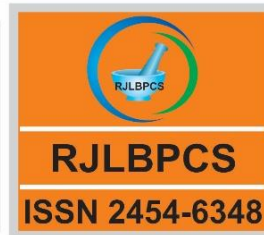


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FLOCCULATION CHARACTERISTICS OF TAPIOCA STARCH GRAFTED POLYACRYLAMIDE IN KAOLIN AND OPENCAST COAL MINES DUST SUSPENSIONS AND METHYLENE BLUE DYE REMOVAL

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ABSTRACT: This article deals with the synthesis and application in flocculation and methylene blue dye removal of tapioca starch grafted polyacrylamides (TAP-g-PAM) and their partially hydrolyzed products (Hyd TAP-g-PAM). And also treatment of water contaminated with haul road coal dust by using Hyd TAP-g-PAM. Five different grades of polymeric flocculants (TAP-g-PAM 1 to TAP-g-PAM 5) have been synthesized by grafting polyacrylamide onto tapioca starch, and their respective hydrolyzed products (Hyd TAP-g-PAM 1 to Hyd TAP-g-PAM 5) prepared by partial alkaline hydrolysis. The flocculation performances of all grades have been evaluated in kaolin suspension by settling and jar test methods. Between TAP-g-PAM 5 and Hyd TAP-g-PAM 3, best performing grades of respective series, the later one has been found to be best in settling and jar tests, whereas the former one in dye removal tests. Further, Hyd TAP-g-PAM 3 has been used in treatment of water contaminated with haul road coal dust.

KEYWORDS: Tapioca; coal mine; dye removal; flocculation

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1.INTRODUCTION

Many people lack access to sufficient amounts of clean water and proper sanitation. To meet their requirements of potable water, contaminated water should be treated [1]. Untreated contaminated water increases suspended solids, dissolved solids particles, turbidity and coloration of water [2]. Methylene blue (MB) being used in paper coloring, temporary hair colorant, dyeing cottons and wools, causes harmful effects in humans such as cyanosis, increase of heartbeat, jaundice, quadriplegia, shock vomiting and tissue necrosis [3]. Thus removal of MB has become one of the major challenges of wastewater treatment [4]. It can be removed from contaminated water by adding some adsorbent like kaolin and bentonite, but this unnecessarily produces water with unwanted wastes [5,6]. Flocculation is an efficient, eco friendly and economical process in particular for primary removal of dyes, suspended solid particles, toxic heavy metals, etc. [7-10]. Natural polymers, such as polysaccharides, can be used as flocculants as they are biodegradable, cheap, easily available, and shear stable. Tapioca, one of the natural polysaccharides, is easily available and cheaper. The commercial tapioca pearls, also known as sago, contain about 60% starch and the main content present in tapioca starch is amylopectin, which is in the range of 69 to 76% [11]. Amylopectin is a highly branched polymer of α -D-glucopyranosyl units linked together by 1 \rightarrow 4 linkages and having branches linked with main chain with 1 \rightarrow 6 linkages [12, 13]. The biodegradability of the natural polymers acts as a drawback in that it reduces storage life as well as performance and they are required at high doses in flocculation process. On the other hand high molecular weighted synthetic polymers, such as polyacrylamides (PAM), are very effective flocculating agents. But, these are unstable in shear fields and thus lose their flocculating effectiveness [14]. To combine the best properties of both natural and synthetic polymers, many attempts have been made by grafting synthetic polymers onto the natural polymer's backbone [15-19]. The great advantages thus obtained are high flocculation efficiency, controlled biodegradation, viscosifying and shear resistance characteristics of the developed graft copolymers [20-22]. Graft copolymers based on polysaccharide and PAM are more effective flocculants due to the greater approachability of the dangling stretchable PAM chains grafted onto rigid polysaccharide branches towards the contaminant particles [23-26]. On the other hand, coal mining is the process used to obtain coal from the ground. Coal is a valuable resource being widely used in thermal power plants. Many manufacturing industries use coal as a source of fuel for extraction of metal from their ores [26]. Apart from its advantages, coal mining has disastrous impacts on the environment in which water and air pollutions are of major concern. Water pollution from the disposal of wastewater is an important problematic environmental issue associated with coal mining [27]. In the process of mining, to facilitate the mining operation, huge amounts of

water are discharged on surface. Deterioration of stream quality results from toxic trace elements, acid mine drainage, high content of dissolved solids in mine drainage water, and increased sediment load discharged to streams [28]. Therefore, the waste water should be treated before its reuse. The present article reports the synthesis of different grades of cheaper and ecofriendly graft copolymers based on starch extracted from tapioca, and polyacrylamide. The partial hydrolysis of the graft copolymers has been done and studied application of these hydrolyzed and unhydrolyzed graft copolymers in flocculation and dye removal. The best grade chosen depend on flocculation performance has been used for the settling of dissolved and suspended solids using coal dust samples.

2. MATERIALS AND METHODS

Materials : Tapioca starch was extracted from pearls of tapioca by making them fine flour, then dissolved in water and precipitated in ethanol. Thus, obtained starch was dried under vacuum at room temperature up to constant weight. Acrylamide, acetone and hydroquinone were supplied from S.D. Fine Chemicals, Mumbai, India. Ceric ammonium nitrate (CAN) was purchased from LobaChemie, Mumbai, India. Kaolin was obtained as a gift from Rajmahal Quartz-Sand, Kolkata, India. Three different samples of road dust i.e., Jammunia, Dragline and Coal face haul road dust samples were collected from different places in India.

Synthesis of graft copolymers based on tapioca starch and polyacrylamide (TAP-g-PAM) In a 50 mL conical flask, under nitrogen purging, 0.5 g of tapioca starch was dissolved in 20 mL of distilled water at 50 °C to get a homogeneous solution and then the reaction mixture was cooled to room temperature. Then anrequired amount of acrylamide was added. The mixture was allowed to stir continuously for 30 minutes under nitrogen atmosphere at room temperature, followed by the addition of 25 mg of CAN. The reaction was carried out until the solution became viscous and then the polymerization was terminated by the addition of 1 mL saturated solution of hydroquinone. The resulting polymers were precipitated, washed in excess amounts of acetone and dried up to constant weight under vacuum at 50 °C. Same procedure was followed to synthesize five grades of graft copolymers based on tapioca starch and PAM i.e., TAP-g-PAM 1 to TAP-g-PAM 5 and the synthesis details are given **Table 1(a)**.

Synthesis of partially hydrolyzed graft copolymers of TAP-g-PAM (Hyd TAP-g-PAM)

Five grades of partially hydrolyzed tapioca grafted polyacrylamides viz., Hyd TAP-g-PAM 1 to Hyd TAP-g-PAM 5, were synthesized by alkaline partial hydrolysis of TAP-g-PAM 1 to TAP-g-PAM 5, respectively. For this, 1 g of TAP-g-PAM (desired grade) was dissolved in 50 mL of distilled water in a 100 mL beaker and 2 mL of 1N NaOH solution was added keeping the solution temperature at 50 °C. The solution was stirred for 3 hours. Finally the reaction mixture was added to a beaker containing

300 mL of acetone with stirring to precipitate the hydrolyzed product. The polymer thus formed was washed with acetone 4 times and dried in vacuum oven at 50 °C. The synthesis details are tabulated in **Table 1(b)**.

Characterization

FT-IR spectroscopy

The IR spectra of tapioca, TAP-g-PAM 5 and Hyd TAP-g-PAM 3 were recorded by Thermo Nicolet FT-IR spectrophotometer (Model JASCO FT-IR-5300), in solid state using KBr pellet method. The IR spectra were recorded within the range of 4000-400 cm^{-1} (**Figure 1(a)**).

^1H NMR Spectroscopy

^1H NMR spectra of tapioca, TAP-g-PAM 5 and Hyd TAP-g-PAM 3 were recorded by FT-NMR spectrometer (Model JEOL AL 300). The sample solutions were prepared in D_2O and tetramethylsilane (TMS) was used as an internal reference (**Figure 1(b)**).

Intrinsic viscosity measurement

The viscosity measurement of the aqueous polymer solutions was done using an Ubbelohde viscometer with a capillary diameter of 0.58 mm (CS/S: 0.00386) at 25 ± 0.1 °C. The viscosities were measured in dilute aqueous solution, at neutral pH. The flow time of the solutions was measured at five different concentrations (0.5%, 0.25%, 0.125%, 0.0625 and 0.03125%). And the intrinsic viscosities were determined from the point of intersection of plots of inherent viscosity and reduced viscosity plotted against concentration. The intrinsic viscosities of the graft copolymers and their hydrolyzed products are reported in **Table 1(a)** and **1(b)** respectively. Through the intrinsic viscosities of the graft copolymers (TAP-g-PAM 1 to TAP-g-PAM 5), their molecular weights were calculated by Mark Houwink equation i.e., intrinsic viscosity, $[\eta] = K[M]^\alpha$ where K and α are constants and M is molecular weight of the polymer and are reported in **Table 1(a)**.

Flocculation study

Jar test

Jar test method was employed to estimate flocculation performance of all the grades of TAP-g-PAM and Hyd TAP-g-PAM. The test protocol involved taking 400 mL of the 0.25 wt% kaolin suspension in 1 L beaker. The flocculant (polymer solution) was added in ppm concentrations and immediately after the addition of the flocculant, the suspension was stirred at a uniform speed of 175 rpm for 2 min followed by slow stirring of 100 rpm for 5 min. Then, the suspension was allowed to settle for 10 min. Afterwards, clean supernatant liquid was drawn from a depth of 1.0 cm and its turbidity was measured using a digital nephelometer (Digital nephelometer model: BellstoneHitech International) to express the turbidity in nephelometric turbidity unit (NTU). For each grade, polymer concentration

was plotted against turbidity of the supernatant liquid and the plots of unhydrolyzed and hydrolyzed graft copolymers are shown in **Figure 2(a)** and **2(b)**, respectively.

Settling test

The settling test of all grades of TAP-g-PAM and Hyd TAP-g-PAM were investigated in 1 wt% of kaolin suspension using the column settling test. This test was performed by using a 100 mL stoppered graduated cylinder of 40 cm height and 2 cm inner diameter. At first, the slurry sample was taken in the cylinder and then polymer solution (in ppm) was added into it. For thorough mixing, the cylinder was inverted 10 times. After that the cylinder was set upright and the height of interface between supernatant water and settling solid bed was measured over time. For each grade the settling time was plotted against interface height. And the plots of unhydrolyzed and hydrolyzed graft copolymers are shown in **Figure 3(a)** and **3(b)**, respectively. The settling velocities of unhydrolyzed and hydrolyzed graft copolymers are reported in **Table 2**.

Dye Removal

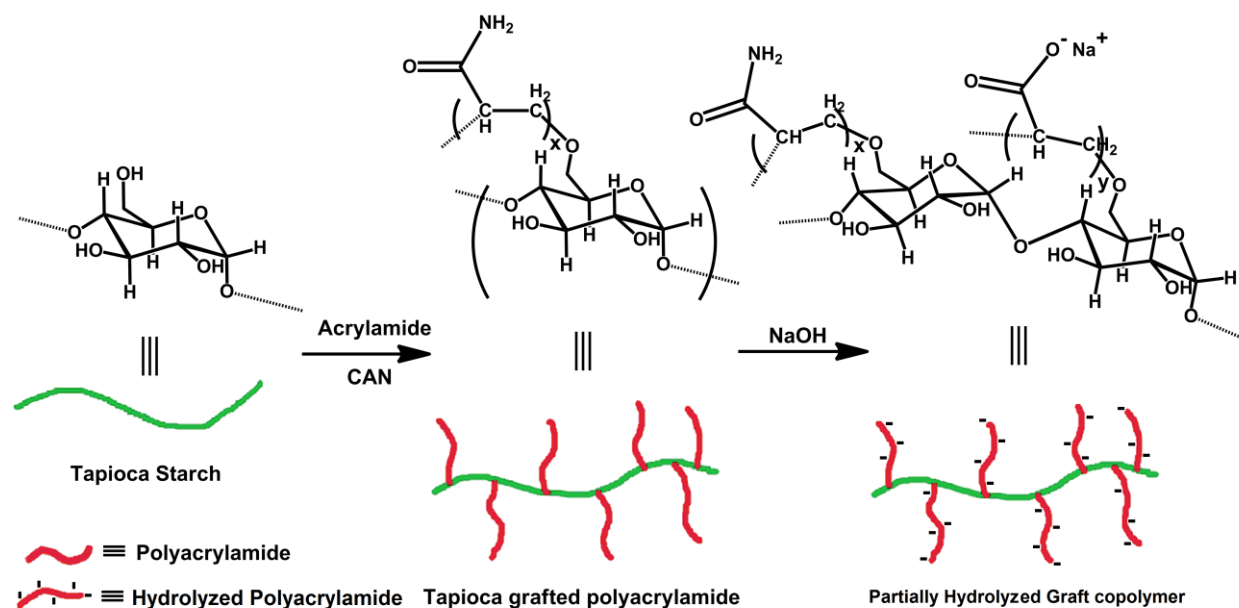
TAP-g-PAM 5 and Hyd TAP-g-PAM 3 were employed in the removal of methylene blue dye from water, using kaolin as an adsorbent. For this, to each 1L beaker containing 400 mL of 400 ppm methylene blue dye, 0.25 g of kaolin was added and then the flocculant was added in ppm concentrations. Immediately after the addition of the flocculant, the suspension was stirred at a uniform speed of 175 rpm for 2 min followed by 100 rpm for 5 min. Afterwards, the suspension was allowed to settle down for 10 min and then 3 mL of clean supernatant liquid was drawn from a depth of 1.0 cm. This, treated water was used for UV analysis, by using UV-Visible Spectrophotometer (Shimadzu UV-1700 pharماسpec, Kyoto, Japan), to estimate the percentage of dye removed. The UV-vis absorption spectra of TAP-g-PAM 5 and Hyd TAP-g-PAM 3 are shown in **Figure 4(a)** and **4(b)**, respectively and the bar graph showing the percentages of dye removal is shown in **Figure 4(c)**.

Treatment of water contaminated by haul road dust in opencast mines

Hyd TAP-g-PAM 3 was used in the treatment of water contaminated by haul road dust in opencast coal mines. Three different samples of road dust (Jammunia, Dragline and Coal face haul road dust samples) collected from different places in India were used for this study. The average percentages of coal present in Jammunia, Dragline and Coal face haul road dust samples are 36, 35 and 56% respectively. Jar and settling tests were performed to study the performance of the flocculant (Hyd TAP-g-PAM 3). The similar methodology as discussed above in the jar and settling test methods was used by using haul road dust instead of kaolin.

3. RESULTS AND DISCUSSION

The schematic representation of synthesis of tapioca starch grafted polyacrylamides and their partially hydrolyzed products is shown in **Scheme 1**.



Scheme 1. Schematic representation of synthesis of TAP-g-PAM and Hyd TAP-g-PAM.

Synthesis of graft copolymers based on tapioca starch and polyacrylamide

Five different grades of graft copolymers (TAP-g-PAM 1 to TAP-g-PAM 5) were synthesized by varying the acrylamide concentration. The generation of free radicals by Ce(IV) involved the following mechanism: Ce(IV) formed a chelate complex among the secondary hydroxyl groups of the tapioca starch and the complex so formed disproportionate to form free radicals on the tapioca starch. These free radical sites then reacted with acrylamide monomer to form TAP-g-PAM. The amount of AM was varied in order to observe the effect with varying chain length of grafted PAM. At fixed concentration of CAN, fixed number of grafting sites on the polysaccharide backbone was expected. Thus, difference in AM concentration would lead to different chain length of PAM. The average length of PAM depended on the concentration of AM and tapioca starch. At high concentration of AM, longer PAM chains were expected, whereas shorter chains were expected at lower concentration of AM. At optimum concentration of AM, longest PAM chains were obtained. This was determined by intrinsic viscosity values. Among the various grades, synthesized by solution polymerization technique, TAP-g-PAM 5 was observed to have maximum intrinsic viscosity i.e., 4.793 dL/g and was the grade with maximum grafting efficiency (G.E %) (**Table 1(a)**).

Table 1. Synthesis details of (a) graft copolymers based on polyacrylamide and tapioca and (b) hydrolyzed graft copolymers.**Table 1(a)**

Polymer	Tapioca (g)	AM (g)	CAN (mg)	GE (%)	Intrinsic Viscosity (dL/g)	Molecular Weight (Da×10 ⁵)
TAP-g-PAM 1	0.5	3	25	91.2	3.674	4.03
TAP-g-PAM 2	0.5	5	25	93.5	3.473	3.77
TAP-g-PAM 3	0.5	7	25	94	4.505	5.13
TAP-g-PAM 4	0.5	9	25	95.4	2.406	2.45
TAP-g-PAM 5	0.5	11	25	97.6	4.793	5.51

Table 1(b)

Polymer	TAP-g-PAM (1g)	1N NaOH (mL)	Yield (%)	Intrinsic Viscosity (dL/g)
Hyd TAP-g-PAM 1	TAP-g-PAM 1	2	70	25.279
Hyd TAP-g-PAM 2	TAP-g-PAM 2	2	71.2	47.043
Hyd TAP-g-PAM 3	TAP-g-PAM 3	2	62.5	22.798
Hyd TAP-g-PAM 4	TAP-g-PAM 4	2	67.6	26.725
Hyd TAP-g-PAM 5	TAP-g-PAM 5	2	68.3	20.362

Synthesis of partially hydrolyzed tapioca starch grafted polyacrylamide

Five different grades of alkaline hydrolyzed graft copolymers i.e., Hyd TAP-g-PAM 1 to Hyd TAP-g-PAM 5 were synthesized by partial hydrolysis of TAP-g-PAM 1 to TAP-g-PAM 5, respectively (**Table 1(b)**). Alkaline hydrolysis of graft copolymers led to the expansion of PAM side chains. Among the various grades synthesized, Hyd TAP-g-PAM 2 was considered as the optimum grade as it had highest intrinsic viscosity in which maximum number of amide groups had converted to carboxyl groups.

FT-IR spectroscopy

The IR spectra of tapioca, TAP-g-PAM 5 and Hyd TAP-g-PAM 3 are shown in **Figure 1(a)**. In the FT IR spectrum of tapioca, the characteristic stretching signals of O–H, C–H and C–O were observed at 3313, 2927 and 1157cm⁻¹, respectively. The bands at 1082 cm⁻¹ and 1024 cm⁻¹ were assigned to –CH₂–O–CH₂– stretching vibrations. In case of TAP-g-PAM 5, stretching bands of hydroxyl group of tapioca starch and N–H of amide group of polyacrylamide overlapped with each other and a broad

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band was observed at 3413 cm^{-1} . The appearance of two signals at 1662 cm^{-1} and 1608 cm^{-1} were attributed to C=O stretching and N–H bending vibrations respectively. Thus, the presence of these additional peaks in case of TAP-g-PAM 5 supported the successful grafting of PAM chains onto tapioca starch. In the case of Hyd TAP-g-PAM 3 a new signal was observed at 1716 cm^{-1} indicating the carbonyl stretching of carboxylate ions. The smoothening of broad stretching band, at 3425 cm^{-1} , of hydroxyl group and N–H of amide group supported the loss of NH_3 during hydrolysis. Thus FTIR spectrum confirms the partial hydrolysis of TAP-g-PAM.

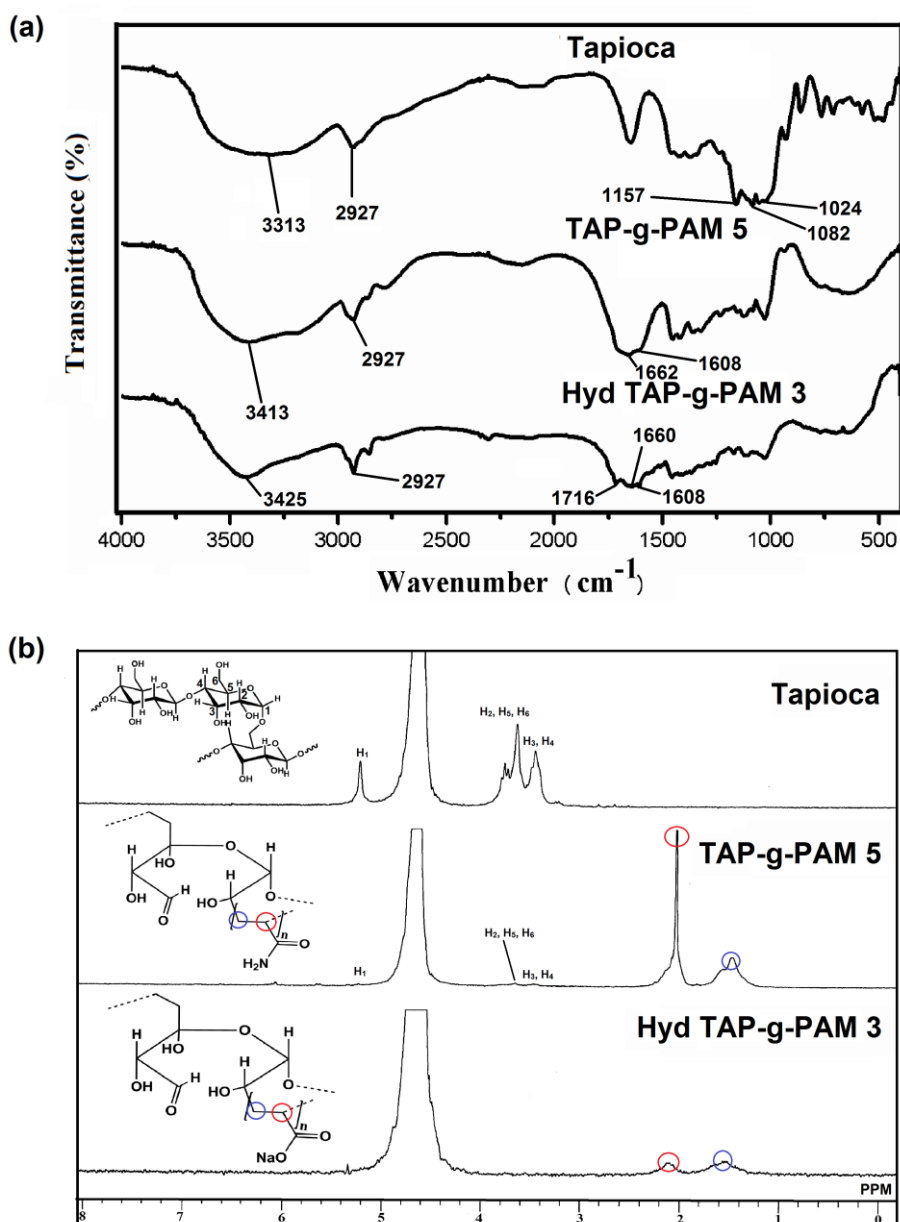


Figure 1. (a) FTIR spectra recorded at room temperature in KBr pellet and (b) ^1H NMR spectra recorded at room temperature in D_2O , of tapioca, TAP-g-PAM and Hyd TAP-g-PAM.

¹H NMR Spectroscopy

Figure 1(b) shows the ¹H NMR spectra of tapioca, TAP-g-PAM 5 and Hyd TAP-g-PAM 3 in D₂O solvent. In ¹H NMR spectrum of tapioca, the peak at 3.49 ppm was attributed to the C–H protons of C₃ and C₄ carbons of glucose units in tapioca. The signals present in the region of 3.67 to 3.8 ppm were due to the protons of C₂, C₅, and C₆. A peak at 5.24 ppm was attributed to anomeric proton of C₁. In case of TAP-g-PAM, along with the characteristic peaks of tapioca back bone, the observed additional peaks at 2.06 and 1.49 ppm were due to the –CH and –CH₂ protons, of polyacrylamide chains, respectively. Whereas, for Hyd TAP-g-PAM 3 the –CH and –CH₂ protons of polyacrylamide chains were shifted to 2.12 and 1.56 ppm respectively. Thus ¹H NMR spectra proved the grafting of PAM onto tapioca starch and partial hydrolysis of graft copolymer.

Intrinsic viscosity measurement

The intrinsic viscosities of all grades of TAP-g-PAM and Hyd TAP-g-PAM were determined and are tabulated in Table 1(a) and (b), respectively. The molecular weights of TAP-g-PAM 1 to TAP-g-PAM 5 were estimated by employing Mark Houwink equation (**Table 1(a)**). Among the different grades of TAP-g-PAM, TAP-g-PAM 5 was observed to have highest intrinsic viscosity. This could be attributed to the presence of longer chains of PAM, as in the case of branched polymers, the longer the branching, higher would be its intrinsic viscosity and vice versa. For the series of Hyd TAP-g-PAM, as the amide groups were converted to carboxyl groups, the repulsions between the COO[–] groups enhanced the chain length. Thus, presence of longer chains led to the increase in intrinsic viscosity than that of parental graft copolymer. Among the grades of Hyd TAP-g-PAM, Hyd TAP-g-PAM 2 was observed to have highest intrinsic viscosity due to conversion of maximum number of amide groups to carboxyl groups.

Flocculation study

Jar test

The flocculation performances of tapioca, PAM, all grades of TAP-g-PAM and Hyd TAP-g-PAM, were estimated in 0.25% kaolin suspension. The plots of polymer concentration vs turbidity of supernatant liquid are shown in **Figure 2**.

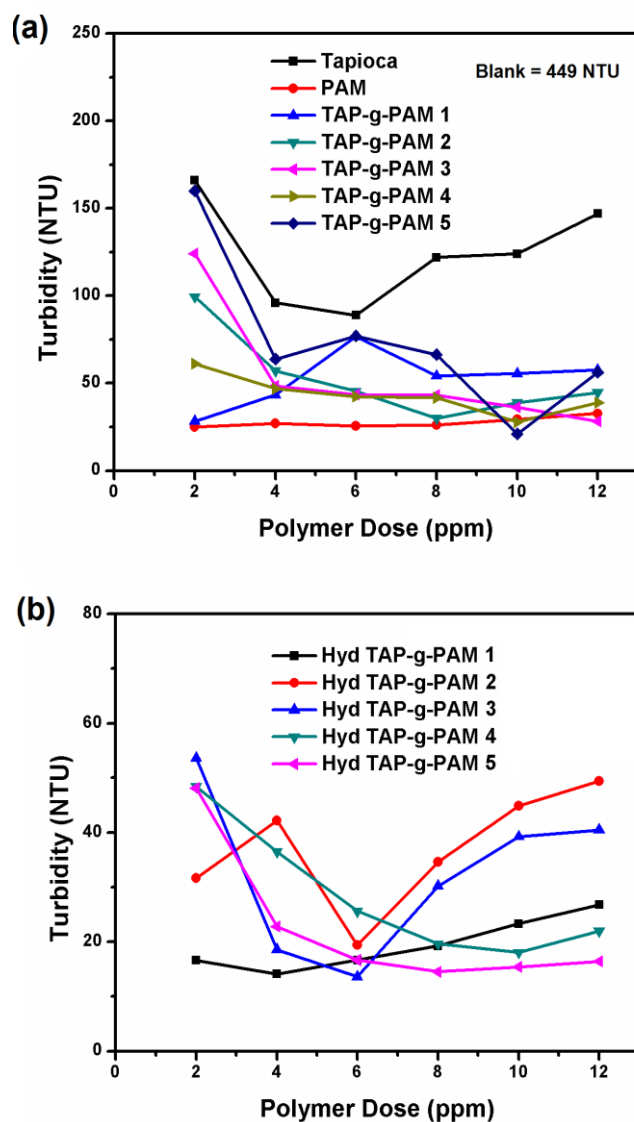


Figure 2. Plots depicting jar test results of
(a) Tapioca, PAM, all grades of TAP-g-PAM, and
(b) all grades of Hyd TAP-g-PAM.

TAP-g-PAM 5 and Hyd TAP-g-PAM 3, showed better flocculation efficiency than that of other grades. The presence of longer chains led to better approachability towards the contaminant and hence better flocculation efficiency was observed for TAP-g-PAM 5 and Hyd TAP-g-PAM 3. Initially there was decrement in turbidity attributed to flocculation at a low dose of flocculant. At optimum dose lowest turbidity and hence maximum flocculation efficiency was observed. As the dose was further increased, restabilization of colloidal flocs occurred and thus there was increase in the turbidity of supernatant liquid. When TAP-g-PAM 5 was compared to Hyd TAP-g-PAM 3 the later one showed better flocculation performance. The expanded side chains of PAM, due to repulsion between the existing negative charges on the polysaccharide backbone, led to increased flocculation performance.

Settling test

The settling tests of all grades of TAP-g-PAM, Hyd TAP-g-PAM and PAM were carried out in 1 wt% kaolin suspension at neutral pH. **Figure 3(a)** and **3(b)** depict the settling behaviors of all grafted grades (TAP-g-PAM 1 to TAP-g-PAM 5) and hydrolyzed grades (Hyd TAP-g-PAM 1 to Hyd TAP-g-PAM 5), respectively. The settling velocities of all grades of TAP-g-PAM and Hyd TAP-g-PAM are reported in **Table 2**. The flocculation efficiencies of all the grades were compared correlating their settling velocities and the grade showing best settling efficiency was determined. Among the grafted grades, TAP-g-PAM 5 exhibited highest settling velocity whereas among the hydrolyzed grades, Hyd TAP-g-PAM 3 exhibited highest settling velocity.

Table 2. Settling velocities of TAP-g-PAM and Hyd TAP-g-PAM in kaolin suspension.

Polymer	Optimum dose (ppm)	Settling velocity (cm/s)
TAP-g-PAM 1	20	1.93
TAP-g-PAM 2	20	1.43
TAP-g-PAM 3	20	1.77
TAP-g-PAM 4	20	1.96
TAP-g-PAM 5	20	2.43
Hyd TAP-g-PAM 1	10	0.65
Hyd TAP-g-PAM 2	10	0.63
Hyd TAP-g-PAM 3	10	2.88
Hyd TAP-g-PAM 4	10	1.24
Hyd TAP-g-PAM 5	10	0.60

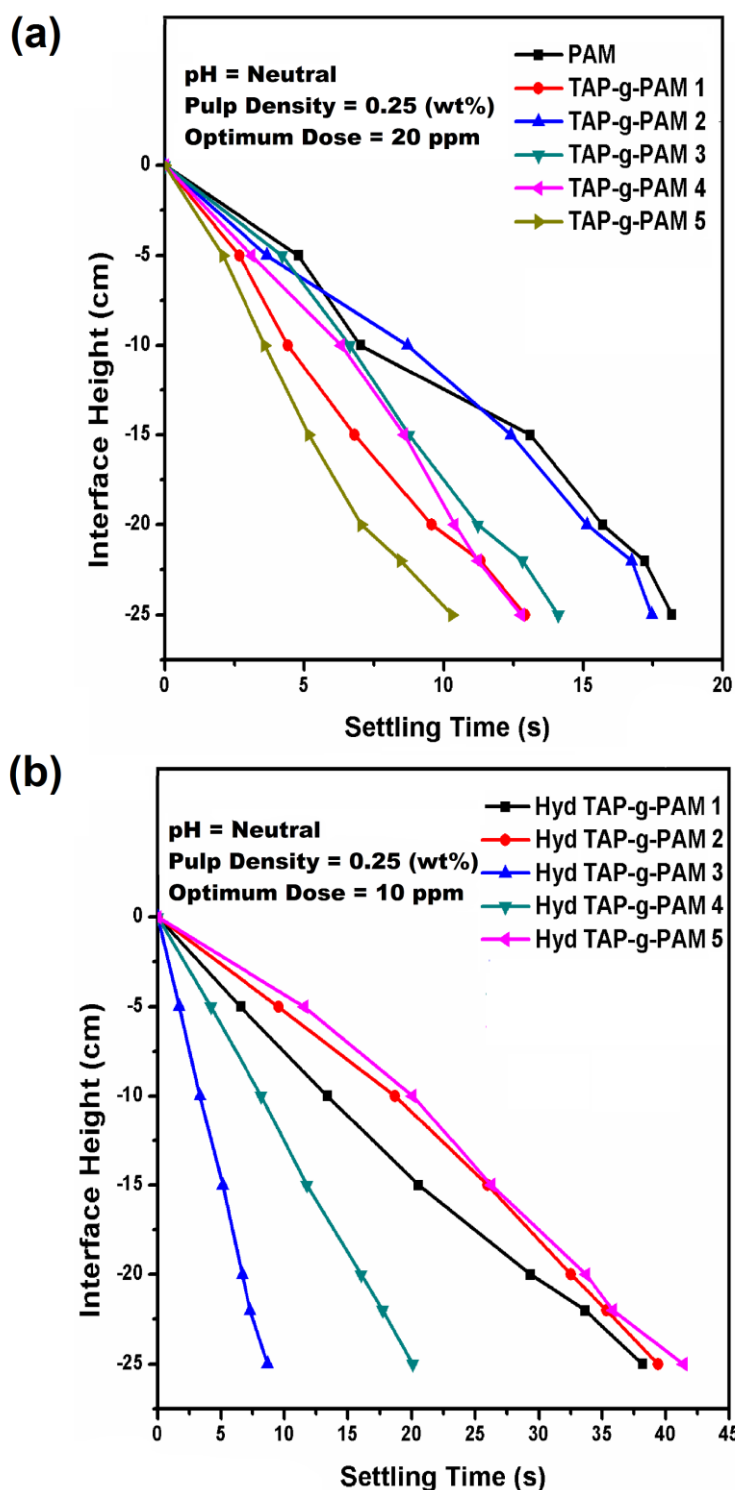


Figure 3. Plots depicting settling test results of
(a) PAM, all grades of TAP-g-PAM, and
(b) all grades of Hyd TAP-g-PAM.

Between TAP-g-PAM 5 and Hyd TAP-g-PAM 3, the later one had longer chains, and thus, observed to have more settling velocity. This was because, during conversion of TAP-g-PAM to Hyd TAP-g-PAM, the side chains of PAM expanded because of repulsion among carboxylate groups. Thus, it was evident that, with longer side chains of PAM in hydrolyzed graft copolymer, the flocculation performance increased.

Dye Removal

TAP-g-PAM 5 and Hyd TAP-g-PAM 3 were chosen, based on their best flocculation performance, for removal of methylene blue dye. Kaolin is also known to be an adsorbate of dye. During the dye removal tests in the laboratory, when kaolin alone was employed for dye removal, only 43.6% of dye was removed. Also unsettled kaolin in the suspension led to water contamination. When the synthesized flocculants were added along with kaolin, all the kaolin particles settled down as floc and efficient removal of dye was observed.

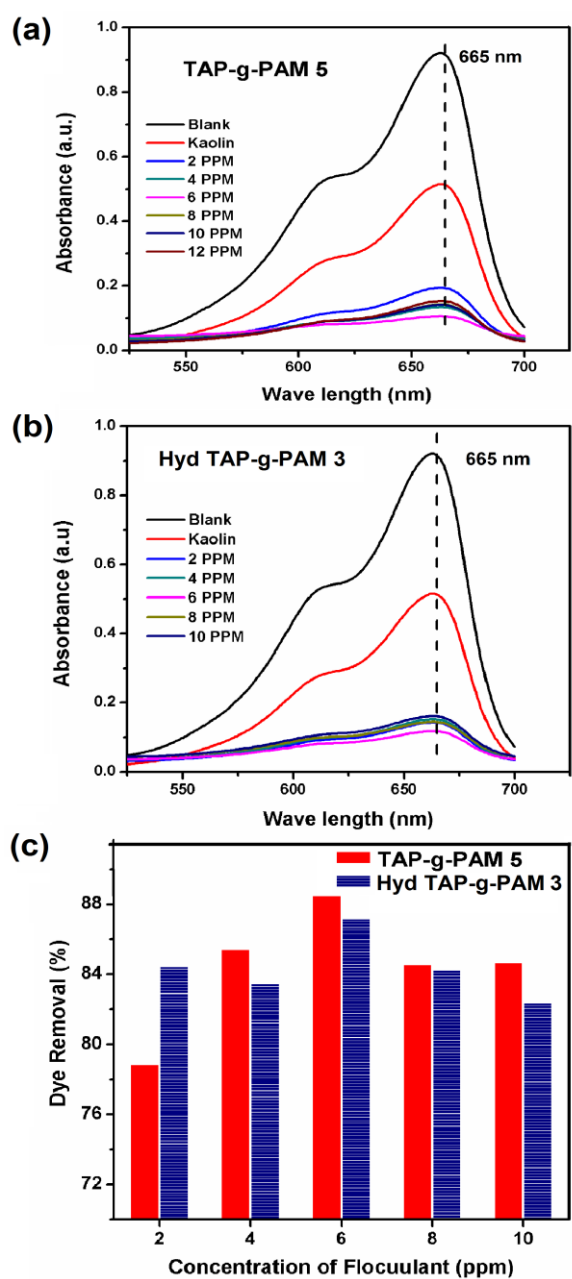


Figure 4. The UV–vis absorption spectra of

(a) TAP-g-PAM 5 and

(b) Hyd TAP-g-PAM 3, and

(c) bar graph showing the percentages of dye removal by both TAP-g-PAM 5 and Hyd TAP-g-PAM 3, using kaolin as adsorbent.

It was observed that, when TAP-g-PAM 5 and Hyd TAP-g-PAM 3 were used 88.5 and 87.2% of dye was removed, respectively (**Figure 4(c)**). This can be explained in the way that better approachability of the grafted chains helped at the easy binding of the colloidal particles through bridging. The optimum grades formed more bridges between the colloidal particles to form flocs. It was expected that, Hyd TAP-g-PAM 3 should show better dye removal than that of TAP-g-PAM 5, due to the presence of anionic carboxylate ions. But it showed nearly same performance as TAP-g-PAM 5. This was because of electrostatic attractions between cationic dye and anionic moieties of hydrolyzed PAM chains which led to less repulsion between carboxylate ions and thus decreased chain lengths of hydrolyzed PAM. Thus, contraction of PAM side chains resulted in a decrease of flocculation performance.

Treatment of water contaminated by haul road dust

As Hyd TAP-g-PAM 3 showed better performance in flocculation tests, it was used in the treatment of water contaminated by haul road dust in opencast mines. To study the performance of the flocculant, jar and settling tests were performed. The results of settling and jar tests are reported in Table 3. From both tests it was observed that in case of coal face haul road dust sample (which contains more percentage of coal) the performance of flocculant was good enough in both ways of turbidity remained and settling velocity. In coal mines water is being mainly polluted by coal particles. As the flocculants could settle the solid wastes having coal easily, it can be employed in the real time practices of water treatment in the coal mines.

Table 3. The settling and jar test results in suspension of coal dust using Hyd TAP-g-PAM 3 as flocculants

Haul road dust sample	Settling test		Jar Test		
	Optimum dose (ppm)	Settling velocity (cm/s)	Optimum dose (ppm)	Turbidity (NTU)	Turbidity of blank solution (NTU)
Jammunia	7	1.58	7	65	271
Dragline	7	1.09	7	54	254
Coal face	4	1.63	5	21.5	236

Thus in short, a series of tapioca grafted polyacrylamide (TAP-g-PAM 1 to TAP-g-PAM 5) was synthesized by solution polymerization method, using CAN as initiator and another series of hydrolyzed tapioca grafted polyacrylamide (Hyd TAP-g-PAM 1 to Hyd TAP-g-PAM 5) was synthesized by alkaline hydrolysis of TAP-g-PAM. The FTIR, ¹HNMR spectra, SEM, TGA and XRD studies confirmed the grafting and then hydrolysis of graft copolymers. TAP-g-PAM 5 had highest molecular weight than other grades of same series. The flocculation efficiencies of the polymers were evaluated in kaolin suspension, through jar and settling tests. TAP-g-PAM 5 and Hyd TAP-g-PAM 3 were found to show better flocculation performance and were chosen as flocculants for removal of methylene blue dye. TAP-g-PAM 5 and Hyd TAP-g-PAM 3 showed 88.5 and 87.2% removal of dye, respectively. Between TAP-g-PAM 5 and Hyd TAP-g-PAM 3, Hyd TAP-g-PAM 3 showed best performance in settling and jar tests, whereas TAP-g-PAM 5 in dye removal test. Moreover, Hyd TAP-g-PAM 3 could settle coal dust easily; it can be employed as flocculants in water treatment in the coal mines.

CONFLICT OF INTEREST

The authors have no conflict of interest.

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REFERENCES

1. Brostow W, Lobland HEH, Pal S, Singh RP. Polymeric Flocculants for Wastewater and Industrial Effluent Treatment. *J Mater Edu.* 2009; 31:157–166.
2. Dao VH, Cameron NR, Saito K. Synthesis, properties and performance of organic polymers employed in flocculation applications. *Polym Chem.* 2016; 7:11-25
3. Zendehtdel M, Barati A, Alikhani H, Hekmat A. Removal of Methylene Blue Dye from Wastewater by Adsorption Onto Semi-Inpenetrating Polymer Network Hydrogels Composed of Acrylamide and Acrylic Acid Copolymer and Polyvinyl Alcohol. *Iranian J Environ Health Sci Eng.* 2010; 7:423–428.
4. Namvari M, Namazi H. Synthesis of magnetic citric-acid-functionalized graphene oxide and its application in the removal of methylene blue from contaminated water. *Polym Int.* 2014; 63:1881–1888.
5. Kumar K, Adhikary P, Karmakar NC, Gupta S, Singh RP, Krishnamoorthi S. Synthesis, characterization and application of novel cationic and amphoteric flocculants based on amylopectin. *Carbohydr Polym.* 2015; 127:275–281.

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6. Narimani F, Lakouraj MM. Synthesis and characterization of super dye adsorbent hydrogels based on acrylic acid and acryloyltetrasodiumthiacalix[4]arenetetrasulfonate. *Polym Int.* 2015; 64:1482–1490.
7. Renault F, Sancey B, Badot PM, Crini G. Chitosan for coagulation/flocculation processes – An eco-friendly approach. *Eur Polym J.* 2009; 45:1337–1348.
8. Crini G. Recent developments in polysaccharide based materials used as adsorbents in wastewater treatment. *Prog Polym Sci.* 2005; 30:38–70.
9. Kumar K, Adhikary P, Krishnamoorthi S. Synthesis, characterization and application of water-soluble star polymers based on 2,4,6-tris-hydroxymethyl phenol and polyacrylamide. *Polym Int.* 2014; 63:1842–1849.
10. Singh RP, Karmakar GP, Rath SK, Karmakar NC, Pandey SR, Tripathy T, Panda J, Kanan K, Jain SK, Lan NT. Biodegradable drag reducing agents and flocculants based on polysaccharides: Materials and applications. *Polym Eng Sci.* 2000; 40:46–60.
11. Yadav R, Garg G. A Review on Indian Sago Starch and its Pharmacuetical Applications. *Int J Pharm Life Sci.* 2013; 3:99–106.
12. Sen G, Kumar R, Ghosh S, Pal S. A novel polymeric flocculant based on polyacrylamide grafted carboxymethylstarch. *Carbohydr Polym.* 2009; 77:822–831.
13. Sen G, Mishra S, Day KP, Bharti S. Synthesis, Characterization and Application of Novel Polyacrylamide-Grafted Barley. *J Appl Polym Sci.* 2014; 131:41046–41054.
14. Adhikary P, Singh RP. Synthesis, characterization, and flocculation characteristics of hydrolyzed and unhydrolyzed polyacrylamide grafted xanthan gum. *J Appl Polym Sci.* 2004; 94:1411–1419.
15. Krishnamoorthi S, Mal D, Singh RP. Characterization of graft copolymer based on polyacrylamide and dextran. *Carbohydr Polym.* 2007; 69:371–377.
16. Azmeera A, Rastogi PK, Adhikary P, Ganesan V, Krishnamoorthi S. Synthesis, characterization and cyclic voltammetric study of copper(II) and nickel(II) polymer chelates. *Carbohydr Polym.* 2014; 110:388–395.
17. Krishnamoorthi S, Singh RP. Synthesis, Characterization, Flocculation, and Rheological Characteristics of Hydrolyzed and Unhydrolyzed Polyacrylamide-Grafted Poly(vinyl alcohol). *J Appl Polym Sci.* 2006; 101:2109–2122.
18. Krishnamoorthi S, Adhikary P, Mal D, Singh RP. Novel polymeric flocculants based on polyacrylamide grafted dextran in kaolin suspension. *J Appl Polym Sci.* 2010; 118:3539–3544.

19. Willett JL, Finkenstadt VL. Starch-poly(acrylamide-co-2-acrylamido-2-methylpropanesulfonic acid) graft copolymers prepared by reactive extrusion. *J Appl Polym Sci.* 2015; 132:42405–42411.
20. Adhikary P, Krishnamoorthi S, Singh RP. Synthesis and characterization of grafted carboxymethyl guar gum. *J Appl Polym Sci.* 2011; 120:2621–2626.
21. Azmeera V, Adhikary P, Krishnamoorthi S. Synthesis and characterization of graft copolymer of dextran and 2-Acrylamido-2-methylpropane sulphonic acid. *Int J Carbohydr Chem.* 2012; 2012:1–7.
22. Borascchi S, Calucci L, Geppi M, Terra FL, Pinzino C, Bertoldo M. Characterization of an amylose-graft-poly(n-butyl methacrylate) copolymer obtained by click chemistry by EPR and SS-NMR spectroscopies. *Carbohydr Polym.* 2014; 112:245–254.
23. Krishnamoorthi S, Mal D, Singh RP. Characterization and Solution Properties of a Partially Hydrolyzed Graft Copolymer of Polyacrylamide and Dextran. *J Appl Polym. Sci.* 2008; 110:1297–1303.
24. Tungala K, Adhikary P, Azmeera V, Kumar K, Krishnamoorthi S. Dendritic star polymer of polyacrylamide based on a β -cyclodextrin trimer: a flocculant and drug vehicle. *New J Chem.* 2017; 41:611–618
25. Adhikary P, Tiwari KN, Singh RP. Synthesis, characterization, and flocculation characteristics of polyacrylamide-grafted glycogen. *J Appl Polym Sci.* 2007; 103:773–778.
26. Silva LFO, Wollenschlager M, Oliveira MLS. A preliminary study of coal mining drainage and environmental health in the Santa Catarina region, Brazil. *Environ Geochem Health.* 2011; 33:55–65.
27. Tiwary RK. Environmental impact of coal mining on water regime and its management. *Water Air Soil Pollut.* 2000; 132:185–199.
28. Tiwary RK, Dhar BB. Environmental pollution from coal mining activities .in damodar river basin, India. *Mine Water Env.* 1994; 13:1–10.