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Drilling Fluid Waste Treatment Using Polysaccharide Grafted Copolymers

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Abstract

A massive quantity of drilling fluid waste is produced as effluents all through exploration and manufacturing of oil and gas. Such effluents want to be dealt with earlier than their very last disposal. Efficient coagulation/flocculation can lessen the overall quantity of disposed effluent, and each coagulation via way of means of inorganic salts and flocculation via way of means of artificial flocculants are determined to be very effective. The graft-copolymers-primarily based totally flocculants have been organized the use of a potassium persulfate initiator answer made via way of means of grafting copolymerisation of polyacrylamide onto polysaccharide backbones (starch, guar gum and amylose) in our laboratory. The synthesised graft copolymers were characterized the use of numerous instrumental strategies of analysis. The outcomes of numerous artificial flocculants and their concentrations were studied in mixture with the coagulants on coagulation/flocculation of bentonite-primarily based totally drilling fluid waste were studied.

Introduction

Oil and natural gas industries devour a big amount of water for getting ready water based drilling fluids. The drilling fluids play an crucial position in secure drilling operations. Various forms of drilling fluids are used for the drilling technique, which include water based, oil based ,

synthetic-based, pneumatic or air-based drilling fluids. Drilling fluids encompass a base fluid and diverse stable and liquid components to permit for desirable drilling performance. Drilling fluids are pumped via the downhole tubing all through the drilling technique and are circulated returned to the floor via the casing annulus and accumulated withinside the go back pit. After the quit of recycling of the drilling fluids, portions of drill cuttings or stable substances are generated from the drilling fluid waste. In the drilling technique of oil and gas wells there are commonly forms of wastes which might be generated: liquid drilling fluids waste and drill cuttings. A unique trouble related to the oil drilling fluid is the disposal of big portions of drilling fluid waste. Besides water, the oilfield drilling fluids waste produces the second one biggest extent of overall waste. The disposal of the drilling fluid wastes have confirmed to be one of the maximum tough environmental troubles withinside the international as they may be product of diverse minerals, clays, natural substances and different solids. The not unusualplace techniques to do away with drilling fluid waste and drilling wastewater are gravity separation, baffle and vacuum separation. In deep drilling wells, while the additives of drilling fluid waste are extra complex, the density of drilling fluid waste will become higher. Minimising the environmental effect of drilling fluid waste is one of the maximum critical demanding situations withinside the petroleum industry. Effective waste control strategies consist of waste minimisation, recycling, solids control, remedy and disposal. Solid-liquid separation with the aid of using coagulation and flocculation performs an critical position in waste control. The time period flocculation and coagulation are frequently used interchangeably, however the tactics are pretty different.

Table-1

Item	Numerical value
Density (g/mL)	1.62
Appalent Viscosity (mPa·s)	36.50
Plastic Viscosity (mPas)	26.70
Dynamic cutting (Pa)	9.80
Solid Content (%)	54.40
Oil Content (%)	5.00
PH	11.64

Table-2

Pollutant	Concentration (mgL^{-1})
Overall Cr	1.55
Xexad Cr	<0.004
Hg	0.0004
Cd	0.22
As	0.024
Pb	1.2
Zn	0.12
Cu	<0.1
Content of Solid	344
Fluoride	5.24

MATERIALS AND METHODS FOR THE SYNTHESIS

Starch, amylose, guar gum, hydroquinone and KPS (K2O2S8) were procured from Lobe Chemie, Mumbai, India. Acetone, hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium chloride (NaCl), aluminium sulfate (Al2(SO4)3.16H2O) and acrylamide were procured from Merck Life Science Private Limited Mumbai, India. A drilling fluid waste sample was collected from the Oil and Natural Gas Corporation Limited (ONGC) Kadi oilfied, Ahmedabad Gujarat, India. The zeta potential of the drilling fluid waste sample was found to be –23.1 mV at pH 4

Table -3

Graft Copolymer	Polysaccharides (gm)	Acrylamide (gm)	Amount of KPS	% Conversion
St-g-PAM-I	1	8	0·1	93
St-g-PAM-II	1	15	0·1	97
Am-g-PAM-I	1	8	0·1	92.8
Am-g-PAM-II	1	15	0·1	99.63
Gr-g-PAM-I	1	8	0·1	94

SHAFT SYNTHESIS

The graft copolymers of starch, amylose and guar gum has been synthesised in inert atmospheric of nitrogen the use of KPS as an initiator. During synthesis, 1 g of starch/amylose/guar gum were slowly dissolved into eighty mL double distilled water in a threenecked spherical backside flask. The flask became equipped with an electrically operated magnetic stirrer (REMI, Model-2 MLH Magnetic Stirrer) and keptin a water baththat became maintained at a temperature of 75 1 C with a consistent stirring pace of 250 rpm. Then, nitrogen fueloline became purged for 15 min, and afterwards, 0.1 g of KPS became dissolved in 10 mL double distilled water and delivered to the solution. Then, after 15 min, the favored amount of acrylamide dissolved in 50 mL double distilled water became poured slowly to the homogenous solution. The response became persevered for some other hour under 75+- 1 C situations with a stirring pace of 250 rpm.

Characteristics of Graft Copolymers

The synthesised graft copolymers have been characterized through XRD evaluation to decide the qualitative mineral contents withinside the samples. XRD analyses have been done the use of a Philips PW 1040 Model diffractometer with Cu goal at 30 kV and a present day of 10 mA. The scattering angle (2q) changed into numerous from 0 to 80 .

Fourier-transform infrared (FTIR) spectroscopy

FTIR spectra of numerous polymer samples have been recorded the use of a Perkin Elmer version Spectrum Two (USA). The frequency tiers are measured as wave numbers generally over the variety 500–4000 cm–1 . 1 mg of pattern changed into combined with a completely small quantity of potassium bromide (KBr), and KBr pellets have been organized the use of a hydraulic press through making use of a stress of a 100 psi for 60 s. The infrared spectrum of the KBr pellets have been recorded, and 100 scans had been collected.

Scanning electron microscopy (SEM) analysis

The morphologies of the diverse polymer samples used on this take a look at had been analysed the usage of a ZESIS Model EVO 60 SEM with an air lock chamber to study the morphology of various polymers samples. The samples had been charged with a platinum coating to supply clearer images. The elemental analyses of graft copolymers had been completed the usage of an Energy-dispersive X-ray spectroscopy (EDX) analyser. The SEM, coupled with the EDX analyser, turned into used decide the fundamental composition of the synthesised graft copolymers and estimate carbon, oxygen and nitrogen.

Flocculation research of drilling fluid waste

The flocculation research of diverse polymers had been completed the usage of widespread jar check methods. The equipment contained six spindles with blades (duration 46 mm, width 17 mm and thickness 3 mm) and a virtual display, with a variable velocity potential starting from 0 to 200 rpm. Each spindle is attached concurrently with the aid of using a chain of stirrers connectedto an electric powered motor thru gears. The drilling fluid waste turned into diluted the usage of distilled water (50% v/v). The adjustment of pH starting from 4 to 10 turned into made with the aid of using including HCL or NaOH (0.1M HCl or 0.1M NaOH awareness). The pH values of the samples had been measured the usage of a virtual pH meter. Afterwards, the diluted samples had been placed into 500 mL glass beakers. Required portions of coagulant/flocculants/NaCl (0.001M to 0.1M) had been brought and the stirring velocity turned into managed with the aid of using a velocity selector switch. The answer turned into blended

unexpectedly with the aid of using growing the velocity (75 rpm) of the stirrer for 1 to 2 min. After this speedy mixing, the answer turned into subjected to gradual mixing (20–25 rpm) for 10 min. Finally, the flocs shaped had been allowed to accept a length of 25 min.

Turbidity measurements

After the settling of the flocs, supernatant liquid turned into cautiously withdrawn from the pinnacle of the jar for the turbidity measurements the usage of a syringe. The turbidity values had been recorded in Nephelometric Turbidity Units (NTU) the usage of a virtual turbidity meter. Determination of general solids, general dissolved solids and general suspended solids withinside the drilling fluid wastes had been completed gravimetrically.

Table-4

Graft Copolymer	C (% wt)	O (% wt)	N (% wt)
St-g-PAM-I	59.81	49.19	0.00
St-g-PAM-II	53.69	37.72	8.59
Am-g-PAM-I	64.71	35.29	0.00
Am-g-PAM-II	56.45	28.81	7.04
Gr-g-PAM-I	51.00	33.86	15.14

Results and Discussions

The graft copolymers had been synthesised the usage of KPS as a loose radical initiator in nitrogen atmospheric, preserving the response temperature at 75 1 C. Monomer (acrylamide), initiator and 2.5 g of polysaccharides starch/amylose/guar gum had been used to synthesise the graft copolymers. Initially, the quantity of monomer and polysaccharide had been taken as 20.0 and 2.5 g, respectively, and had been dissolved in 80 and 50 mL double distilled water, respectively. But, because of excessive viscosity of the answer, the graft copolymerisation couldn't be achieved nicely whilst the initiator turned into brought to the answer. It turned into additionally discovered that the response product broke up whilst washing with acetone. The in all likelihood motives had been that the better awareness of monomer resulted inthe formation of unwanted homopolymers and better awareness of polysaccharides ended in better viscosity of the answer. The above phenomenon hindered everyday graft copolymerisation with the aid

of using limiting the motion of loose radicals, resultinginaless efficientinitiation manner and grafting efficiency. Finally, the quantity of monomer and polysaccharides had been reducedto most appropriate concentrations.

XRD analysis

The XRD sample of all of the polysaccharides grafted copolymers (St-g-PAM-I to Am-g-PAM-II) are proven. In this sample of XRD evaluation, all graft copolymers do now no longer display a unmarried height and imply crystallinity among more than a few 2q . The XRD styles additionally do now no longer display a pointy height. It is in all likelihood that the grafted merchandise do now no longer imply any crystallinity or any sharp height because of acrylamide monomer. Similar outcomes were acquired from the evaluation of grafted merchandise synthesised via way of means of in advance paintings the use of the equal technique.

SEM analysis

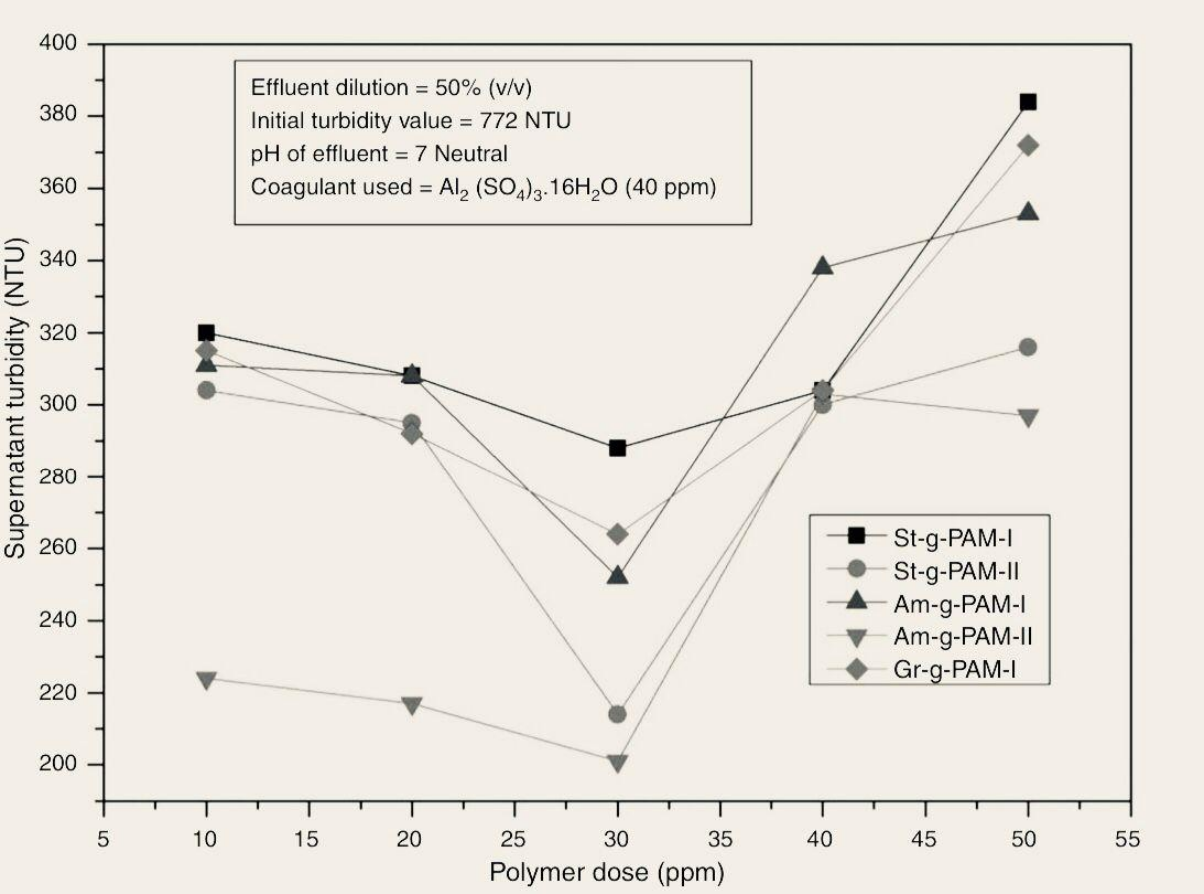
SEM become used to analyze the floor morphological function of starch, amylose and synthesised graft copolymers (St-g PAM-I and Am-g-PAM-I) with acrylamide. The morphological function of starch indicates a cohesive and dense shape. The morphological function of amylose is a easy and non-stop floor with a granular shape and no wonderful perturbations. After grafting, the granular look of starch and amylose had been distorted and modified to fibrillar. The morphology of acrylamide additionally seemed to extrade after grafting with starch and amylose. The SEM micrograph of graft copolymer St-g-PAM-I and Am-g-PAM-I confirmed that the graft copolymerisation of starch and amylose with acrylamide dramatically modified the conformation of the polysaccharides polymer (starch and amylose) chain. The comparable morphological shape extrade become additionally located via way of means of in advance paintings even as appearing the graft copolymerisation the use of chitosan and polyacrylamide. This commentary shows that the grafting of acrylamide influences the morphological association of polymers. The micrograph of graft copolymers confirmed numerous lengthy chains of acrylamide that agglomerated and modified in fibrillar shape .

Flocculation traits

The drilling fluid waste pattern amassed from Kadi oilfield, ONGC Ahmedabad, Gujarat, become handled for coagulation and flocculation research. The preliminary pH of the waste become 8.25, and the turbidity fee become 1589 NTU. While treating the waste, it become located that treating the waste with both alum or polymer on my own via way of means of coagulation or flocculation become very hard. The focused solutions (90% extent of drilling fluid waste in conjunction with 10% extent of distilled water) couldn't be handled effectively. This become because of the reality that the oilfield drilling waste particularly contained lignosulfonates, lignin, strong drill cuttings and excessive molecular weight polymeric compounds. The plastic and the obvious viscosity of the drilling fluid wastes had been additionally excessive. It become hard to flocculate the debris with polymeric flocculants on my own. Therefore, the unique waste become diluted with the addition of an equal quantity of distilled water. Afterwards, it become coagulated with coagulant Al2(SO4)3.16H2O after which flocculated with grafted copolymers. Technique become accompanied for flocculation and the supernatant turbidity values in NTU had been measured after a particular settling duration following flocculation.

Effect of flocculants

The diluted drilling fluid waste become first coagulated with Al2(SO4)3.16H2O via way of means of speedy blending at seventy five rpm for 1 min. Then flocculants (graft copolymers) had been delivered and stirred for some other minute. Afterwards, the drilling waste become subjected to sluggish blending at 20 rpm for 10 min and settling for 25 min. Initially, the 10 ppm awareness of polyacrylamide/graft copolymer become constant even as various the alum awareness from 10 to 80 ppm. Increasing the alum awareness led to deceasing the turbidity of the waste as much as a positive awareness of the alum. Further boom in alum awareness led to growing the turbidity fee. The turbidity fee of the supernatant liquid become recorded 320 NTU at 40 ppm, after which a similarly boom in alum awareness led to restabilisation of the debris with the turbidity fee of 546 NTU at 80 ppm. Hence, 40 ppm of alum awareness wasfixed even as varyingthe graft copolymer concentrations from 10 to 50 ppm for the following set of experiments. It become located that after the polymer awareness expanded from 10 to 30 ppm the turbidity fee of supernatant liquid reduced from 224 to 201 NTU. Further boom withinside the awareness of graft copolymer as much as 50 ppm noticed the turbidity fee of supernatant liquid boom from 304 to 384 NTU (St-g PAM-I). The turbidity fee become located to be lowest (201 NTU) while 30 ppm of the Am-g-PAM-II polymer become used. The outcomes of flocculation overall performance of grafted copolymers. It is apparent that the Am-g-PAM-II indicates higher flocculation overall performance in evaluation with different graft copolymers.



As mentioned in advance, for powerful flocculation, the drilling fluid waste become diluted with addition of equal quantity of distilled water. The pH of the machine become adjusted via way of means of including HCl or NaOH (0.1M HCl/z 0.1M NaOH awareness). The coagulation-flocculation research had been performed the use of 40 ppm of alum and 10 ppm of graft copolymer/polyacrylamide the use of the same old jar check technique. After flocculation, the turbidity values of the supernatant drinks had been decided below numerous pH conditions. The supernatant turbidity values in NTU had been recorded as a characteristic of pH of the machine. It become located that because the pH fee of the machine expanded the supernatant turbidity fee reduced.

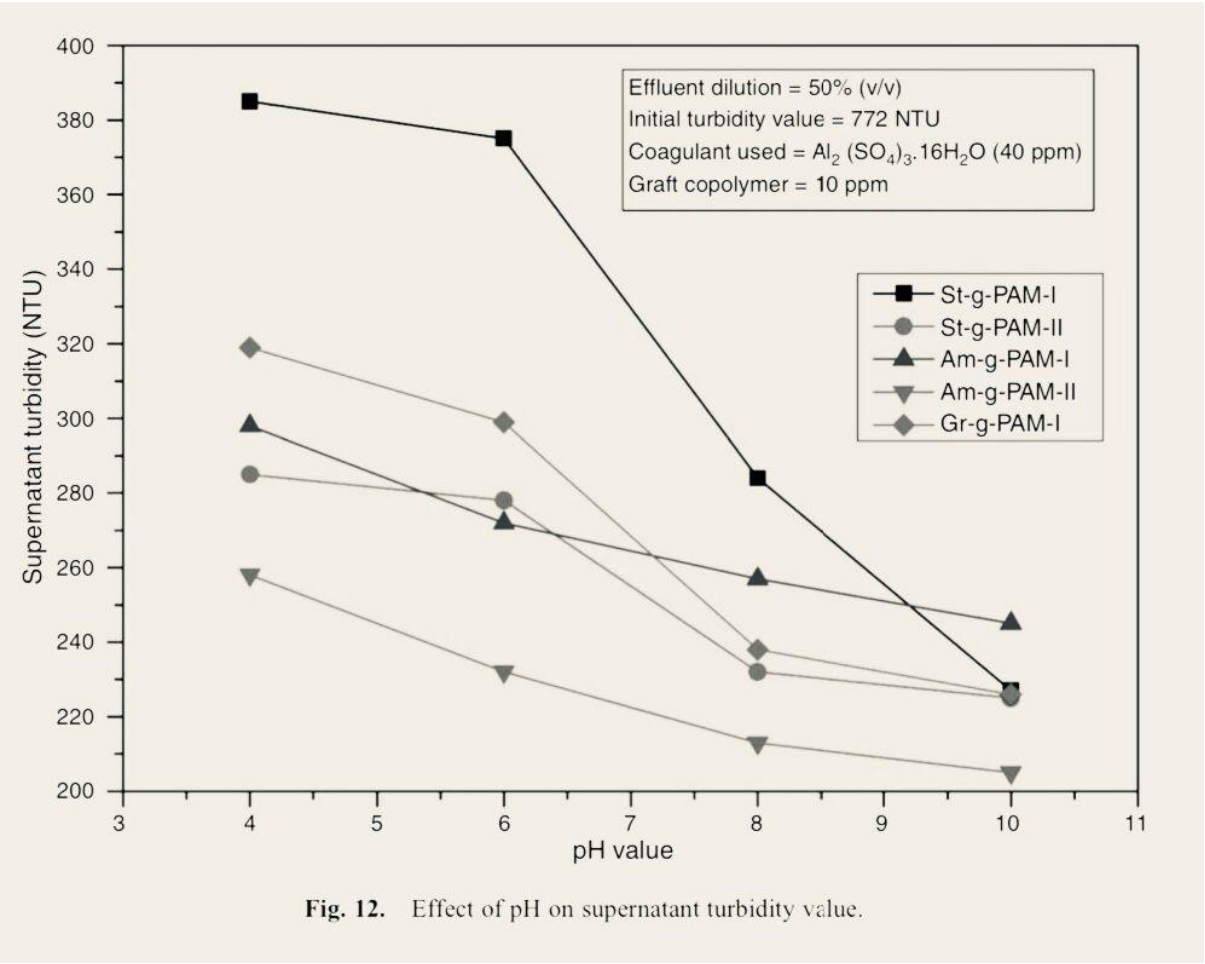


Fig. 12. Effect of pH on supernatant turbidity value.

This become because of an boom withinside the nice rate density of the ions found in alkaline media (at pH 9). The appeal among the definitely charged ions and negatively charged hydroxyl companies ofthe alkali enhancedthe aggregation of the debris. The turbidity fee of the supernatant liquid become recorded maximum at 320 NTU the use of 10 ppm of St-g-PAM-I at pH 4 of the machine. It additionally become located that the turbidity fee become lowest at 204 NTU the use of 10 ppm of Am-g-PAM-II at pH 10

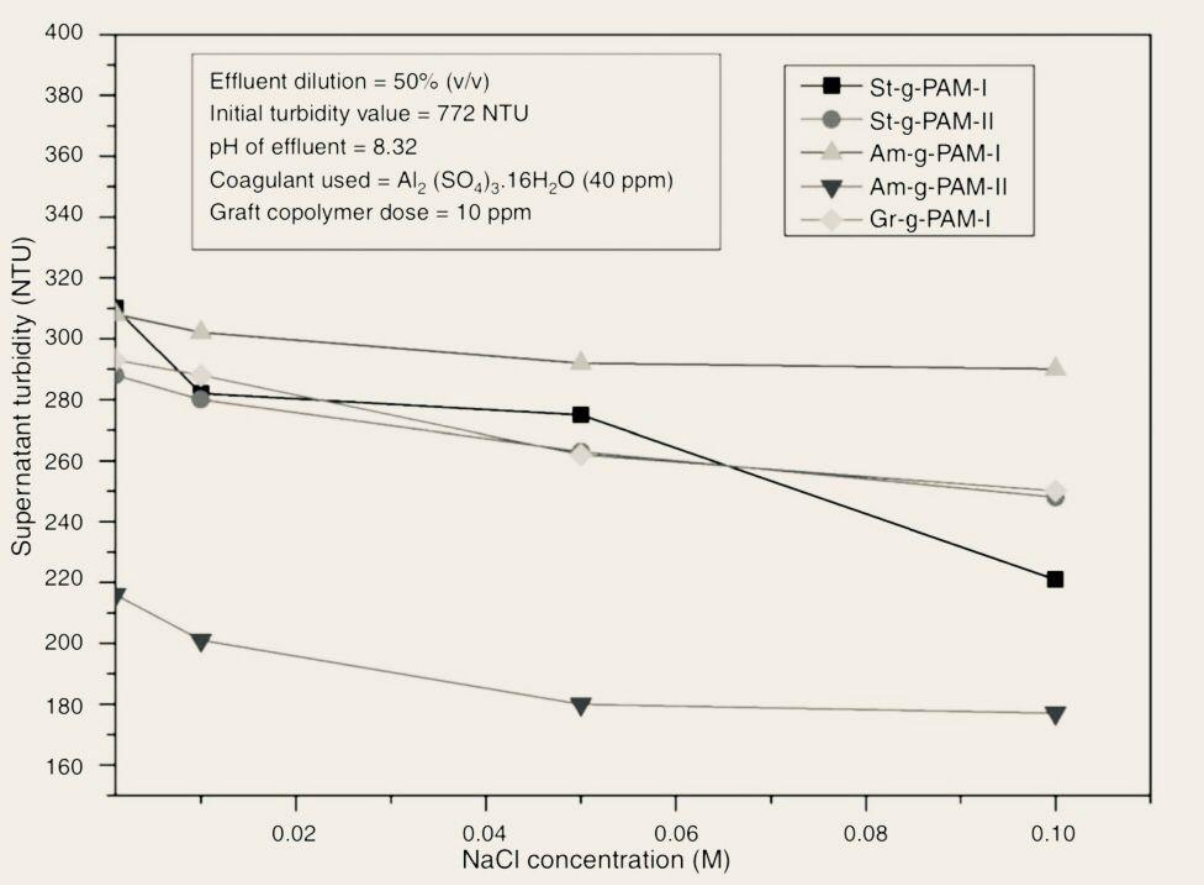


Table-5

Polymer	Turbidity value	Ts	TDS	TSS
Without	772	126	81	45
St-g-PAM-I	320	33	28.32	4.68
St-g PAM-II	304	29.7	26.56	3.14
Am-g PAM-I	311	37.22	39.97	4.25
Am-g PAM-II	224	17.22	14	3.2
Gr-g-PAM-I	315	28.28	19.07	3.21

Conclusion

(1) Grafting of acrylamide monomer on starch, amylose and guar gum polysaccharide backbones have been successfully executed the use of KPS as an initiator.

(2) The syntheses of the above graft copolymer have been confirmed through the instrumental analyses in their products.

(3) While treating the drilling fluid waste, it became determined that neither a coagulant nor a flocculant by myself can completely flocculate this kind of complicated system. After destabilising such waste with a appropriate coagulant, polysaccharide grafted polymers may be used as flocculant aids for the whole flocculation of the contaminants gift in the system.

(4) Polysaccharide-primarily based totally grafted copolymers have been determined to be green flocculant aids for remedy of the drilling fluid waste withinside the presence of NaCl and at better pH conditions.

(5) The synthesised Am-g-PAM-II became determined to be the most green flocculant a number of the different synthesised graft copolymers

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