Flocculation properties of polyacrylamide grafted carboxymethyl guar gum (CMG-g-PAM) synthesised by conventional and microwave assisted method

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ABSTRACT

A novel polymeric flocculant based on polyacrylamide grafted carboxymethyl guar gum (CMG-g-PAM) has been synthesised by grafting polyacrylamide chains onto CMG backbone using conventional redox grafting and microwave assisted grafting methods. Under optimum grafting conditions, 82% and 96% grafting efficiencies have been observed in case of conventional and microwave assisted methods respectively. The optimum sample has been characterized using viscometry, spectroscopic analysis, elemental analysis, molecular weight and radius of gyration determination. The flocculation characteristics of grafted and ungrafted polysaccharides have been evaluated in kaolin suspension, municipal sewage wastewater and decolourization efficiency of a dye solution (methylene blue). It is evident from results that CMG-g-PAM synthesised by microwave assisted grafting method is showing best flocculation characteristics.

1. Introduction

The chemical contamination of water from a wide range of toxic derivatives, in particular heavy metals, suspended particles, aromatic molecules and dyes, is a serious environmental problem owing to their potential human toxicity. Strict legislation on discharge of these toxic materials make it necessary to develop efficient technologies for the removal of toxic pollutants present in wastewater. The wastewaters emanated from various industries contain very fine suspended particles having size in the range of 0.001–10 μm. Because of very small size and the presence of surface charge, it is very difficult to bring these particles closer to make heavier mass for settling [1]. Sometimes these particles remain suspended for years. Hence, removal of these colloidal particles from wastewaters becomes a serious challenge for the industries [2,3]. Out of various wastewater treatment processes, flocculation is an economical and effective technique, plays a dominant role in wastewater treatment, in particular for removal of suspended particles, dyes and heavy metals [4,5]. Flocculation is a process that makes finely divided or dispersed particles aggregate and form large flocs so as to be settled and separated from wastewater [6]. The chemicals used in flocculation are known as flocculants.

Most of the inorganic particles carry charge in neutral aqueous medium. To destabilize the system, inorganic coagulants such as alum, polyaluminium chloride, ferric chloride, ferrous sulphate,

magnesium chloride etc. have been used for decades [7]. However, this process is strongly pH dependent and decreases the alkalinity of the water [8]. Moreover, the inorganic coagulants are required in large amount to achieve effective settling rate. As a consequence, large volume of metal hydroxide sludge is produced. This again creates disposal problem [9]. Apart from this disposal problem, the uses of inorganic salts such as alum and polyaluminium chloride are now very much controversial because of the possible impact of residual aluminium in the recycled water on Alzheimer disease [10,11].

To minimize the drawbacks of inorganic coagulants, synthetic flocculants are used as an alternative because of its rapid settling and reduced sludge production [8]. The flocculants neutralize the surface charge of the hydrated colloidal particles, thus reducing the electrical repulsion between the approaching particles. It also bridges the approaching particles by the polymer chains. Water soluble synthetic flocculants, mainly polyacrylamide based flocculants, with different molecular weights and charge densities find extensive utility in industries because of its economic advantage and easy tailorability [12]. However, these synthetic polymers are not biodegradable and their degradation products are considered to be hazardous because of the release of toxic monomers, which may cause potential health hazards [13].

Because of increasing demand for eco-friendly and healthy technologies, natural polymer based flocculants have been used widely as flocculants in order to replace inorganic and synthetic polymer based flocculants [14,15]. Among the natural polymer based flocculants, graft copolymers of natural polysaccharide and synthetic polymer are becoming an important resource for developing

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Nomenclature

GG	Guar gum
CMG	Carboxymethyl guar gum
AM	Acrylamide
PAM	Polyacrylamide
CMG-g-PAM	Polyacrylamide grafted carboxymethyl guar gum
%GE	Percentage of grafting efficiency
%DE	Percentage of decolourization efficiency
TS	Total solid
TDS	Total dissolved solid
TSS	Total suspended solid
COD	Chemical oxygen demand

advanced materials as it can improve the functional properties of natural polysaccharides. As a tailor-made material, graft copolymers find various applications as matrix for controlled drug release [16,17], gums with improved properties [18], flocculants [12,14,15], etc. Synthesis of graft copolymers essentially involves free radical mechanism. The free radicals can be generated in a variety of ways; the most effective approaches are the use of free radical initiator [14,15] and using high energy radiations such as microwave irradiation [19]. Further, microwave based grafting is of two types. The most commonly used method employs microwave in the presence of a free radical initiator (microwave assisted grafting) [14,19]. The lesser-known method involves microwave radiation in the absence of any free radical initiator (microwave initiated method) [20]. Microwave assisted method exhibits the best potential for synthesising graft copolymers, because the free radicals are generated using microwave photons as well as free radical initiators, leading to a much higher percentage of grafting efficiency as compared to the conventional method of synthesis. Moreover, the microwave irradiation as a source of efficient thermal energy constitutes an original method of heating materials, different from the classical one. Main advantage is that, it results in almost instantaneous homogeneous heating of materials in a selective manner.

Guar gum (GG) is one of the most important industrial gums. It has been extracted from the seeds of *Cyamopsis tetragonoloba*, which belongs to the *Luguminosoe* family. GG is a linear polymannose with pendent galactose sugars on alternating mannose units. On the average, there are between 1.5 and 2 mannose residues for every galactose residue, with few, if any, non-substituted regions. Carboxymethyl guar gum (CMG) is a derivative of guar gum, synthesised by inserting carboxymethyl groups onto the backbone of guar gum [21].

In this present study, an efficient polymeric flocculant has been crafted by grafting polyacrylamide chains onto carboxymethyl guar gum backbone using redox grafting and microwave assisted grafting methods. Varying the reaction conditions, graft copolymer samples of different %grafting efficiency (%GE) have been prepared. The applicability of these graft copolymers as novel polymeric flocculants for the treatment of simulated wastewater (Kaolin suspension), municipal sewage wastewater and decolourization efficiency of methylene blue dye solution has been reported.

2. Experimental

2.1. Materials

Carboxymethyl guar gum was used as synthesised earlier [21]. Acrylamide was procured from E. Merck, Germany. Potassium persulphate was purchased from Qualigens Fine Chemicals, Mumbai,

India. Analar grade acetone and hydroquinone were supplied by S. D. Fine Chemicals, Mumbai, India. All the chemicals were used as received, without further purification.

Methylene blue was supplied by Loba Chemie Pvt. Ltd., Mumbai, India. Kaolin was purchased from B. D. Pharmaceutical Works Pvt. Ltd., Howrah, India. Municipal sewage wastewater was collected from main sewage system of Birla Institute of Technology, Mesra, Ranchi, India.

2.2. Synthesis

2.2.1. Synthesis of graft copolymer by conventional method [CMG-g-PAM (C)]

The graft copolymerization of polyacrylamide onto CMG has been carried out in a 250 mL three necked round bottom flask. The flask was fitted with an electrically operated magnetic stirrer (Tarsons, Model: Spinot Digital), maintained at temperature $70 \pm 1\,°C$. Required amount of CMG was dissolved in 100 mL of distilled water with constant stirring and bubbling of a slow stream of nitrogen for about 15 min. Desired quantity of acrylamide listed in Table 1 was dissolved in 20 mL of distilled water and mixed with the CMG solution. Afterwards, oxygen free nitrogen gas was purged through the solution mixture for 30 min. At this stage, 5 mL of potassium persulphate solution of desired concentration listed in Table 1 was added and nitrogen gas purging was continued for another 1 h, after which it was terminated by adding saturated solution of hydroquinone. The reaction mixture was stirred at a constant speed (300 rpm) to avoid the adverse effect of stirring on graft copolymerization. The resultant graft copolymer was precipitated by adding 400 mL of acetone, dried in a hot air oven at $60\,°C$ for 6 h, pulverized and sieved through a 125 μm sieve.

2.2.2. Synthesis of the graft copolymer by microwave assisted method [CMG-g-PAM (MA)]

Microwave irradiation and potassium persulphate were used to generate the free radical sites on the polysaccharide as well as monomer backbone. The detailed synthesis process is as follows.

Required amount of CMG was dissolved in 35 mL of distilled water. Desired quantity of acrylamide and $S_2O_8{}^{2-}$ as listed in Table 1 was dissolved in 10 mL and 5 mL water respectively and was mixed with the CMG solution. Afterwards the mixture was transferred to the reaction vessel (1000 mL Borosil beaker) which was then placed on the turntable of a microwave oven (LG Microwave oven Model: MG-577B). An electronic thermometer with an alarm set at $70\,°C$ temperature was incorporated into the reaction vessel. Whenever the temperature of the reaction mixture reached $70\,°C$, the alarm would sound and the microwave was immediately paused and the reaction vessel was cooled. Microwave irradiation at power density $1.64\,W/cm^2$ was performed for the time listed in Table 1. The reaction vessel and its content were allowed to cool and left undisturbed for 1 h and the reaction was being terminated using saturated solution of hydroquinone. The mixture was poured into 250 mL of acetone; the resulting precipitate was collected and dried in a hot air oven at $60\,°C$ for 6 h, pulverized and sieved through a 125 μm sieve.

2.2.3. Purification of the graft copolymer by solvent extraction method

Occluded polyacrylamide (PAM) formed by competing homopolymer formation reaction was removed from the graft copolymers by solvent extraction using a mixture of formamide and acetic acid (1:1 by volume).

Table 1
Synthesis details of polyacrylamide grafted carboxymethyl guar gum.

Synthetic details of CMG-g-PAM by conventional method [amount of CMG[a] (=0.0061 mol) is fixed]

Polymer grade	Amount of monomer (mol)	Amount of $S_2O_8{}^{2-}$ ($\times 10^{-5}$ mol)	%GE[b]	Intrinsic viscosity (dL/g)	Mol. Wt. (g/mol)	Radius of gyration (nm)
CMG-g-PAM 1(C)	0.07	0.37	64%	13.70	2.24×10^6	78.2
CMG-g-PAM 2(C)	0.07	1.85	71%	16.50	3.05×10^6	80.4
CMG-g-PAM 3(C)	0.07	3.70	67%	15.09	3.23×10^6	83.6
CMG-g-PAM 4(C)	0.14	1.85	77%	19.78	4.40×10^6	87.0
CMG-g-PAM 5(C)	0.21	1.85	82%	23.80	5.26×10^6	90.1
CMG-g-PAM 6(C)	0.28	1.85	79%	22.06	4.97×10^6	88.9

Synthesis details of CMG-g-PAM by microwave assisted method [amount of CMG[a] (=0.0061 mol) is fixed]

Polymer grade	Amount of monomer (mol)	Amount of $S_2O_8{}^{2-}$ ($\times 10^{-4}$ mol)	Time (min)	%GE[b]	Intrinsic viscosity (dL/g)	Mol. Wt. (g/mol)	Radius of gyration (nm)
CMG-g-PAM1(MA)	0.07	0.37	1	84%	17.90	3.67×10^6	84.5
CMG-g-PAM 2(MA)	0.07	0.37	2	89%	25.45	5.10×10^6	89.6
CMG-g-PAM 3(MA)	0.07	0.37	3	81%	24.02	4.80×10^6	88.4
CMG-g-PAM 4(MA)	0.07	1.85	2	90%	31.25	6.28×10^6	96.6
CMG-g-PAM 5(MA)	0.07	3.70	2	93%	30.50	5.60×10^6	94.2
CMG-g-PAM 6(MA)	0.14	1.85	2	96%	46.01	7.40×10^6	102.9
CMG-g-PAM 7(MA)	0.17	1.85	2	91%	41.50	6.80×10^6	98.4
CMG	–	–		–	11.60	4.10×10^5	71.1

[a] Calculated on the basis of anhydroglucose unit (AGU). 1 mol of AGU = 162 g.
[b] % grafting efficiency = ((wt. of graft copolymer − wt. of polysa ccharide)/wt. of monomer) × 100.

2.3. Characterization

CMG and various grades of CMG-g-PAMs were characterized through intrinsic viscosity measurement (using Ubbelodhe viscometer, with capillary diameter of 0.58 mm at 25 °C in 1 M NaNO$_3$ solution), determination of molecular weight and radius of gyration using SLS analysis (Zetasizer Nano ZS, Malvern, UK) and elemental analysis with an Elemental Analyzer (Make – M/s Elementar, Germany; Model – Vario EL III). ^{13}C nuclear magnetic resonance (NMR) spectroscopic analysis was done in solid state using 500 MHz Bruker Advance II-500 spectrometer. Morphological analysis was done using scanning electron microscopy (SEM, Model: JSM-6390LV; JEOL, Japan).

2.4. Flocculation studies

2.4.1. Flocculation characteristics in simulated wastewater (kaolin suspension)

The flocculation efficiency of various polymer samples was carried out using standard Jar Test Method.

A conventional jar test apparatus comprises a flocculator and a turbidity meter. The flocculator was supplied by Gon Engineering Works, Dhanbad, India and the turbidity meter was procured from Systronics, Ahmedabad, India. 0.25 wt% suspension of kaolin (prepared by mixing 1 g in 400 mL of distilled water) was used for flocculation study. The suspensions were taken in each of six 1-L beakers and the flocculant was added in solution form. The following procedure was uniformly applied–immediately after the addition of flocculant; the suspension was stirred at a constant speed of 75 rpm for 2 min, followed by low stirring at 25 rpm for 5 min. The flocs were then allowed to settle down for 15 min [22]. At the end of the settling period, clean supernatant liquid was drawn from a depth of 1 cm, and its turbidity was measured using turbidity meter. Distilled water served as reference. The relationship between polymer concentration and residual turbidity of the supernatant liquid was plotted. The flocculant concentration was varied from 0.025 to 0.5 ppm.

2.4.2. Flocculation of municipal sewage wastewater

The experiment was carried out in four sets. In the control set, 500 mL of municipal sewage wastewater was stirred at a constant speed of 75 rpm for 2 min followed by 25 rpm for 5 min, left to settle for 15 min, and the supernatant liquid was collected from the top portion. The remaining sets were treated in the same way, but in the presence of 9 ppm of CMG, CMG-g-PAM 5 (C), CMG-g-PAM 6 (MA) respectively. The supernatant was subjected to trace metal analysis for total iron, total manganese and total chromium after nitric acid digestion [23] using an Atomic Absorption Spectrophotometer (AA-680, Atomic Absorption/Flame Emission Spectrophotometer, Shimadzu Corporation, Japan). Total nickel was determined by a spectrophotometric method using NiSO$_4$ solutions as standards and absorbance measurements at 445 nm [23]. Determination of total solid (TS), total dissolved solid (TDS) and total suspended solid (TSS) were carried out gravimetrically [23]. COD was determined by mixing of each 5 mL sample with 2 mL digestion solution (sulphuric acid/mercuric sulphate/potassium dichromate/water) and 1.5 mL acid reagent (sulphuric acid + silver sulphate) followed by heating in a Digital Reactor Block 200 at 150 °C for 2 h. The mixture was cooled and the COD value was measured with a HACH Portable spectrophotometer (Model – DR/2400) [23].

2.4.3. Flocculated decolourization of dye

1–10 ppm of various flocculants (CMG and grafted CMGs) were added into 400 mL of methylene blue solution (0.1 wt %). Then the mixture was vortexed for 1 min and allowed to stand for 60 min at room temperature (25 °C). The absorbance of the clarified layer was measured before and after flocculation at the end of the settling period using a UV-Visible spectrophotometer (Electronic Corporation of India, India) at a maximum absorbance wavelength (λ_{max} = 650 nm). Distilled water was used as reference. % decolourization efficiency (%DE) [24] was calculated using the following equation:

$$\%DE = \frac{A_0 - A}{A_0} \times 100 \tag{1}$$

where A and A_0 are the absorbances of the supernatant liquid after and before addition of flocculant, respectively.

COD of simulated dye solution was measured in the same way as discussed in Section 2.4.2. %COD removal was determined using the following equation:

$$\%\text{COD removal} = \frac{C_0 - C}{C_0} \times 100 \tag{2}$$

where C_0 and C are COD values before and after addition of flocculant, respectively.

3. Results and discussions

3.1. Synthesis

3.1.1. Synthesis of CMG-g-PAM by conventional method

CMG-g-PAM was synthesised by conventional method, using potassium persulphate as a free radical initiator, in an inert atmosphere of nitrogen. Table 1 shows various grades of graft copolymers prepared using conventional process, by varying the monomer (acrylamide) and the initiator concentration. The optimized grade [CMG-g-PAM 5 (C)] was determined through its higher percentage of grafting efficiency, intrinsic viscosity, molecular weight and radius of gyration. Potassium persulphate generates free radical sites on the polysaccharide (CMG) backbone as well as monomer (AM) backbone. These active free radicals are then recombining with each other to generate graft copolymers.

A series of six graft copolymers have been synthesised by conventional method. For the first three graft copolymers (1–3), the catalyst concentration was varied with the concentration of monomer and CMG fixed. For the second set of four graft copolymers (2, 4–6), only acrylamide concentration was varied keeping the other parameters constant.

3.1.1.1. Effect of initiator concentration.
It is desirable that a low concentration of catalyst should initiate a few grafting sites, which results in longer polyacrylamide chains, compared to a high concentration of catalyst, which will initiate a larger number of grafting sites, thus making the average polyacrylamide chains shorter for the same acrylamide concentration. So by grafting polyacrylamide chains onto CMG, two possibilities are there – one can either have a small number of long polyacrylamide chains or a large number of short polyacrylamide chains in the graft copolymer. In the former case, the compact shape of the graft copolymer would be changed, because of the presence of long polyacrylamide chains. This would result in larger hydrodynamic volume, leading to higher intrinsic viscosity, molecular weight and radius of gyration (Table 1). On the other hand, a large number of short polyacrylamide chains will not alter the original compact shape to a great extent and hence lower would be hydrodynamic volume (i.e. intrinsic viscosity) and radius of gyration (Table 1). This result in the reduction of flocculation efficiency, since decrease in radius of gyration reduces the flocculation efficacy (Section 3.3).

3.1.1.2. Effect of monomer concentration.
With increase in monomer concentration (From 0.07 mol to 0.28 mol), %GE increased continuously and achieved the maximum when the concentration of acrylamide is 0.21 mol. Afterwards, the %GE decreased. This behaviour can be explained by the fact that an increase in monomer concentration lead to the accumulation of monomer molecules in close proximity to the polymer backbone. The decrease in the %GE after optimization could be associated with the reduction in the active sites on the CMG backbone as graft copolymerization proceeds. In addition to this, with excess monomer concentration, the competing homopolymer formation reaction becomes significant, leading to depletion in %GE as well as viscosity.

### 3.1.2. Synthesis of CMG-g-PAM by microwave assisted (MA) method

Polyacrylamide grafted carboxymethyl guar gum was synthesised using microwave assisted (microwave energy as well as potassium persulphate was used to generate free radicals) method.

When small polar molecules like water are irradiated with microwave, it results in rotation of the molecules, leading to generation of heat. No free radical is produced as such. However, if bigger molecules or macromolecules are present, rotation of the entire molecule is not possible. In that case, the microwave is absorbed by the polar groups present (e.g. –OH groups attached to CMG molecule) which then behave as if they were anchored to an immobile raft and its immobile localized rotations [25,20] will occur in the MW region. Consequently, the severing of bond takes place, leading to formation of free radical sites.

Further, the microwave energy absorbed by water molecules is quickly transferred to the acrylamide molecules, causing dielectric heating [26] which results in severing of the double bonds, producing another set of free radicals. The free radicals generated on the polar –OH groups of the CMG backbone and on the monomer then recombine with each other through initiation, propagation and termination steps to produce the graft copolymer.

3.1.3. Explanation for using hydroquinone as inhibitor

Inhibitors react with chain radicals to terminate chain propagation and hydroquinone (HQ) radical, which is formed, is stable and cannot initiate further polymerization. The stability of the HQ radical is because of the delocalization of electron charge density throughout the aromatic structure. Hence addition of hydroquinone quenches the grafting reaction which supports the free radical mechanism:

$$\text{reaction (i):} \quad \text{CMGO}^* + \text{HQ} \rightarrow \text{CMGOH} + \text{HQ}^*$$
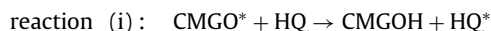
3.2. Characterization

The intrinsic viscosity was determined for CMG and different grades of CMG-g-PAMs and is presented in Table 1. It has been observed that intrinsic viscosity of all grades of CMG-g-PAMs is greater than that of CMG. This is because of grafting of polyacrylamide chains onto the polysaccharide backbone. Among various grades of graft copolymers, CMG-g-PAM 6 (MA) is having highest % grafting efficiency and intrinsic viscosity. This is because of the presence of longer PAM chains grafted onto CMG backbone, leading to higher hydrodynamic volume.

It is obvious that all grafted products have higher molecular weight and radius of gyration than CMG (Table 1). Also, it is interesting to note that higher the % grafting efficiency, higher is the molecular weight and radius of gyration as a consequence of grafted PAM chains.

The elemental analysis of CMG (% C = 37.1, % N = 0.12, % H = 9.8), PAM (% C = 50.80, % N = 19.76, % H = 7.69) and optimized grade of CMG-g-PAMs (optimization with respect to percentage grafting, intrinsic viscosity and molecular weight) i.e. CMG-g-PAM 5 (C) [% C = 42.21, % N = 8.45, % H = 8.20]; CMG-g-PAM 6 (MA) [% C = 41.80, % N = 9.41, % H = 7.12], demonstrates that considerable percent of nitrogen was present in the grafted products compared to the polysaccharide (CMG). This confirms that PAM chains have been grafted on the backbone of CMG.

The ^{13}C NMR spectrum of CMG (Fig. 1a) shows four distinct peaks in the region of 70.5–108.2 ppm. The absorption peak at δ = 108.2 ppm is for anomeric carbon atom and the peak at δ = 80.6 ppm is for carbon atoms connected to –OH groups (i.e. carbon atoms in the six membered ring except anomeric carbon atom). Peaks at δ = 70.5 and 76.2 ppm are assigned
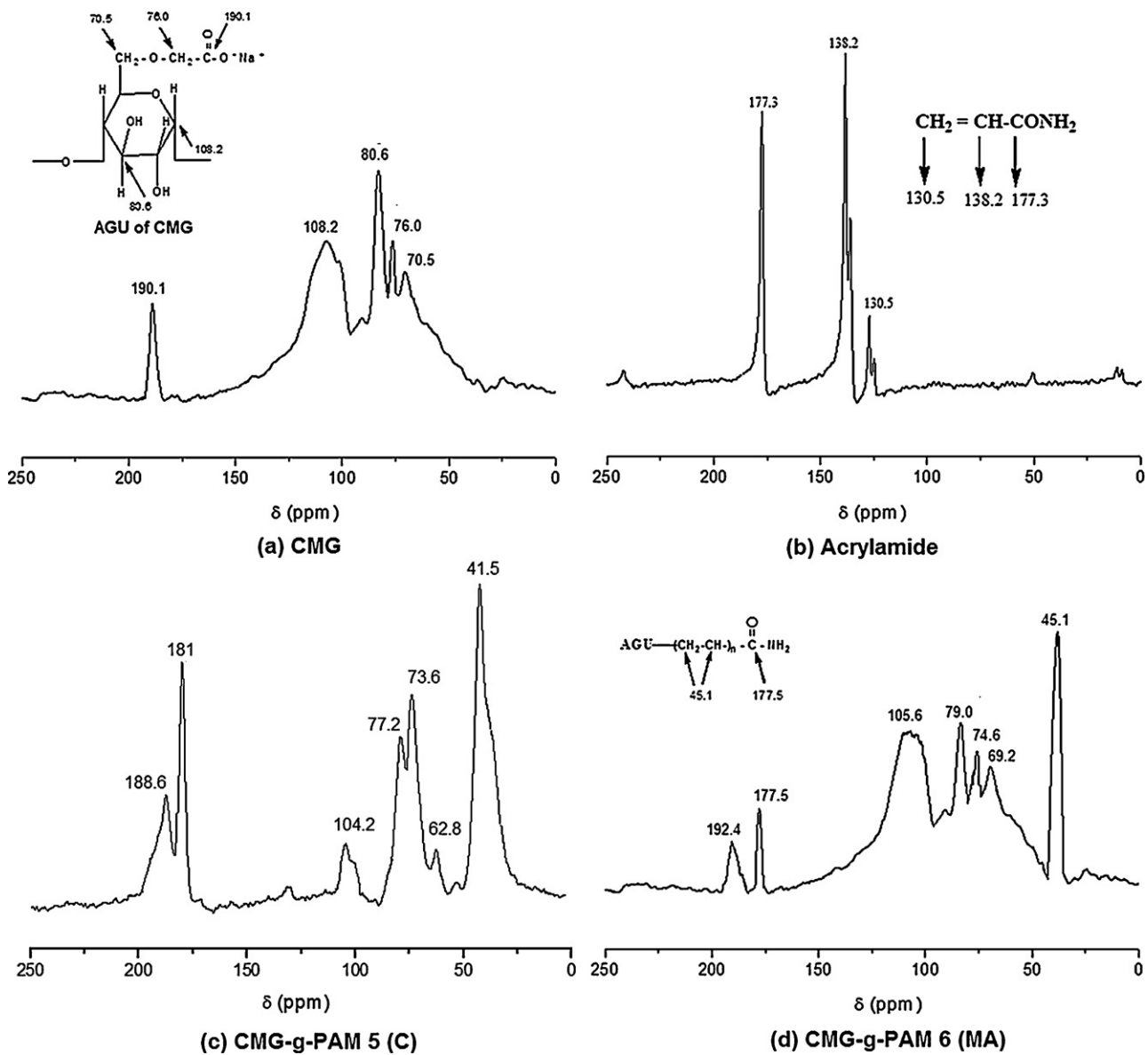
Fig. 1. ^{13}C NMR spectra of (a) CMG, (b) acrylamide, (c) CMG-g-PAM 5 (C) and (d) CMG-g-PAM 6 (MA).

for –CH$_2$–O–CH$_2$–COO–Na$^+$ and the carbon atom of –O–CH$_2$ of the inserted carboxymethyl group. The absorption peak at δ = 190.1 ppm is for the carboxyl carbon atom of COO–Na$^+$ group. The ^{13}C NMR spectrum of acrylamide has three major peaks (Fig. 1.b). The peak at δ = 177.3 ppm is from the amide carbonyl carbon. Peaks at δ = 130.5 and 138.2 ppm are for two sp^2 hybridized carbon atoms (i.e. CH$_2$=CH–). In the ^{13}C NMR spectrum of grafted products (Fig. 1c and d), there are two additional bands present, compared to base polysaccharide (CMG). The presence of a very intense peak at δ = 177.5 ppm [CMG-g-PAM 6 (MA)] is because of carbonyl groups, along with an additional peak at δ = 45.1 ppm which is attributed to methylene groups; confirms that grafting of polyacrylamide chains onto CMG backbone has been taken place. As obvious in the ^{13}C NMR spectrum of the graft copolymer and acrylamide, acrylamide had two peaks at δ = 130.5 and 138.2 ppm for two sp^2 hybridized carbon atoms which were absent in the graft copolymers. Moreover, one additional peak was present for the graft copolymer at δ = 45.1 ppm, which is for the sp^3 hybridized carbon atoms (i.e. –(CH$_2$–CH)$_n$ units in the graft copolymer). Nei-

ther the CMG nor the acrylamide spectrum had this peak. Therefore, the absence of peak at δ = 130.5 and 138.2 ppm and the presence of a peak at δ = 45.1 ppm is evidence of covalent attachment of the polyacrylamide chains onto the CMG backbone.

Scanning electron microscopy (Fig. 2) was used to investigate the morphological features (Magnification – 800×) of CMG and CMG-g-PAM. CMG is having granular morphology. After grafting, the granular appearance of CMG was distorted. This observation suggests that grafting of polyacrylamide affects the structural arrangement of CMG and causes granular disintegration. The micrographs of CMG-g-PAMs showed a unique feature where a number of long chain polyacrylamides got agglomerated and was observed to be as fibrillar structure.

3.3. Flocculation characteristics

3.3.1. Flocculation characteristics in kaolin suspensions
The flocculation characteristics of various grades of graft copolymers synthesised by conventional (Fig. 3) and microwave assisted
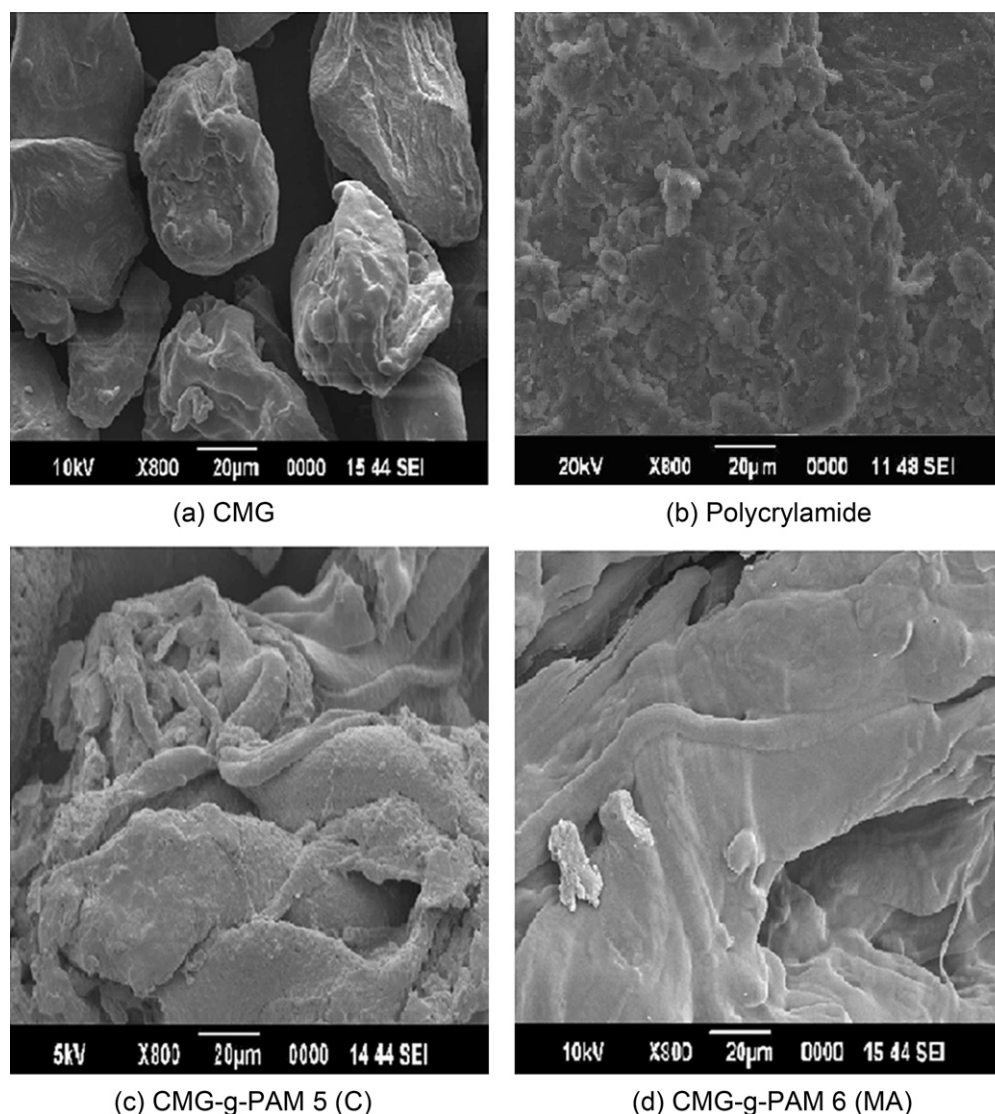
Fig. 2. Scanning electron microscopy of (a) CMG, (b) polyacrylamide, (c) CMG-g-PAM 5 (C) and (d) CMG-g-PAM 6 (MA).

methods (Fig. 3) were compared in 0.25 wt% kaolin suspension. In each case, the turbidity of the supernatant liquid after flocculation was plotted against polymer concentration. It is obvious from Fig. 3 that the performance of CMG-g-PAM 5 (C) and CMG-g-PAM 6 (MA); which are having higher percentage of grafting efficiency, higher pervaded volume i.e. longer grafted PAM chains, higher radius of gyration and higher molecular weight; are better flocculants than other graft copolymers for kaolin suspension.

The mechanism of kaolin suspension flocculation with polyacrylamide grafted CMGs may be explained by a combination of charge neutralization and polymer bridging. The charge neutralization occurs if the charge of the flocculant is opposite in sign to that of the suspended particles. The addition of such polymers to the suspension will result in an aggregation caused by specific ion adsorption. For neutral flocculants/slightly ionic flocculants [27,28], the major mechanism of flocculation is the polymer bridging. Bridging flocculation occurs when segments of the same polymer molecule are attached to more than one particle, thereby linking the particles together. This type of flocculation mechanism has been found to be very efficient. In polymer bridging, the high molecular weight polymer chains are adsorbed onto the particle surface and form bridges between adjacent particles. Adsorption occurs by electrostatic forces, van-der Wall forces, hydrogen bonding and chemical bonding. When long chain polymer molecules are adsorbed on the surface of the particles, they tend to form loops that extend some distance from the surface into the aqueous phase and their ends

Table 2
Flocculating effect for treatment of municipal sewage wastewater.

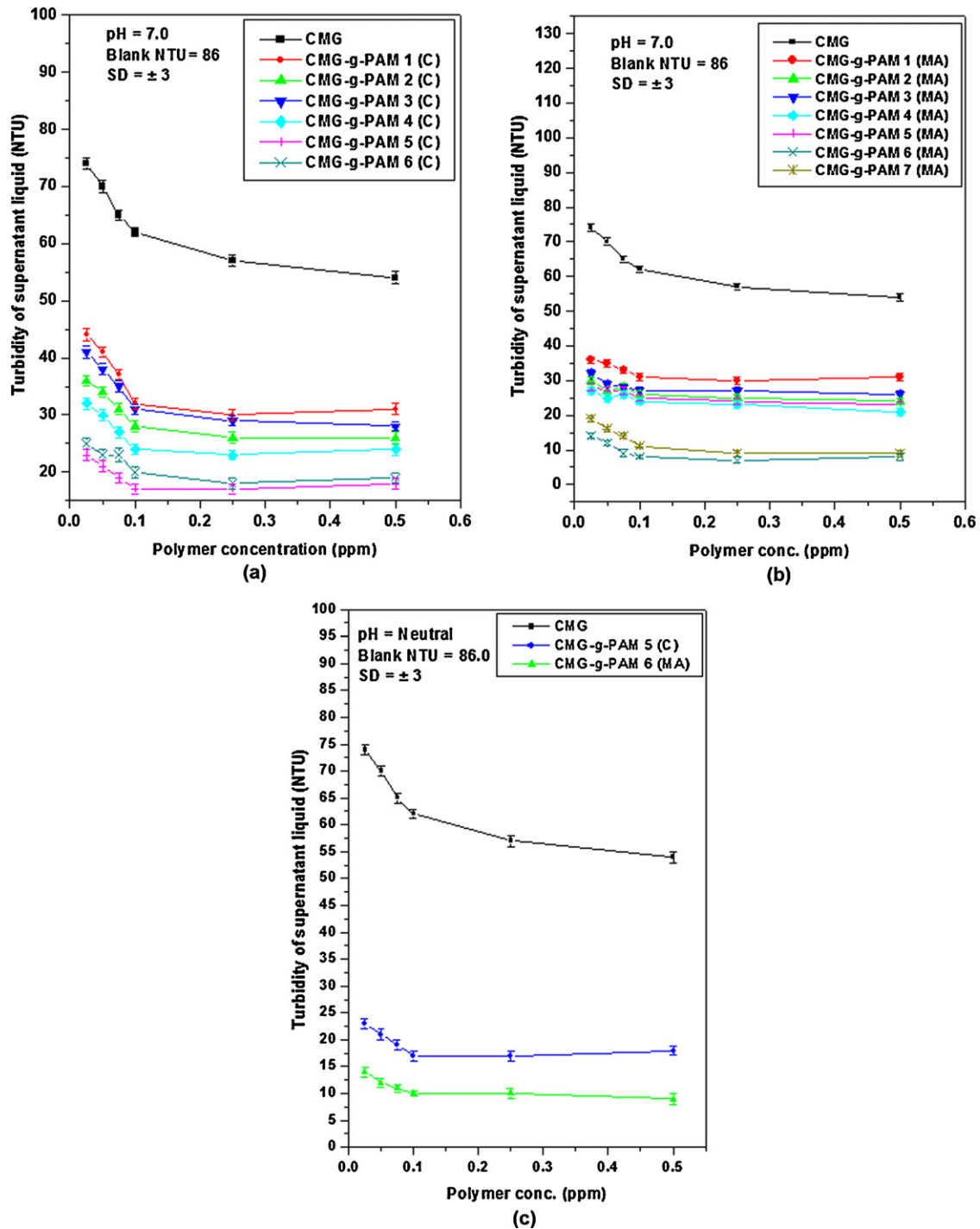| Flocculant	Turbidity (NTU)	TS (ppm)	TDS (ppm)	TSS (ppm)	COD (ppm)	Total Fe^{3+} (ppm)	Total Mn^{2+} (ppm)	Total Cr^{2+} (ppm)	Total Ni^{2+} (ppm)
Without flocculant	64	630	280	350	540	5.44	2.4	1.12	0.88
CMG	49	505	230	275	480	4.2	1.5	0.95	0.74
CMG-g-PAM 5 (C)	15	265	205	60	295	0.45	0.09	0.06	0.05
CMG-g-PAM 6 (MA)	9	230	200	30	210	0.08	0.02	0.00	0.00

Fig. 3. Flocculation characteristics of (a) CMG and various grades of CMG-g-PAMs (C), (b) CMG and various grades of CMG-g-PAMs (MA) and (c) CMG, CMG-g-PAM 5 (C), CMG-g-PAM 6 (MA) in 0.25 wt% kaolin suspension.

may dangle [29]. These loops and ends may come in contact with and get attached to another particle forming a bridge between the two particles. The reason for better flocculating power of the graft copolymers over linear polymer is essentially the polymer bridging occurring due to segments of polymer chain adsorbing on different particles, linking the particles together. In order for effective bridging to occur, the length of polymer chains should be long, so that they can extend from one particle to another [29]. Hence the polymers with longer chains would be more efficient than that with shorter chains. Among all of the grafted polymers, CMG-g-PAM 6

(MA) is having highest percentage of grafting efficiency, radius of gyration and intrinsic viscosity (i.e. highest pervaded volume i.e. longer grafted polyacrylamide chains), hence it outperforms other graft copolymers as well as CMG in kaolin suspension. Further, the best performing graft copolymers were compared with each other (Fig. 3) and it is obvious that the CMG-g-PAM 6 (MA) surpasses the flocculation efficacy of others. The reason why microwave assisted based synthesis results in generation of better flocculant is that chain opening of the polysaccharide backbone does not take place hence rigidity of the polysaccharide chain is maintained giving
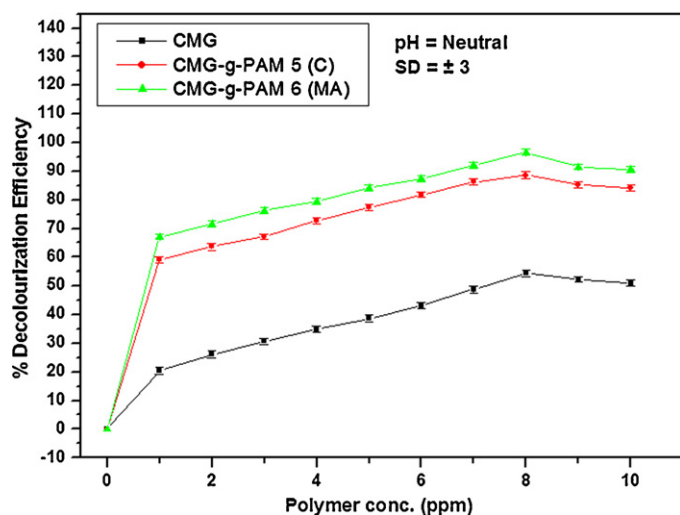
Fig. 4. Effect of flocculant concentration onto %DE of simulated dye (methylene blue) solution.

Fig. 5. Effect of flocculant concentration onto %COD removal of simulated dye (methylene blue) solution.

higher efficiency. The higher rigidity extends the polymer chain and hence the pendant PAM chains will be able to capture more contaminants. The higher molecular weight and radius of gyration of the best performing graft copolymer, CMG-g-PAM 6 (MA) (Table 1), was likely the reason why it outperformed the conventional one (Fig. 3), as it has already been established qualitatively and quantitatively that with increase in molecular weight and radius of gyration of a flocculant, the approachability of the contaminant particles towards the polymeric flocculant is enhanced and thereby increasing the flocculation efficacy [30,31].

3.3.1.1. Application of synthesised graft copolymer as flocculant for the treatment of municipal sewage wastewater.

It is well known that municipal sewage wastewater constitutes an important part of the total wastewater from various sources. The amount of pollutants contained in the municipal sewage wastewater is around 28.6% of the average daily pollutant generation, which becomes a dominant factor. Proper treatment of municipal sewage wastewater becomes top priority enforcement in recent years. Because of dwindling supply and increasing demand for quality water resources in the agricultural and industrial sectors, a better alternative to direct discharge of treated municipal sewage wastewater is to elevate its water quality further to an appropriate level for possible agricultural and industrial reuse. Flocculation is an important phenomenon for further purification of municipal sewage wastewater for its reuse, as it can decrease the total pollutant content from the wastewater.

Table 2 gives the results of analysis for treatment of municipal sewage wastewater. It clearly indicates that CMG-g-PAM 6 (MA) considerably reduce the overall pollutant load (i.e. TS, TSS, TDS, Turbidity, COD). Also, the total content of various metals are drastically reduced using CMG-g-PAM 6 (MA) as flocculant, in case of total chromium and total nickel, practically all of the metal got removed.

3.3.1.2. Decolourization efficiency of methylene blue dye.

Fig. 4 illustrates the effect of flocculant concentration and % grafting efficiency onto % of decolourization efficiency (%DE) of methylene blue dye at pH 7. Initially with an increase in flocculant concentration up to optimum dosage (i.e. 8 ppm), %DE of the simulated dye suspension increased followed by a decreasing trend in dye removal with further increase in concentration. This is particularly a flocculation system controlled by a charge neutralization mechanism. The cationic dye is electrostatically attracted by the carboxylate groups of CMG and CMG-g-PAMs. This reaction neutralizes the cationic
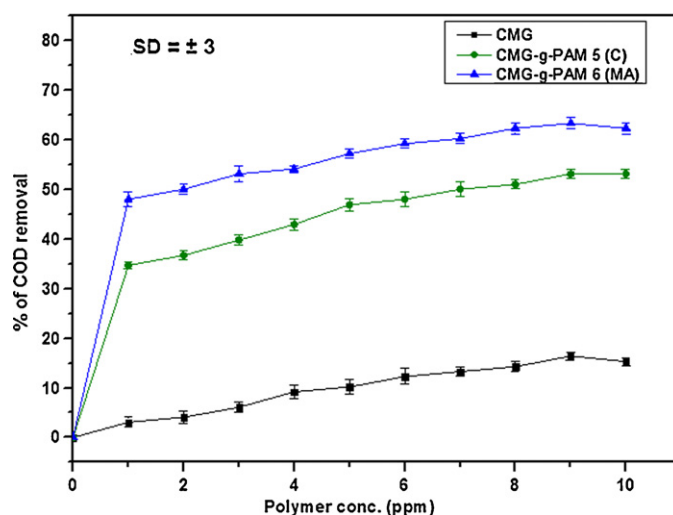
charges of dye that can bind together and settle. When the carboxylate groups had completely neutralized the cationic charges of dye, the decolourization efficiency reached its maximum. However, destabilization took place by the electrostatic repulsion among the cationic dye, which is already bound with flocculants, when the optimal concentration is exceeded. This is a well known phenomenon in flocculation. CMG-g-PAMs are showing better colour removal property compared to CMG, because of the presence of grafted polyacrylamide chains, which enhanced its hydrodynamic volume i.e. radius of gyration and thereby increasing its flocculation ability. The higher molecular weight and radius of gyration of CMG-g-PAM 6 (MA) may be the reason for its better performance of removal of colour in comparison to CMG-g-PAM 5 (C).

Fig. 5 explains the performance of developed flocculants on the % COD removal of simulated dye solution. It is evident that CMG-g-PAM 6 (MA) surpasses the % COD removal (63.48%) ability of other flocculants. This further confirms the superiority of this novel flocculant for the treatment of simulated dye solution.

4. Conclusion

Polyacrylamide grafted carboxymethyl guar gum (CMG-g-PAM) was prepared and studied as flocculant in suspended particle separation, treatment of municipal sewage wastewater and removal of colour from dye solution. The flocculation results demonstrate that all grafted CMGs were effective flocculants. Further, the graft copolymer synthesised by microwave assisted method showed maximum %DE (97.1%) and reduced the total pollutant content drastically after treatment of municipal sewage wastewater. This novel polymeric flocculant can be used universally for the treatment of wastewater.

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