.8	61.0	77.9	1.18	88.70	ND
10	6.78	3 8.12	217.4	80.25	77.77	1.19	88.75	ND
20	6.78	36.90	217.0	60.25	80.71	1.18	88.75	ND
40	6.80	36.44	217.7	60.25	79.50	1.20	88.75	ND
80	6.87	32.00	217.9	60.25	84.25	1.19	88.75	ND
120	6.98	24.07	217.9	60.25	59.10	0.98	88.75	ND
500	6.98	7.61	217.8	60.25	64.58	0.98	88.75	ND
1000	7.10	6.39	217.9	60.25	60.42	0.91	88.75	ND
5000	7.00	4.82	217.6	60.25	59.70	0.96	88.75	ND

A, The CMC -g- PAAM graft polymer used has a graft level of 527. 21% grafted PAAM chains Mv of 1.22 x 10^5 and 35.15mmoles of grafted chains per anhydroglucose unit.

alkaline region to varying degrees dependent on solution concentration.

The pH values obtained were all within WHO maximum allowable levels of pH 6.8 – 8.2 for portable water. On the basis of turbidity results, the order of effectiveness as coagulation/flocculation agent is aluminium sulphate > ferric sulphate > PAAM -g- CMC graft polymer > polacrylamide as shown in Fig.2. To moderate the test water turbidity of 43.4 NTU to WHO maximum allowable level of 10 NTU, a polyacrylamide concentration of a least 5000ppm will be required in treating the test water and a likelihood of depositing a polymer residue of about 4.50ppm in the process.

Whereas at a concentration of 500ppm, PAAM-g-CMC can effectively remove turbidity to allowable level without any detectable polymer residue. Both polyacrylamide and PAAM-g- CMC graft polymer solutions do not seem to have any net effect on the levels of total dissolved solid (TDS), bicarbonate content and chloride ions in the treated water. However, at concentrations above 120ppm of PAAM-g-CMC graft

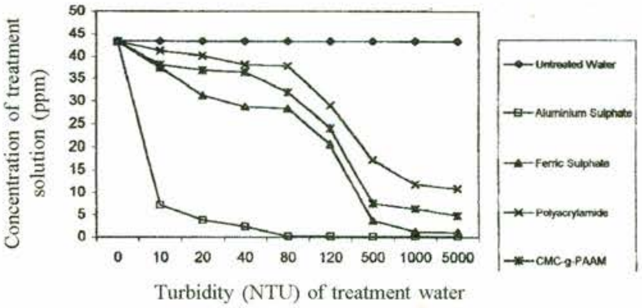

Fig 2. Effect of treatment solution concentration on the turbidity (NTU) of Warri River.

Table 6
Effect of aluminium sulphate and polymer blend treatment on the pH value and turbidity of Warri River water

Blend of aluminium sulphate and synthetic polymer solutions	pH value	Turbidity (NTU)
20% polyacrylamide	6.37	3.06
30% polyacrylamide	6.40	1.81
50% polyacrylamide	6.00	2.57
10% CMC – PAAM graft polymer	6.60	0.09
20% CMC – PAAM graft polymer	6.60	0.08
30% CMC – PAAM graft polymer	6.43	0.12
50% CMC – PAAM graft polymer	6.40	1.14

polymer solution, the sulphate and nitrate levels are slightly reduced.

The observed trend in the coagulation/flocculation properties of the materials considered may be attributed to the fact that polyacrylamide is a non-ionic polymer which exists in solution as a random coil (Cheremisinoff and Young 1975) and as such relatively lower suspended particles bridging effect as compared to the inorganic agents used which exists as polyaluminium hydrates and polyferric hydrate complexes in solution, coupled with the latter is the inherent abilities of these essentially positive complexes to readily neutralize negatively charged suspended solids in water (Cheremisinoff and Young 1975). The superior flocculation effect of PAAM-g- CMC graft polymer as compared with polyacrylamide may not be unrelated to the higher molecular weight and improved floc formation.

The results of using aluminium sulphate and polymer blend treatment are presented in Table 6. There is no improvement in turbidity results on blending aluminium sulphate and polycarylimide (1.8 – 3.6 NTU) in the ratios considered. On the contrary, there is slight loss in the turbidity moderating effect of aluminium sulphate. At below 50% PAAM–CMC graft polymer solution in the blends, significant improvements in treated water turbidity were obtained. The results suggested that at a ratio of 4:1 aluminium sulphate/graft polymer blend, the graft polymer seen to function as an excellent flocculation aid since a turbidity as low as 0.08 NTU and a pH 6.6 were achieyvable. This finding may be due to the complementary enhancement in inter-particle bridging and macro-floc agglomeration by the graft polymer, after the destabilization of the colloids by charge neutralization actions of the aluminum salt.

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