Flocculation Performance of Grafted Xanthangum: A Comparative Study

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ABSTRACT

Ceric ion induced graft copolymerization of N,N-dimethylacrylamide (DMA) and acrylamide (AM) were carried out onto Xanthangum (XAN) backbone. The graft copolymers were characterized by different characterization techniques. Flocculation performances of the graft copolymers were evaluated in kaolin, silica and iron ore suspensions. A detailed comparative study of the flocculation properties of the synthetic graft copolymers was with some commercial flocculants also made in the same suspensions. The result showed that graft copolymers based on N,N-dimethylacrylamide perform better than those based on acrylamide and as well as some commercial flocculants.

Keywords: Flocculation; N, N-dimethylacrylamide; Xanthangum; Silica suspensions; Graft copolymer.

1. Introduction

Polymeric flocculants are extensively used for treatment of industrial effluents and mineral processing [1, 2]. Polymers are convenient to use and do not affect the pH of the medium. They are used in very small quantities and the flocs formed during flocculation are bigger and stronger. Anionic, cationic and nonionic synthetic as well as natural polymers are widely used. Among the natural polymers, polysaccharides have been used extensively but their performance is not good[3]. On the other hand polyacrylamide based synthetic polymers are very efficient flocculating agents but they are shear

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degradable. Polysaccharides are easily biodegradable, inexpensive and fairly shear stable. By grafting polyacrylamide chains on polysaccharides, it is therefore, possible to develop efficient as well as shear stable and biodegradable flocculants for the treatment of industrial effluents and mineral processing. In these flocculants, the flexible polyacrylamide chains are grafted on the rigid backbones of polysaccharides, hence the approachability of polyacrylamide chains to colloidal contaminates is significantly increased. Thus, they offer highly efficient flocculating attributes[4, 5, 6, 7, 8].

It was reported that Poly (N,N-dimethylacrylamide) (PDMA) is highly water soluble, biocompatible[9] and its copolymer was used in oil recovery [10]. Graft copolymer based on N,N-dimethylacrylamide and polysaccharide[11, 12] and the flocculation performance of k-carrageenan-g-N,N-dimethylacrylamide in coal suspension have been reported recently[12]. But no attempt has been made to investigate the flocculation performance of graft copolymers based on N,N-dimethylacrylamide and polysaccharides in detail. Between acrylamide and N,N-dimethylacrylamide, the latter has two methyl groups at the 'N' atom, which increases the electron density and hence polarity of the amide functionality as the methyl group has electron donating effect. Again in polymeric chain of the acrylamide the $-NH_2$ groups take part in intramolecular hydrogen bonding with the   groups of the neighboring amide groups which reduce the water solubility of the polyacrylamide graft copolymers to some extent. But no such intramolecular hydrogen bonding is possible in the poly (N, N-dimethyl acrylamide) which makes easy water soluble.   C=O

The present investigation was undertaken to investigate the effect of methyl groups at the 'N' atom of the amide groups in the flocculation performance of the graft copolymers based on polysaccharides and N,N-dimethylacrylamide in detail. A detail comparative study of the flocculation performances of the synthetic graft copolymers were also made in iron ore slime, kaolin and silica suspensions. One polysaccharides namely Xanthangum was chosen for the grafting reaction with DMA and AM.

2. Experimental
2.1.   Materials
Polyacrylamide (M.W $5x10^6$) was procured from Himedia Chemicals Pvt. Ltd., Mumbai, India. N,N-dimethylacrylamide (DMA) was procured from Aldrich chemical company, USA. N,N-dimethylacrylamide was purified by vacuum distillation and the middle fraction was used for the study. Ceric ammonium nitrate (CAN), Xanthangum (XAN), Acetone and silicon dioxide were procured from Loba Chemie, Bombay, India. Acrylamide, sodium nitrate were supplied by E. Merck, Bombay, India. Iron ore slime was

obtained from TISCO mine, (Jharkhand, India). Kaolin clay was obtained from Famous Minerals and Chemical Pvt. Ltd., Mumbai, India. The average particle size of kaolin clay is 79.6 nm, and the suspension zeta potential is -3.9 mV at pH 7.6. The average particle size of iron ore slime is 104.6 nm and the suspension zeta potential is -31.72 mV at pH 7.2. The average particle size of silica is 101.4 nm and the suspension Zeta potential is -52.3 at pH 7.2. Magnafloc-1011 was obtained from BASF India Limited, Mumbai, India. Telfloc-2230 was obtained as a gift from Balaji Paper & Newsprint Pvt. Ltd. Manikpara, W.B, India. The commercial flocculants are polyacrylamide (PAM) based linear homopolymer and their structures are totally classified by their manufacturer. Doubly distilled water was used for the synthesis. Poly (N, N-dimethylacrylamide) (M.W is the order of 10^6) was procured from Scientific Polymer Product, Inc. USA.

3. Synthesis of the Graft copolymer

The graft copolymers of polysaccharides and DMA were synthesized by the use of ceric ion induced redox initiation method [13]. The typical experimental details for one graft copolymer involving XAN and DMA are as follows; 1.5g of XAN was dissolved in 100 ml of distilled water at 100^oC with constant stirring and bubbling of nitrogen for about 15 min. 10 cc (0.109 moles) of N,N-dimethylacrylamide was added to the XAN solution. Then nitrogen gas was purged through the solution for 20 min. at this stage 40 cc of the required CAN solution was added to the reaction mixture followed by further purging with nitrogen for 15 mins. The reaction was allowed to continue for 24 hours after which it was terminated by adding saturated solution of hydroquinone. At the end of the reaction the polymer was precipitated by adding excess quantities of acetone. The homopolymer PDMA was removed by soxhlet extraction using methanol as a solvent. The precipitated polymer was then dried under vacuum. Afterwards it was pulverized and sieved. The PAM grafted polysaccharides were also synthesized by ceric ion induced redox initiation method under the similar condition as stated above. The detailed synthetic process was given in our previous article[4]. The synthetic details of all the graft copolymers are given in Table I and Table II.

Table I: Synthetic details of the graft copolymers based on N, Ndimethylacrylamide (DMA)

Polymer	Polysaccharide (g)	DMA (mol)	Amount of CAN (mol x 10^{-4})	Percentage of conversion [a]	Intrinsic Viscosity (dl/g)
XAN-g-PDMA	1.5	0.109	4.564	83.24	6.4

[a] Percentage conversion is calculated from the relation,
% Conversion = [(wt of graft copolymer – wt of polysaccharide) / amount of DMA] x 100

Table II: Synthetic details of the graft copolymers based on acrylamide (AM)

Polymer	Polysaccharide (g)	AM (mol)	Amount of CAN (mol x 10^{-4})	Percentage of conversion [a]	Intrinsic Viscosity (dl/g)
XAN-g-PAM	1.5	0.140	4.564	84.11	6.5

[a] Percentage conversion is calculated from the relation,
% Conversion = [(wt of graft copolymer – wt of polysaccharide) / amount of AM] x 100

4. Isolation of grafted PDMA and PAM Chains

The grafted PDMA chains were isolated by hydrolyzing the graft copolymers in 70 % (v/v) H_2SO_4 [14] for 12 h at boiling point. The mixture was poured into excess acetone and hexane mixture (1:1 by volume). The PDMA thus precipitated was re-dissolved in water and precipitated again in acetone and hexane mixture.

The PDMA was dried in vacuum. The grafted PAM chains were also isolated from the polysaccharides backbone by treatment with 70% (v/v) aqueous sulfuric acid for 24 h at the temperature of 25^0C. The mixture was poured into excess acetone and the polyacrylamide precipitated was re-dissolved in water and re-precipitated in acetone. Then it was dried in vacuum. The graft copolymers, the isolated PDMA and PAM were used for the IR study.

5. Characterization of the graft copolymers
5.1. Viscosity measurement

Viscosity measurement of polymer solutions was carried out using an Ubbelhode viscometer (constant 0.00527) at 27^0C. The viscosities were measured in 1 (M) $NaNO_3$ solution. The flow time was measured for the solutions at five different concentrations. The intrinsic viscosity was calculated by plotting η_{sp} vs. c and η_{inh} vs. c; and then taking the common intercept at c = 0 of the best fitted straight lines through the two sets of points[15]. Here c is the polymer concentration in g/dl; η_{sp} and η_{inh} are the specific and inherent viscosity calculated from the following equations. $\eta_{rel} = t/t_0$ where η_{rel} is the relative viscosity, t is the time of flow of the solution and t_0 is the time of flow of solvent (here water) at the same temperature $\eta_{sp} = (t-t_0)/t_0$ $\eta_{inh} = \ln \eta_{rel} /c$. The values of intrinsic viscosities of all the graft copolymers are given in Table I and Table II.

6. FTIR-Spectroscopy
The homopolymer PDMA was removed from all the PDMA graft copolymers by soxhlet extraction using methanol as solvent. The homopolymer PAM was also removed by the same procedure using a mixture of formamide and acetic acid (1:1 by volume) [16] from the PAM graft copolymers. Then the graft copolymers, PDMA and PAM were subjected to IR spectral analysis. A Perkin-Elmer-883 Infrared spectrophotometer (UK) was used and the potassium bromide (KBr) pellet method was followed for IR spectrum. The spectra are shown in Figure 1 and 2.

7. Thermal analysis
The thermal analysis (TGA / DTGA) of all the graft copolymers based on DMA and AM along with the polysaccharide was carried out with Stanton Red Croft (STA625) Thermal analyzer. TGA analysis of the samples was performed upto a temperature of 800^0C starting from 10^0C in an atmosphere of nitrogen. The heating rate was uniform in all cases at 10 deg / min. the TGA curves are shown in Figures 3, 4, 5 and 6.

8. Flocculation study
Flocculation Jar Test [3] was carried out in standard flocculation Jar apparatus supplied by Scientific Engineering Corporations, New Delhi, India. Turbidity measurements were carried out with a Digital Nephelo Turbidity meter procured from EI Products, Haryana, India. The detailed flocculation procedure was given in our previous article[4]. A 1.0 wt% kaolin clay and 0.25 wt% iron ore slime and 0.25 wt% silicon dioxide were used for flocculation studies. The dose of flocculant varied in the range of 1-10 ppm for iron ore slime; 1-8 ppm for kaolin clay suspension and 1-12 ppm for silicon dioxide suspension.

9. Results and Discussion

9.1. Synthesis and intrinsic viscosity of the graft copolymers

The synthetic details of the graft copolymers are shown in Table I and Table II. Two graft copolymers were synthesized namely XAN-g-PDMA, using DMA as the monomer and XAN-g-PAM using AM as the monomer keeping all the reaction parameters constant. The mechanism of ceric ion action involves the formation of a chelate complex that decomposes to generate free-radical sites on the polysaccharide backbone. These active free-radical sites in the presence of acrylic monomers generate graft copolymers. The reaction parameters were fixed according to our previous experience.

It is known that the intrinsic viscosity of a polymer is a measure of its hydrodynamic volume in solution, which in turn is a function of the polymer molecular weight, its structure, nature of the solvent, and the temperature of the medium. Keeping the other factors constant, two polymers of approximately similar intrinsic viscosity will have approximately similar molecular weight [17].

9.2. FTIR Spectroscopy

The grafting is supported by IR spectroscopy. The IR spectra of XAN-g-PDMA and PDMA are shown in Figure 1. The IR spectrum of PDMA shows a peak at 1648 cm^{-1} for amide group, the peak at 1416 cm^{-1} is for C-N group, a peak at 2933 cm^{-1} is for aliphatic C-H group. The peak at 3450 cm^{-1} is due to the presence of absorbed moisture. The graft copolymer XAN-g-PDMA shows characteristic absorption on 1632 cm^{-1} which is for amide group, and 1455 cm^{-1} is for the C-N group. Since the DMA and PDMA were removed, the presence of peaks at 1632 cm^{-1} and 1455 cm^{-1} in the graft copolymer is a strong evidence for grafting.

In Figure 2 the IR spectrum of XAN-g PAM and PAM are shown. Here the peaks which remain in PAM molecule 3370 cm^{-1} for –NH$_2$ group 1680 cm^{-1} for amide C=O group, 1427 cm^{-1} for C-N group are also present in the graft copolymer at 2918 cm^{-1}, 1650 cm^{-1} and 1410 cm^{-1}. Since the acrylamide and polyacrylamide were removed, the presence of peaks at 2918 cm^{-1}, 1650 cm^{-1}, and 1410 cm^{-1} in the graft copolymer is a strong evidence for the grafting.
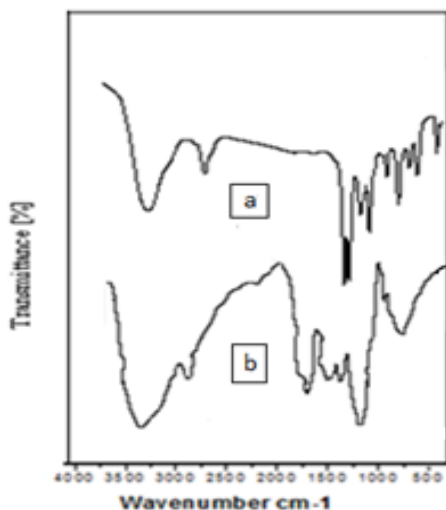
Figure 1 IR Spectra of
(a) PAM (b)XAN-g-PAM
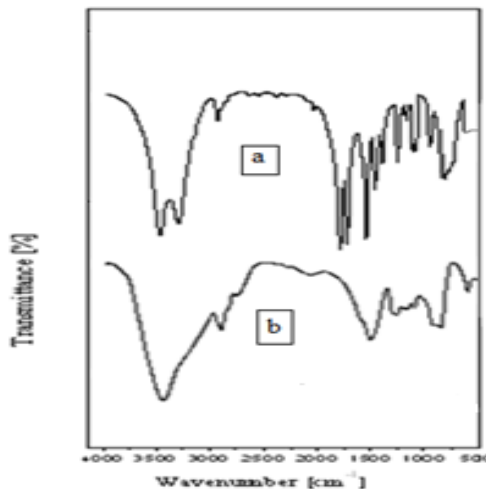
Figure 2 IR Spectra of
(a) PDMA (b) XAN-g-PDMA

10. Thermal analysis

The TGA / DTGA curves of XAN-g-PAM and XAN-g-PDMA are shown in Figure 3 and 4 respectively. It is obvious from the TGA / DTGA curve of XAN-g-PAM that it has four decomposition regions. The initial weight loss of the polymer may be due to the presence of moisture. In the second region the weight loss is due to the loss of hydroxyl groups from the polysaccharide backbone. In the third zone the weight loss is due to the elimination of $-NH_3$ from the polyacrylamide chains. In the last zone the weight loss might be due to the loss of carbon monoxide (CO) and the loss of abundant hydroxyl groups by the degradation of polysaccharide chain. In the XAN-g-PDMA the weight loss at the third zone (at 437 ^{0}C) is due to the elimination of Me_2NH groups.
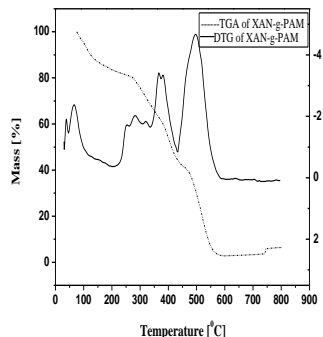
Figure 3 TGA and DTGA curves of XAN-g-PAM
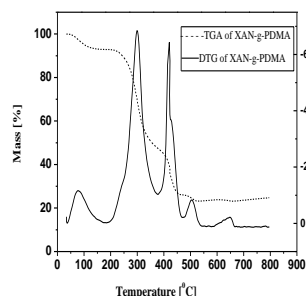
Figure 4 TGA and DTGA curves of XAN-g-PDMA

10. Flocculation study

The flocculation efficiencies of the synthesized graft copolymers XAN-g-PAM and XAN-g-PDMA were tested in 1.0 wt% of kaolin clay, 0.25 wt% of silica and 0.25 wt% of iron ore slime suspensions. The results are shown in Figures 5-14. In each case, the turbidity of supernatant liquid after flocculation was plotted against the polymer concentration. The flocculation properties of XAN-g-PDMA was compared with XAN-g-PAM in, kaolin clay, silica and iron ore slime suspension as depicted in Figures 5 for kaolin clay, Figures 6 for silica and Figures 7 for iron ore slime suspensions. In all the above three cases graft copolymers based on DMA showed better performance than those based on AM. In all cases the performance of a particular flocculants was expressed in terms of turbidity. The lower the turbidity, the better the performance will be. The reason for the better flocculation performance of PDMA grafted polysaccharides will be as follows.
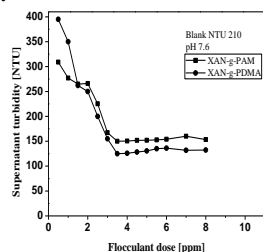
Figure 5 Comparison of flocculation characteristics of XAN-g-PAM and XAN-g-PDMA in 1.0 wt%
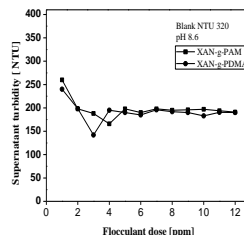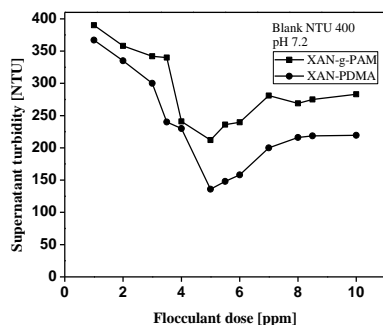

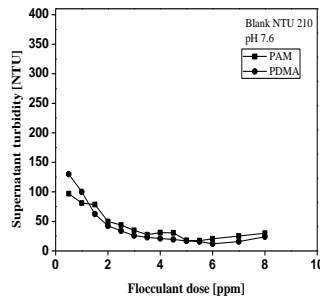**Figure 6** Comparison of flocculation characteristics of XAN-g-PAM and XAN-g-PDMA in 0.25 wt% silica

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Kaolin clay suspension   Suspension

Figure 7 Comparison of flocculation characteristics of XAN-g-PAM and XAN-g-PDMA in 0.25 wt% iron ore slime suspension

Figure 8 Comparison of flocculation characteristics of PAM and PDMA 1.0 wt% kaolin clay suspension

The major mechanisms of flocculation of polyelectrolytes are surface charged neutralization and bridging. Surface charged neutralization occurs, if the charge of flocculant is opposite in sign to that of the suspended particles. For neutral flocculants, the major mechanism of flocculation is the polymer bridging. When very long chain polymer molecules are absorbed on the surface of particles, they tend to form loops that extend some distance from the surface into the aqueous phase, and their ends may also dangle. These loops and ends may come into contact with, and attach to other particles. This is the bridging mode of flocculation. Essentially, a polymer bridging occurs because segments of a polymer chain get absorbed in various particles, thus bringing the particles together. For effective bridging to occur, there must be a sufficient polymeric chain length, which extends far enough from the particle surface to attach to other particles and also the flexibility of the polymeric chains.

In water medium, in the polyacrylamide chains, strong intramolecular hydrogen bonding between the –CO and –NH$_2$ groups occurs, which makes the chain stiffen and helical[26]. Thus the approachability of the grafted PAM chains to the contaminant particle becomes less. But in case of PDMA chains, the intramolecular hydrogen bonding does not occur. The absence of hydrogen bonding increases the flexibility of the grafted PDMA chains. So, in the PDMA grafted polysaccharides due to the better flexibility of the dangling grafted PDMA chains, the approachability of the grafted chains to the colloidal particles becomes higher than that of the grafted PAM chains. Hence, for PDMA grafted polysaccharides bridging will be better and easier than that of PAM grafted polysaccharides.

Again, in the amide functionality ($-\overset{\overset{O}{\|}}{C}-N\diagup$) the electron delocalization of the lone pair of nitrogen into the adjacent carbonyl group places a partial (+)ve charge on the nitrogen atom and a partial negative charge on the oxygen atom
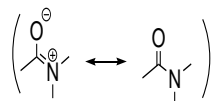
which makes the amide group polar. Hence, the colloidal particles are attracted by the amide groups in a polymer chain irrespective of surface charges (Zeta potential) of the suspended colloidal particles. The polarity of

$$-\overset{\overset{O}{\|}}{C}-NMe_2$$
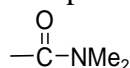
group (present in DMA molecule) is higher than that of the $-CONH_2$ group (present in acrylamide molecule) due to the presence of electron donating methyl (-Me) groups at the nitrogen atom of the former, which helps the absorption of the colloidal particles into the grafted PDMA chains resulting strong bridging. For this effective intense bridging capabilities of the PDMA chains, PDMA grafted polysaccharides showed better flocculation performance over PAM grafted polysaccharides. This finding is further supported by the following fact. When the flocculation performance of the homopolymer PAM and PDMA were compared in all the three suspensions, kaolin clay, silica and iron ore slime suspensions it was observed that the performance of PDMA is better than the PAM. The results are shown in Figures 8, 9 and 10 respectively.

The flocculation performances of the two synthesized graft copolymers were compared in kaolin clay, silica and iron ore slime suspensions also. The results are shown in Figures 5, 6 and 7 respectively. In all the three cases it was observed that
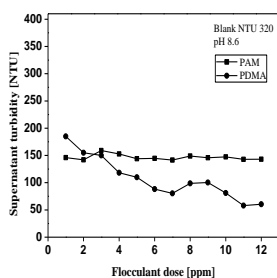
Figure 9 Comparison of flocculation characteristics of PAM and PDMA 1.0 wt% kaolin clay suspension
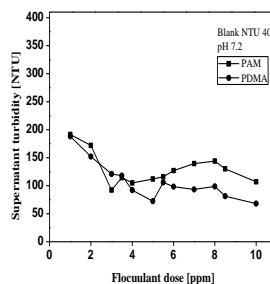
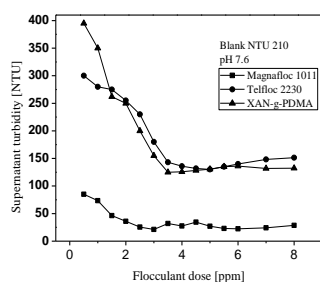**Figure10** Comparison of flocculation characteristics of PAM and PDMA in 0.25 wt% silica suspension

the flocculation performance of XAN-g-PDMA is better than that of the XAN-g-PAM.

In Figures 11, 12 and 13 the flocculation performance of the better performing graft copolymer XAN-g-PDMA was compared with two commercially available flocculants Telfloc-2230 and Magnafloc-1011 in kaolin clay, silica and iron ore slime suspensions respectively. From the figures it is obvious that in kaolin clay suspension and silica the performance XAN-g-PDMA is better than Telfloc-2230, whereas in iron ore slime suspension XAN-g-PDMA shows better performance in higher dose where as magnafloc-1011 showed better performance in lower dose.

12.Conclusion

It can be concluded from the above study that PDMA can be grafted successfully at the xanthangum backbone by ceric ion induced redox polymerization technique in aqueous solution. PDMA grafted polysaccharide showed better flocculation performance over PAM grafted polysaccharides. The flocculation performance of XAN-g-PDMA is at par or better than some commercially available flocculants. Hence, by grafting PDMA chains onto the polysaccharide backbones, effective flocculating agents can be developed for the treatment of waste water.

Figure 11 Comparison of flocculation characteristics of XAN-g-PDMA, Magnafloc 1011 and Telfloc 2230 in 1.0 wt% kaolin clay suspension
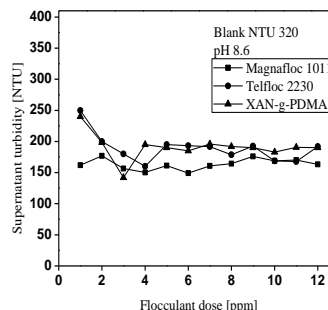
Figure 12 Comparison of flocculation characteristics of XAN-g-PDMA, Magnafloc 1011 and Telfloc 2230 in 0.25 wt% silica suspension
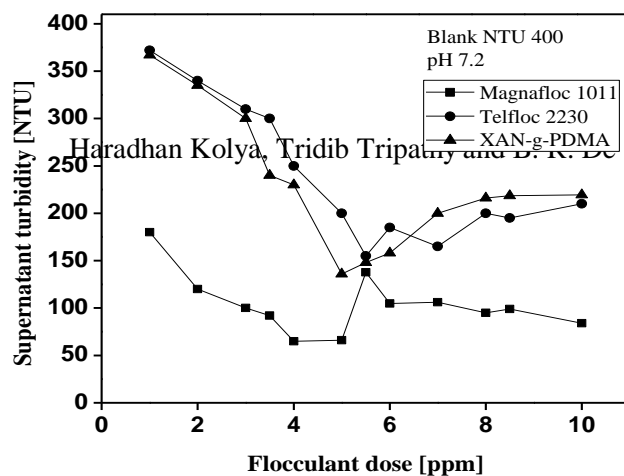
Figure 13 Comparison of flocculation characteristics of XAN-g-PDMA, Magnafloc 1011 and Telfloc 2230 in 0.25 wt% Iron ore slime suspension

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