

# Selective Lead(II) Adsorption and Flocculation Characteristics of the Grafted Sodium Alginate: A Comparative Study

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**Abstract** Synthesis of sodium alginate-*g-poly*(acrylamide-co-*N*-methylacrylamide) [S-III], sodium alginate-*g-poly*(*N*-methylacrylamide-co-*N,N*-dimethylacrylamide) [S-II], sodium alginate-*g-poly*(acrylamide-co-*N,N*-dimethylacrylamide) [S-I]. Sodium alginate-*g-poly*(*N,N*-dimethylacrylamide) [SAG-*g*-PDMA] and sodium alginate-*g-poly*(acrylamide) [SAG-*g*-PAM] were prepared by solution polymerization technique using potassium peroxydisulfate as the initiator at 70 °C in water medium. The graft copolymers were characterized by FTIR and NMR (<sup>1</sup>H and <sup>13</sup>C) spectroscopy, SEM and XRD studies. All the five graft copolymers were used to remove Pb(II) ions from the aqueous solution and also in flocculation studies of kaolin clay (1.0 wt%), silica (1.0 wt%) and iron ore slime (0.25 wt%) suspensions. A comparative studies of all the five graft copolymers were also made in both the two cases. The Pb(II) ion removal capacity of all the graft copolymers follows the order S-III > SAG-*g*-PAM > S-II > SAG-*g*-PDMA > S-I. But the flocculation performance of the graft copolymers follows the order S-II > S-I > S-III > SAG-*g*-PDMA > SAG-*g*-PAM. S-III was also used for the competitive metal ion removal with Hg(II), Cd(II), Cu(II) and Zn(II). Pb(II) adsorption of S-III (the best Pb(II) ion adsorber) follows pseudo second order rate equation and Langmuir adsorption isotherm.

**Keywords** Graft copolymerization · Flocculation · *N,N*-dimethylacrylamide · *N*-methylacrylamide · Sodium alginate · Pb(II) ion removal

## Introduction

Water pollution caused by toxic heavy metal ions is now a serious global problem and received much attention in recent years. Such metal ions come into the water bodies mainly by the effluents and waste water from variety of chemical industries. The major toxic metal ions have been found in surface and ground water are Pb(II), Cd(II), Hg(II), Zn(II), Cu(II) and Ni(II) which are non degradable naturally and causing serious health problems in living organisms. Lead(II) is one of the most toxic and harmful metal ion, causes dangerous effects when it enters into the body of any living organism by any source. It damages kidneys, liver and gastrointestinal system and also affects the central nervous system [1]. Diseases like anaemia, headache irritability, hallucination, hepatitis, insomnia and renal damage are the symptoms of Pb(II) accumulation. Lead(II) comes into the environment mainly by the waste of variety of industries like lead batteries, paint and dyes, electroplating, platings etc. [2]. Therefore, the removal of Pb(II) ions from the waste water has got considerable significance from the environmental point of view. There are various methods to remove Pb(II) ions from water medium including chemical precipitation, reverse osmosis, solvent extraction, membrane filtration etc. These methods are relatively expensive. Among the various methods, adsorption is an effective process for the removal of Pb(II) ions and the suspended particulate materials from the water medium where low cost, efficient and easily available adsorbents were used. Therefore, searching materials of low cost, highly

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effective sorbents for the metal ions and the suspended particulate matters in waste water is an active area of research.

Industrial waste water also contains various toxic elements, suspended solids together with other microbiological and chemical contaminants which are extremely harmful towards human health and aquatic species [3]. Therefore, direct disposal of industrial waste water into the environment without the separation of toxic and harmful elements is not permissible. There are so many waste water treatment methods of which flocculation is an economical and efficient technique for purification and recycling of industrial waste water and effluents [4].

Adsorption of heavy metal ions from aqueous medium by using cost effective efficient metal adsorbing agents is an active area of research now a days [5–8]. Among the various heavy metal ion adsorbents water soluble polymers (polyelectrolytes and polychelator) are found to be most effective. The essential requirements for a polymer to act as metal capturing agent are their high water solubility, chemical stability, strong affinity to interact with the metal ions, metal selectivity and can be prepared easily [9]. The most useful polymers bearing such properties are the polysaccharide based graft copolymers containing one or more metal coordinating functionalities. These groups are placed at the side chains of the polysaccharide backbone resulting comb like structures. Polymers containing functional groups capable of coordinating metal ions are called polychelators. Carboxylic acids ( $-\text{COOH}$ ) and amides  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}$  are two important functional groups present in the polychelators [10].

There are three different types of amide groups namely primary ( $-\text{CONH}_2$ ), secondary ( $-\text{CONHMe}$ ), tertiary ( $-\text{CONMe}_2$ ) with varying electron density at the 'N' as well as at the 'O' centre  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{N} \longleftrightarrow -\overset{\ominus}{\text{O}}-\overset{\oplus}{\text{N}}$ . The electron density at the 'N' and 'O' centres increases on going from primary amide to tertiary because of the increment of electron donating methyl ( $-\text{CH}_3$ ) groups. Poly(*N,N*-dimethylacrylamide) (PDMA) is highly water soluble and biocompatible but graft copolymers based on polysaccharide and dimethylacrylamide (DMA) have poor metal chelating properties because of the steric crowding of two methyl groups at the 'N' centre [11]. Poly(*N*-methylacrylamide) (PNMA) is not water soluble because of the extensive intramolecular hydrogen bonding [12]. Polyacrylamide (PAM) is water soluble and PAM based graft copolymers were used as metal ion adsorbing and flocculating agents. Therefore, the present investigation was undertaken to prepare five graft copolymers containing both  $-\text{CONH}_2$  ( $1^\circ$  amides) and  $-\text{CONHMe}$  ( $2^\circ$  amide),  $-\text{CONHMe}$  ( $2^\circ$  amide) and  $-\text{CONMe}_2$  ( $3^\circ$  amide),  $-\text{CONH}_2$  ( $1^\circ$  amide) and  $-\text{CONMe}_2$  ( $3^\circ$  amide) functionalities into the sodium

alginate backbone by grafting a mixture of acrylamide (AM) ( $\text{CH}_2=\text{CH}-\text{CONH}_2$ ) and *N*-methylacrylamide (NMA) ( $\text{CH}_2=\text{CH}-\text{CONHMe}$ ), *N,N*-dimethylacrylamide (DMA) ( $\text{CH}_2=\text{CH}-\text{CONMe}_2$ ) and NMA and AM and NMA, and by grafting AM and DMA separately onto the sodium alginate backbone which are to be used as Pb(II) coordinating and flocculating agents. The aim was to investigate the water solubility and hence the effectiveness of the graft copolymers to bind the Pb(II) ions and to act as flocculating agents in water medium. A comparative study was also made in both the two applications.

## Experimental

### Materials

Sodium alginate (SAG), potassium peroxydisulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ), acrylamide (AM), lead nitrate [ $\text{Pb}(\text{NO}_3)_2$ ], acetone ( $\text{CH}_3\text{COCH}_3$ ), silicon dioxide (suspension zeta potential  $-52.3$  mV at pH 7.2) and *N*-methylacrylamide (NMA) were procured from Loba Chemie, Bombay, India. *N,N*-dimethylacrylamide (DMA) was purchased from Aldrich Chemical Company, St. Louis, USA. *N,N*-dimethylacrylamide was purified by vacuum distillation and the middle fraction was used for this study. Iron ore slime (suspension zeta potential  $-31.72$  mV at pH 7.2) was obtained from TISCO mine, (Jharkhand, India). Kaolin clay (suspension zeta potential  $-3.9$  mV at pH 7.6) was obtained from Famous Minerals and Chemical Pvt. Ltd., Mumbai, India.

### Synthesis and Purification of Graft Copolymers

Graft copolymers were prepared in water medium by radical polymerization technique where potassium peroxydisulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ) was used as a free radical initiator. A typical procedure was as follows; aqueous solution of sodium alginate (SAG) was prepared first by dissolving 2.5 g SAG in 150 ml water into a stoppered conical flask at  $90^\circ\text{C}$ , after which the solution was cooled to  $30^\circ\text{C}$ . Then 8.0 ml of DMA and 7.0 g of AM were added to the SAG solution. The dissolved oxygen was eliminated by purging  $\text{N}_2$  gas onto the solution for 30 min, then the temperature of the solution was raised to  $70^\circ\text{C}$ . 0.05 g of  $\text{K}_2\text{S}_2\text{O}_8$  was added to the solution and the temperature was fixed at  $70^\circ\text{C}$ . After 6 h of reaction the reaction was terminated by adding saturated solution of hydroquinone. The graft copolymer was isolated by precipitating it from the water medium using acetone as the solvent. The solid polymer after isolation dried in a vacuum oven. After that it was subjected to purification. Similar procedure was followed by preparing SAG-*g-poly*(DMA-co-NMA) and SAG-*g-poly*(AM-co-NMA) by taking a mixture of 8.0 ml

DMA and 6.5 g NMA, 7.0 g AM and 6.5 g NMA onto 150 ml of aqueous solution of SAG containing 2.5 g SAG in each case separately. The synthetic details are shown in Table 1.

The occluded homo-polymers PDMA and PAM were removed from the graft copolymer by solvent extraction technique in a Soxhlet extraction using a mixture of formamide and acetic acid (1:1 by volume) for PAM [12] and methanol for PDMA [13]. Poly(*N*-methylacrylamide) (PNMA) was removed from the PNMA containing graft copolymer by water treatment, since PNMA is water insoluble. SAG-g-PAM and SAG-g-PDMA were prepared by the similar way using 8 ml of DMA and 7.0 g

of AM as the monomers separately in solution containing 2.5 g of SAG in 150 ml of water.

## Characterization of the Graft Copolymers

### FTIR Spectroscopy Study

All the purified polymers namely S-I, S-II, S-III, SAG-g-PAM and SAG-g-PDMA were subjected to FTIR spectral analysis. KBr pellet method was used and the spectra were carried out in a Perkin Elmer (L16000300 Spectrum Two LiTa, Llantrisant, UK) spectrophotometer. The IR spectra of all the graft copolymers are shown in Fig. 1.

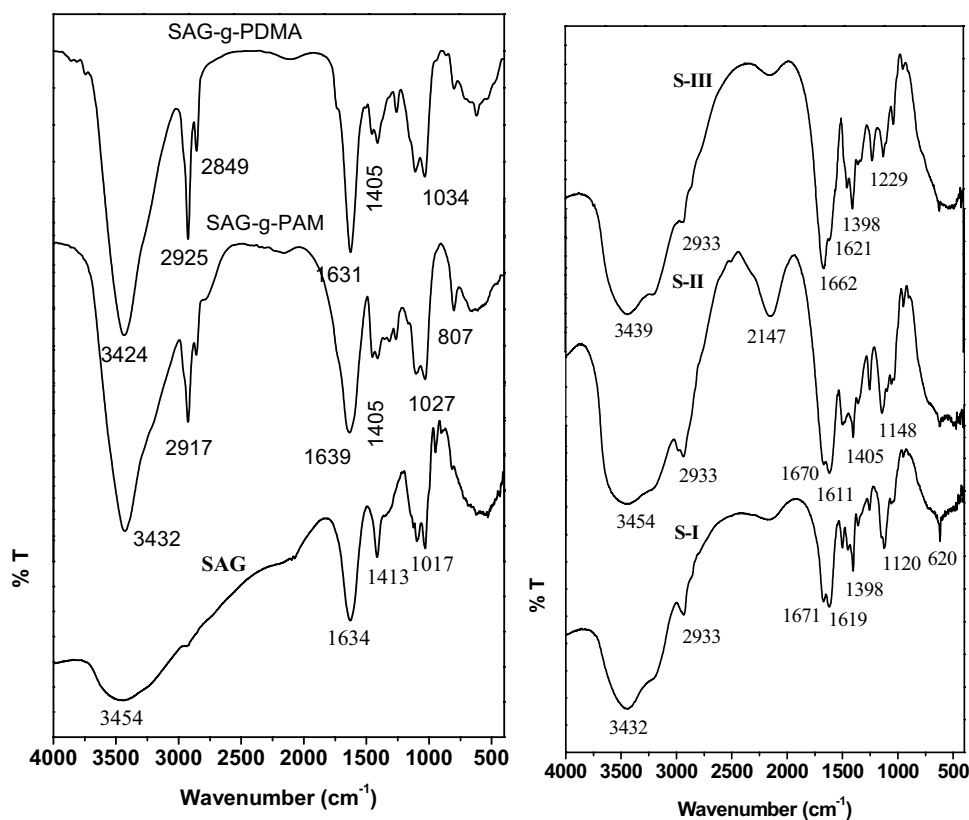
**Table 1** Synthetic details of the graft copolymers S-I, S-II, S-III, SAG-g-PAM and SAG-g-PDMA

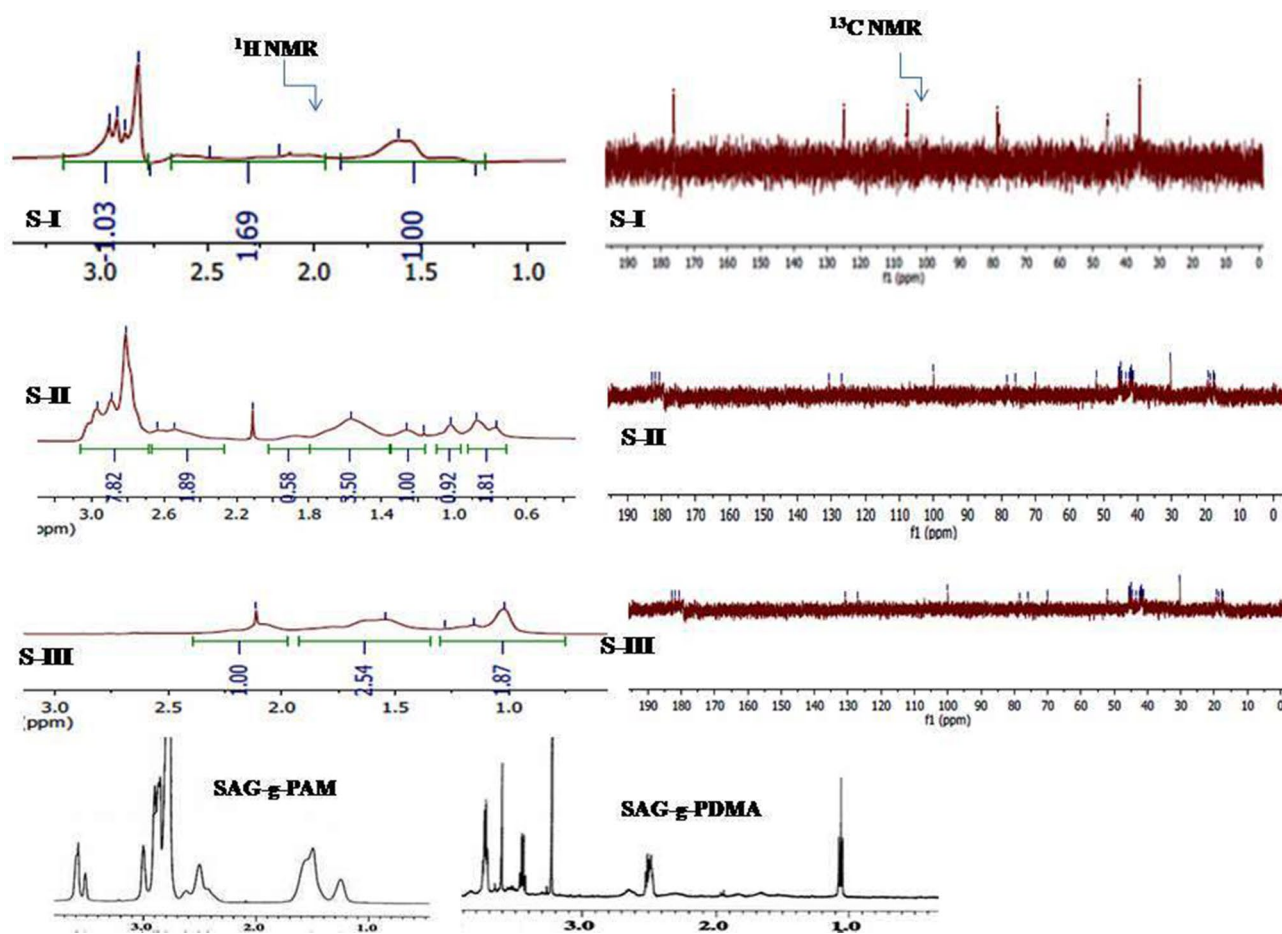
Polymer	Amt. of polysaccharide (g)	Amt. of monomer (g)			Amt. of $K_2S_2O_8$ (g)	Temp. (°C)	Time (h)	Yield (g)	Graft yield (%) <sup>a</sup>	Grafting percentage (%) <sup>b</sup>
		AM	NMA	DMA						
SAG-g-PAM	2.5	7.0	–	–	0.05	70	6.0	9.0	360	92.9
SAG-g-PDMA	2.5	–	–	8.12	0.05	70	8.0	9.2	368	82.5
SAG-g-AM-co-DMA (S-I)	2.5	7.0	–	8.12	0.05	70	10.0	15.5	620	86.0
SAG-g-NMA-co-DMA (S-II)	2.5	–	6.5	8.12	0.05	70	9.0	15.1	604	86.2
SAG-g-AM-co-NMA (S-III)	2.5	7.0	6.5	–	0.05	70	10.0	14.5	584	89.6

<sup>a</sup>% Graft yield = [(wt. of graft copolymer - wt. of SAG) / wt. of SAG] × 100

<sup>b</sup>Grafting percentage (%) = [(wt. of graft copolymer - wt. of SAG) / amount of total monomer] × 100

**Fig. 1** IR spectra of SAG, SAG-g-PAM, SAG-g-PDMA, S-I, S-II and S-III (graft copolymers)





**Fig. 2**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of S-I, S-II and S-III and  $^1\text{H}$  NMR spectra of SAG-g-PAM, SAG-g-PDMA,

### $^1\text{H}$ and $^{13}\text{C}$ NMR Spectroscopy

NMR instruments (JEOL, Tokyo, Japan) was used for this NMR spectral analysis at 500 MHz for  $^1\text{H}$  at and 100 MHz for  $^{13}\text{C}$ . The spectral analysis of graft copolymers were performed in  $\text{D}_2\text{O}$  solvent at  $25^\circ\text{C}$ . The spectra are shown in Fig. 2.

### XRD Analysis

The powder XRD analysis of all the graft copolymers was performed in Rigaku, Miniplex 600 (Japan), X-ray diffractometer using  $\text{CuK}\alpha$  radiation ( $\lambda=0.154056$  nm). The XRD plots are shown in Fig. 3.

### Pb(II) Adsorption

Adsorption experiments were carried out in batch mode in 50 ml stoppered conical flasks by taking 10 ml (0.04 g) of graft copolymer solution and 30 ml of 0.01 M Pb(II) nitrate solution at pH 5.5 in a flask for each graft copolymer

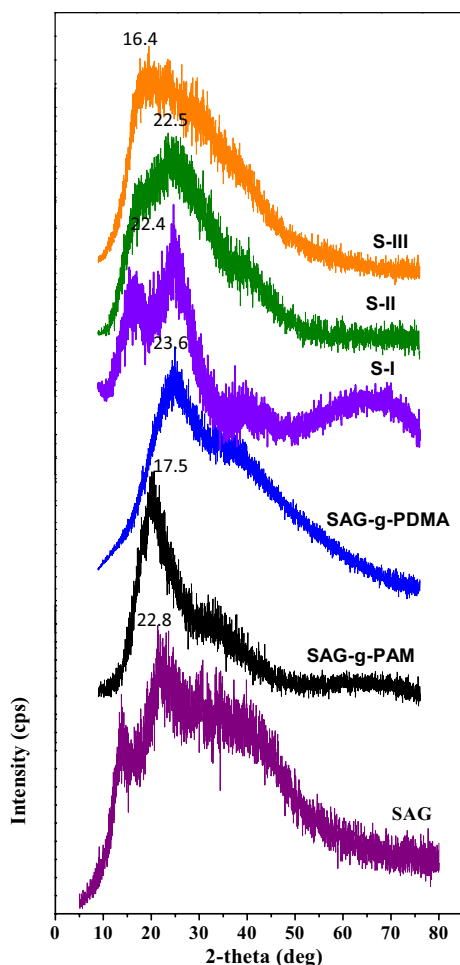
separately. The mixture of each flask was agitated separately by  $40^\circ\text{C}/150$  rpm for 2 h. After 2 h the Pb(II) adsorbed polymer was separated by centrifugation and the concentration of Pb(II) in the supernatant was analysed using atomic adsorption spectrophotometer (Varian-Spectra, AA55B, Australia). The Pb(II) adsorption capacity of the graft copolymer was calculated by using the following equation [14].

$$q = \frac{c_i - c_f}{m} \times v \quad (1)$$

where  $q$  represents the Pb(II) ion adsorption capacity at time  $t$  or at equilibrium (mg/g).  $c_i$  and  $c_f$  are the initial and final concentration of Pb(II) ion (mg/l).  $v$  is the volume of Pb(II) solution used (l) and  $m$  is the mass of the graft copolymer (adsorbent) used (g).

### Desorption of Pb(II) From the Pb(II) Adsorbed Graft Copolymer

Desorption of Pb(II) was carried out by heating with glacial acetic acid [15]. In a 50 ml of conical flask fitted



**Fig. 3** XRD plots of SAG-g-PAM, SAG-g-PDMA, S-I, S-II and S-III graft copolymers

with a condenser 0.3 g of Pb(II) loaded graft copolymer was taken. 30 ml of glacial acetic acid was added to the flask and the mixture was refluxed for 45 min. After refluxation the mixture was cooled and centrifuged. Supernatant was isolated by precipitation using excess quantity of acetone. About 80% of the graft copolymer was regenerated that can be reused and it was found that about 20% adsorption ability was reduced after third cycle.

## Adsorption Dynamics

### Effect of pH

Pb(II) adsorption by all the graft copolymers were studied in the pH range 1–7 keeping all the parameters

affecting the adsorption constant. The result is shown in Fig. 4a.

### Effect of the Amount of Graft Copolymer

The amount of adsorbents was varied for studying Pb(II) adsorption from 8 to 52 mg under constant parameters affecting adsorption. The result is shown in Fig. 4b.

### Effect of Temperature

The Pb(II) adsorption by all the graft copolymers was studied within the temperature range 25–65 °C keeping other parameters affecting the adsorption constant. The result is shown in Fig. 4c.

### Effect of Time

The adsorption of Pb(II) ion by all the graft copolymers were studied at different time intervals (30–150 min) under constant temperature, polymer dose and pH. The result is shown in Fig. 4d.

## Competitive Adsorption Studies of Pb(II) and Other Metal Ions by the S-III Graft Copolymer

Relative competitive metal ion absorption studies were carried out in the mixtures Pb(II)/Hg(II), Pb(II)/Cd(II), Pb(II)/Cu(II) and Pb(II)/Zn(II) to evaluate the selectivity of the metal ion adsorption by the graft copolymer S-III. The adsorption studies were carried out by taking 10 ml of 0.1 (M) of each metal ion solution and 10 ml of polymer solution in 50 cc beaker. The solution mixtures were agitated for 15 min in a magnetic stirrer and then were allowed to stand for 2 h to reach equilibrium. After that the reaction mixtures were centrifuged and supernatants of the reaction mixtures were collected to measure the equilibrium metal ion concentrations. From the equilibrium metal ion concentration the static distribution coefficient ( $K_D$ ), selectivity coefficient ( $\alpha$ ) of the graft copolymer was determined by using the following equations [14].

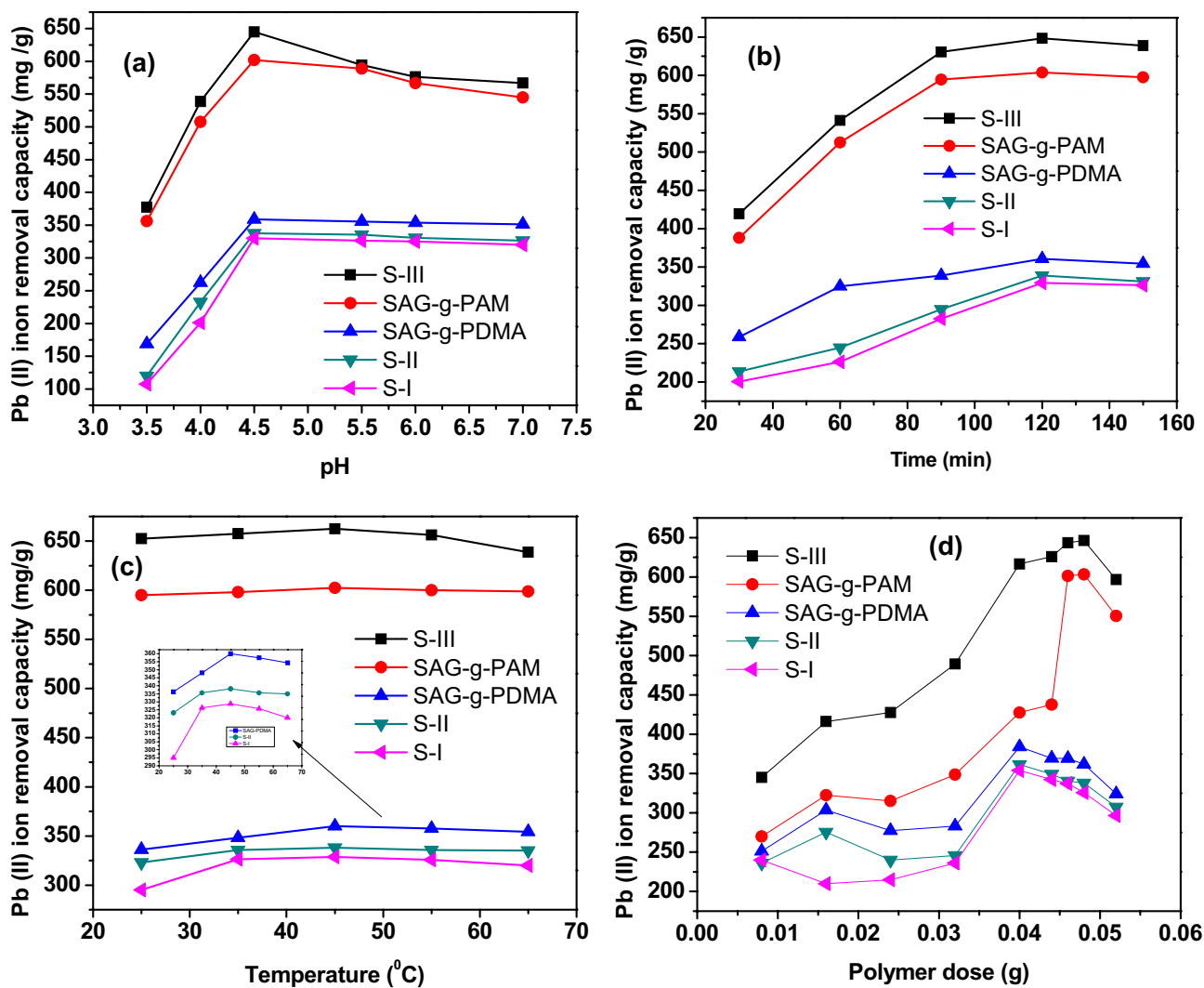
Static distribution coefficient is,

$$k_D = \frac{q_e}{c_e} \quad (2)$$

Selectivity coefficient,

$$\alpha = \frac{K_{D1}}{K_{D2}} \quad (3)$$

where  $q_e$  represents the metal ion removal capacity in equilibrium,  $c_e$  represents the equilibrium concentration



**Fig. 4** **a** Effect of pH, **b** effect of treatment time, **c** effect of temperature, **d** effect of polymer dose of the Pb(II) ion adsorption onto the graft copolymers SAG-g-PAM, SAG-g-PDMA, S-I, S-II and S-III

of Pb(II) ion.  $K_{D1}$  is the distribution coefficient for Pb(II) ion,  $K_{D2}$  is the distribution coefficient for other competitor metal ions [Cd(II), Cu(II), Hg(II), Zn(II)] and  $\alpha$  is the selectivity coefficient of the synthesized graft copolymer. The results are given in Table 2.

**Flocculation Study**

Flocculation experiments were carried out in a standard Jar apparatus supplied by Scientific Engineering Corporation, New Delhi, India [16]. The turbidity of the solution after flocculation was measured by Digital Nephelo Turbidity Meter (E1 products, Haryana, India; Model 331), The turbidity was expressed in NTU unit. 0.25 wt% iron ore slime, 1.0 wt% SiO<sub>2</sub> and 1.0 wt% kaolin clay were used for the flocculation experiments. The detail characterization of

**Table 2** The selectivity of adsorption of S-III for Pb(II) ion in comparison to other metal ions

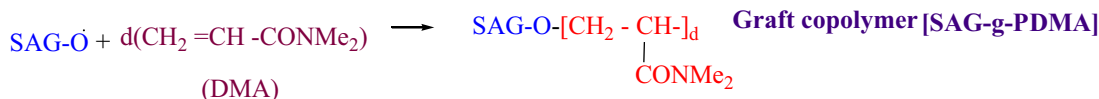
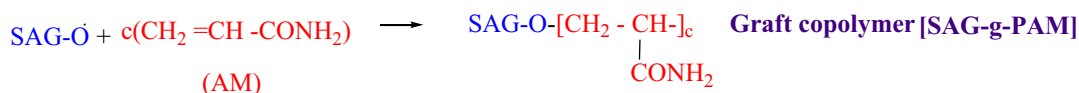
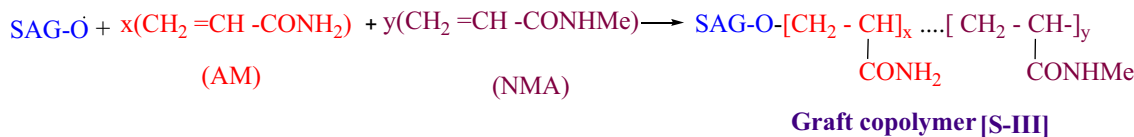
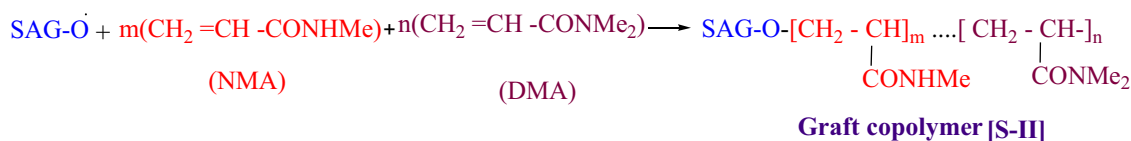
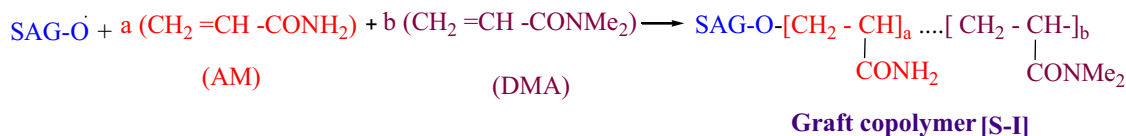
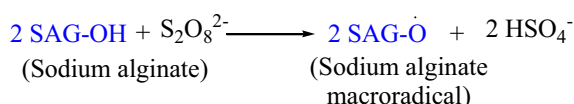
Metal ion	$K_D$	$\alpha$
Pb(II)	104.0	–
Cd(II)	47.11	2.2
Cu(II)	16.00	6.5
Hg(II)	71.32	1.4
Zn(II)	18.98	5.4

iron ore slime, silicon dioxide and kaolin clay was given in our previous communication [12]. A polymer stock solution was prepared by dissolving 0.5 g each graft copolymer in 250 ml distilled water. The solution was prepared by heating the polymer-water mixture at 80 °C for 24 h. In each case the polymer dose was varied from 2 to 16 ppm.

## Results and Discussion

### Synthesis

Grafting reactions onto sodium alginate backbone were carried out in water medium by using potassium peroxydisulfate ( $K_2S_2O_8$ ) as the radical initiator where initially the radical generated by the thermal decomposition by  $S_2O_8^{2-}$  captures electron from  $-OH$  groups of sodium alginate forming macro-radical SAG-O $\cdot$ . This macro-radical now react with the monomers forming graft copolymers. The grafting reactions are shown in the following schemes.



$-\text{CH}_2-\underset{|}{\text{CH}}-$  unit present in the graft copolymers. The peaks at  $1662 \text{ cm}^{-1}$  in S-III,  $1670 \text{ cm}^{-1}$  in S-II,  $1671 \text{ cm}^{-1}$  in S-I are for the  $\nu_{>\text{C}=\text{O}}$  stretching frequencies of the amide  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}-$  carbonyl groups. In SAG the peak at  $1634 \text{ cm}^{-1}$  is for  $>\text{C}=\text{O}$  group of  $-\text{COO}^-$  functionalities which is present in all the graft copolymer with a slight different values. In SAG-g-PAM and SAG-g-PDMA the amide. The  $>\text{C}=\text{O}$  stretching vibration band is superimposed with that of carboxylate ( $-\text{COO}^-$ ) groups.

### Proof of Grafting

#### FTIR Spectroscopy

Figure 1 shows the FTIR spectra of all the five graft copolymers along with sodium alginate. In all the graft copolymers there is a peak appears at  $2900 \text{ cm}^{-1}$  region ( $2933 \text{ cm}^{-1}$  is for S-I, S-II, and S-III,  $2925 \text{ cm}^{-1}$  in SAG-g-PDMA,  $2917 \text{ cm}^{-1}$  is SAG-g-PAM) which is absent in SAG which is due to the  $\text{sp}^3 \text{ C-H}$  stretching vibration for

#### NMR Spectroscopy

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of S-I, S-II, and S-III are shown in Fig. 2. From Fig. 2 it is evident that the peaks at  $\delta_{2.0-2.2\text{ppm}}$  in all the three cases are due to the methyl protons connected to N. The peaks at  $\delta_{2.6-3.0\text{ppm}}$  are due to the methine protons of the repeating units and the peaks at  $\delta_{1.0-1.5\text{ppm}}$  are due to the protons of  $-\text{CH}_2-$  unit of the  $-\text{CH}_2-\underset{|}{\text{CH}}-$  repeating units of the grafted chains. In all the three cases the peaks due to the alkene protons which

are at  $\delta_{5.8\text{ppm}}$  are absent rather the peaks for the  $\text{—CH}_2\text{—CH—}$  (saturated carbon) unit appear which suggest an evidence of grafting. In  $^1\text{H}$  NMR spectrum of SAG-g-PDMA (Fig. 2) the peaks at  $\delta_{2.5\text{--}2.8\text{ppm}}$  are the protons of methyl groups connected to the 'N' atom ( $\text{—NMe}_2$ ) of PDMA chains. In  $^1\text{H}$  NMR spectrum of SAG-g-PDMA and SAG-g-PAM the peaks are at  $\delta_{1.0\text{--}1.6\text{ppm}}$  are due to the protons of the  $\text{—CH}_2\text{—}$  groups of the repeating unit. The peaks at  $\delta_{3.3\text{--}3.8\text{ppm}}$  are attributed by the methine  $\text{—CH—}$  protons of the sodium alginate backbone and also for the  $\text{—CH}_2\text{—CH—}$  repeating unit.

From the  $^{13}\text{C}$  NMR spectra of all the three graft copolymers (Fig. 2) it is obvious that the peak at highest region ( $\delta_{190\text{--}210\text{ppm}}$ ) is due to the carbon atom of the carboxylate ( $\text{—COO}^-$ ) functionalities of the SAG. The peak at  $\delta_{176\text{ppm}}$  for S-II,  $\delta_{182\text{ppm}}$  for S-III and at  $\delta_{176\text{ppm}}$  for S-I is for the carbonyl carbon of the amide functionalities  $\text{—CH}_2\text{—CH—}$  present in the grafted chains. The peaks in the middle region ( $\delta_{70\text{ppm}}\text{--}\delta_{130\text{ppm}}$ ) are the carbon atoms present in the sodium alginate backbone. The peaks at lower regions ( $\delta_{30\text{ppm}}\text{--}\delta_{45\text{ppm}}$ ) are for the carbon atoms present in the  $\text{—CH}_2\text{—CH—}$  repeating unit present in the grafted chains and the  $\text{CH}_3\text{—}$  groups connected to the nitrogen atoms of amide functionalities.  $^{13}\text{C}$  NMR spectra of the graft copolymers show the grafting phenomenon.

## XRD Studies

Figure 3 shows the XRD plots of all the five graft copolymers along with the SAG. It is evident from the figure that the peaks which are originally present in SAG at  $2\theta=25^\circ$  and  $2\theta=15^\circ$  are absent in all the five graft copolymers. More over in the graft copolymers new peaks are observed at  $2\theta=17.5^\circ$  in SAG-g-PAM,  $23.6^\circ$  in SAG-g-PDMA,  $22.4^\circ$  in S-I,  $22.5^\circ$  in S-II,  $16.4^\circ$  in S-III. This is explained by the morphological change of the graft copolymers after grafting onto the SAG backbone, indicating graft copolymerization process.

## Adsorption Dynamics

### Effect of pH

The adsorption capacity of a polymer is greatly dependent on the pH of the medium. The effect of pH of the Pb(II) ion removal capacity by all the graft copolymers is shown in Fig. 4a. It is evident from the figure that the Pb(II) ion adsorption increases with increasing pH up to 4.5 in all the five graft copolymers after that it remains constant. At low

pH the amide functional groups  $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—N}$  get protonated and act as positively charged species. Shifting towards higher pH values, deprotonation of amide functional groups occurs and behave like a negatively charged species. Now, they can chelate Pb(II) ions with them, which results in more adsorption capacity of the graft copolymers. After pH 4.5 the equilibrium is reached and the adsorption remains almost constant. The effect of solution pH was studied within the range 3.0–7.5 because after that pH Pb(II) ions precipitated as lead hydroxide.

### Effect of Time

Figure 4b depicts the effect of adsorption time on Pb(II) removal efficiency of all the five graft copolymers. The figure shows that the initial rate of Pb(II) ion uptake increases with increasing time and reached a maximum at time 120 min after which it levelled off. This is due to the initial greater number of available adsorbing sites on the surface of the graft copolymer which reduced with increasing time of adsorption. Beyond 120 min no further adsorption occurs because of the non availability of the adsorption sites on the adsorbents' surface.

### Effect of Temperature

The effect of temperature on the adsorption capacity of Pb(II) ion by all the graft copolymers was investigated within the temperature range 20–65 °C (Fig. 4c). The maximum adsorption was found at 35 °C after which it remains constant. The enhancement of the adsorption capacity of the adsorbents when temperature is increased to some extent could be due to increased mobility and also increase in surface activity of the adsorbents and diffusion of the ionic species which is continued up to the equilibrium. So, increase of Pb(II) adsorption occurs with increase in temperature up to the equilibrium value.

### Effect of Polymer Dose

The effect of polymer concentration on the Pb(II) ion adsorption by all the graft copolymers is shown in Fig. 4d, which shows that the amount of Pb(II) ion adsorption increases with increasing the amount of polymer initially. After reaching maximum adsorption at 0.04 g of polymer amount the adsorption becomes constant. This is due to increase in adsorption sites with increasing polymer dose before the maximum adsorption, beyond which the



adsorption remains more or less same because of the no availability of Pb(II) ions.

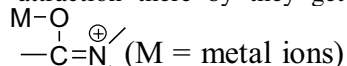
### Comparison Among the Graft Copolymers in Pb(II) Adsorption

The Pb(II) ion removal capacity and Pb(II) ion removal (%) of all the five graft copolymers namely S-I, S-II, S-III, SAG-g-PAM and SAG-g-PDMA is shown in Fig. 5. From Fig. 5 it is obvious that the Pb(II) removal capacity and removal (%) by the graft copolymers follows the order S-III > SAG-g-PAM > S-II > SAG-g-PDMA > S-I. The graft copolymers containing PDMA chains are inferior to the other. Again it is also obvious from the figure that SAG-g-PAM showed better Pb(II) absorbing performances than SAG-g-PDMA. In the polymer containing

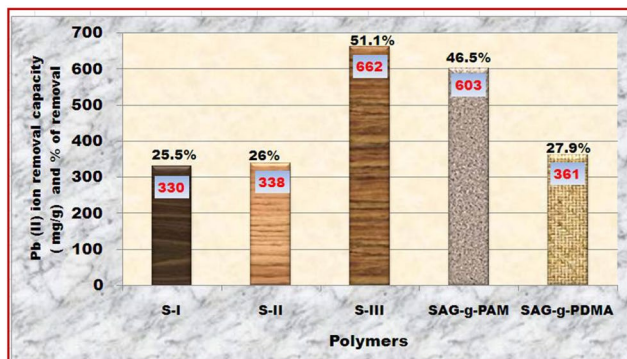
amide  $\left( \begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{N} \end{array} \right)$  functionalities it is the oxygen atom which is responsible for the coordination of the metal ions [17]. Amides are existed in charge delocalised structure

$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{N} \end{array} \text{ (I)} \longleftrightarrow \begin{array}{c} \ominus \text{O} \\ \parallel \\ -\text{C}=\text{N}^{\oplus} \end{array} \text{ (II)}$  of which (II) has

the significant contribution [18]. Since the oxygen atom becomes electron rich metal ions coordinate with oxygen atom by the electrostatic attraction there by they get adsorbed forming



(M = metal ions). Now going from  $1^{\circ} \rightarrow 2^{\circ} \rightarrow 3^{\circ}$  amide i.e. from acrylamide ( $\text{CH}_2=\text{CH}-\text{CONH}_2$ )  $\rightarrow$  *N*-methylacrylamide ( $\text{CH}_2=\text{CH}-\text{CONHMe}$ )  $\rightarrow$  *N,N*-dimethylacrylamide ( $\text{CH}_2=\text{CH}-\text{CONHMe}_2$ ), the number of methyl group increases as a result of which the volume of  $-\text{NH}_2 \rightarrow -\text{NHMe} \rightarrow -\text{NMe}_2$  also increases. As the volume near metal coordination sites increases approaching of the Pb(II) ion to coordinate with oxygen atom becomes



**Fig. 5** Comparison of Pb(II) removal capacity and % of Pb(II) removal of SAG-g-PAM, SAG-g-PDMA, S-I, S-II and S-III

sterically inhibited, this explains why graft copolymers containing PDMA chains become inferior to Pb(II) adsorption than the others. In S-I the steric crowding surrounding the oxygen atom is greatest because of the presence of PNMA and PDMA chains simultaneously, hence its metal coordination power is lowest. The Pb(II) ion adsorption capacity is greatest for S-III where both PNMA and PAM chains are present. In NMA presence of one methyl group at the ‘N’ centre does not create strong steric crowding rather it increases the electron density at the oxygen centre by the positive inductive effect of the  $-\text{CH}_3$  group. Due to the greater electron density of ‘O’ centre of PNMA chains its Pb(II) adsorption power is greater than the PAM chains where only  $-\text{CONH}_2$  functional groups are present. SAG-g-PNMA is water insoluble hence its Pb(II) adsorption performance can not be evaluated. Thus graft copolymer based on the mixture of NMA and AM showed better Pb(II) ion removal capacity than the PAM grafted copolymer, because of the presence more electron denser ‘O’ atom in PNMA moieties. Where as PDMA based graft copolymers are inferior for Pb(II) adsorption because of the steric crowding by the two methyl groups at the ‘N’ centre.

Among all the five graft copolymer since S-III showed best Pb(II) ion removal capacity (best absorption performance) adsorption kinetics and adsorption isotherm were studied only with S-III graft copolymer.

### Adsorption Kinetics

The adsorption of Pb(II) ions by S-III is well explained [19] by considering the pseudo-second order kinetic rate equation which is,

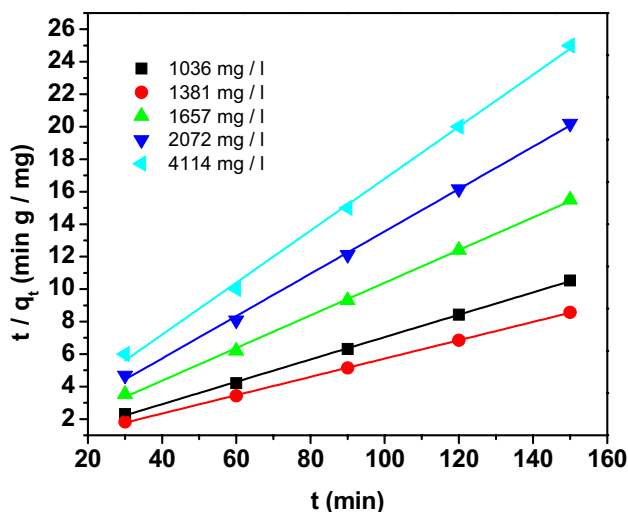
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where  $q_e$  and  $q_t$  are the amount (mg/g) of Pb(II) ion adsorbed by S-III at equilibrium and at time ‘t’ respectively. The  $k_2$  is the pseudo-second-order rate constant (g/mg/min). Figure 6 shows the pseudo-second-order plot and the parameters  $k_2$ ,  $q_e$  and  $R^2$  (correlation coefficient) values are listed in Table 3.

### Adsorption Isotherm

The distribution of Pb(II) ions between the liquid and the solid phase in equilibrium are explained by the adsorption isotherm. The adsorption isotherm of the adsorption of Pb(II) ions by S-III is better explained by the Langmuir isotherm model. The linear mathematical expression of the Langmuir model [20] is

$$q_e = \frac{x}{m} = \frac{k_1 C_e}{1 + a_1 C_e} \quad (5)$$



**Fig. 6** Pseudo-second-order plot of Pb(II) adsorption by S-III (condition; adsorbent mass 0.048 g, solution pH 4.5, time 120 min and temperature 35 °C)

**Table 3** Pseudo-second-order rate constants for Pb(II) ion adsorption onto graft copolymer [S-III] (Conditions: Pb(II) ion concentration 0.01 M, pH 4.5, time 120 min, adsorbent dose 0.048 g, temperature 35 °C)

Polymer	Langmuir constants along with $q_{max}$				
	$q_{max}$ (mg/g)	$k_1$ (l/g)	$a_1$	$R_L$	$R^2$
SAG-g-poly(AM-co-NMA) [S-III]	19.6	1.393	0.071	0.012	0.999

or,

$$\frac{c_e}{q_e} = \frac{1}{k_l} + \frac{a_1}{k_l} C_e \tag{6}$$

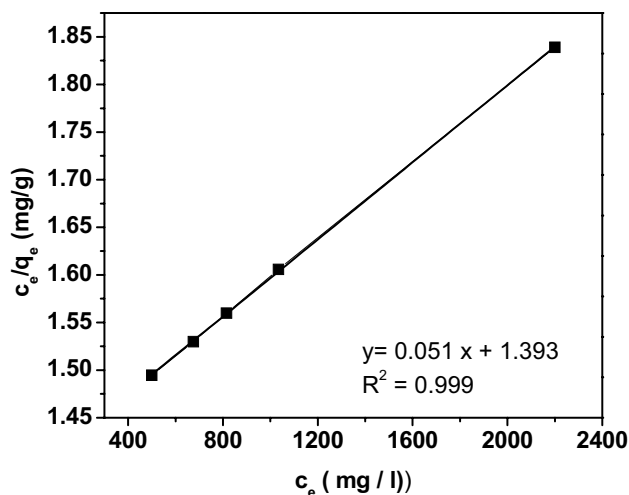
where  $x$  is the amount of metal ion adsorbed (mg),  $m$  is the amount of Pb(II) adsorbent (g) used.  $k_l$  (l/g) and  $a_1$  (l/mg) are the Langmuir constants, which are obtained from the plot of  $\frac{C_e}{q_e}$  versus  $c_e$ . From the intercept  $k_l$  and from the slope  $\frac{a_1}{k_l}$  values are obtained. Numerically  $k_l/a_1$  is equal to  $q_{max}$  i.e. maximum adsorption capacity of the adsorbent.

The feasibility of the adsorption process is calculated using separation factor  $R_L$  [21] which is defined by following equation:

$$R_L = \frac{1}{1 + a_1 C_0} \tag{7}$$

The category of the isotherm is indicated by the value of  $R_L$  where  $R_L > 1$  means unfavourable,  $R_L = 1$  means linear,  $R_L = 0$  means irreversible and for favourability  $0 < R_L < 1$ .

From Fig. 7 it is evident that the Langmuir isotherm model shows a better fit with the experimental data. The



**Fig. 7** Langmuir adsorption isotherm for the adsorption of Pb(II) by S-III (condition; adsorbent mass 0.048 g and pH 4.5, time 120 min)

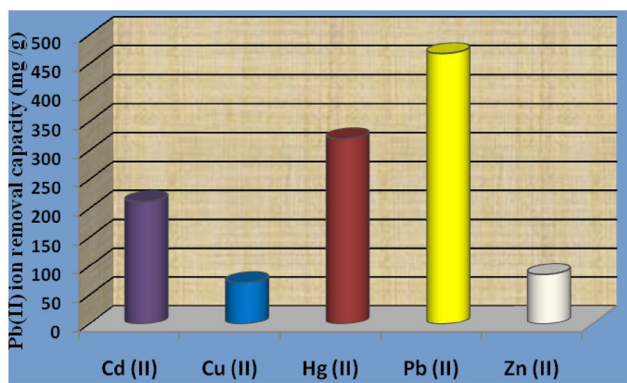
**Table 4** Comparison of maximum adsorption capacities of SAG-g-poly(AM-co-NMA) [S-III] for removal of Pb(II) ion with other reported adsorbents

Adsorbent	$q_{max}$ (mg/g)	References
Polyaniline composite with maize bran	18.75	[15]
Activated carbon from coconut	4.38	[22]
Crown ether (4-vinylbenzo-18-crown-6)	13.54	[14]
<i>Imperata cylindrica</i> leaf powder modified by sodium hydroxide	13.50	[23]
Bagasse fly ash modified by hydrogen peroxide	2.50	[24]
SAG-g-poly(AM-co-NMA) (S-III)	19.6	Present study

$q_{max}$  and  $R_L$  values are given in Table 3. The adsorption capacities for the removal of Pb(II) ion of other reported adsorbents are given in Table 4. It is clear from Table 4 that the prepared adsorbent (S-III) in the present investigation has higher adsorption capacity than some of the other adsorbents reported [14, 15, 22–24].

**Selectivity of S-III Graft Copolymer**

Figure 8 shows the competitive metal ion removal capacity of the synthesized S-III graft copolymer with the other metal ions. From the figure it is clear that the S-III graft copolymer has higher Pb(II) ion removal capacity over the other metal ions. The distribution coefficient and selectivity coefficient values are given in Table 2. The static distribution coefficient of S-III is higher for Pb(II) ion adsorption over other competitor metal ions. The selectivity coefficients of S-III for Pb(II) ion with Cd(II), Cu(II), Hg(II), Zn(II) metal ions are 2.2, 6.5, 1.4 and 5.4 respectively.

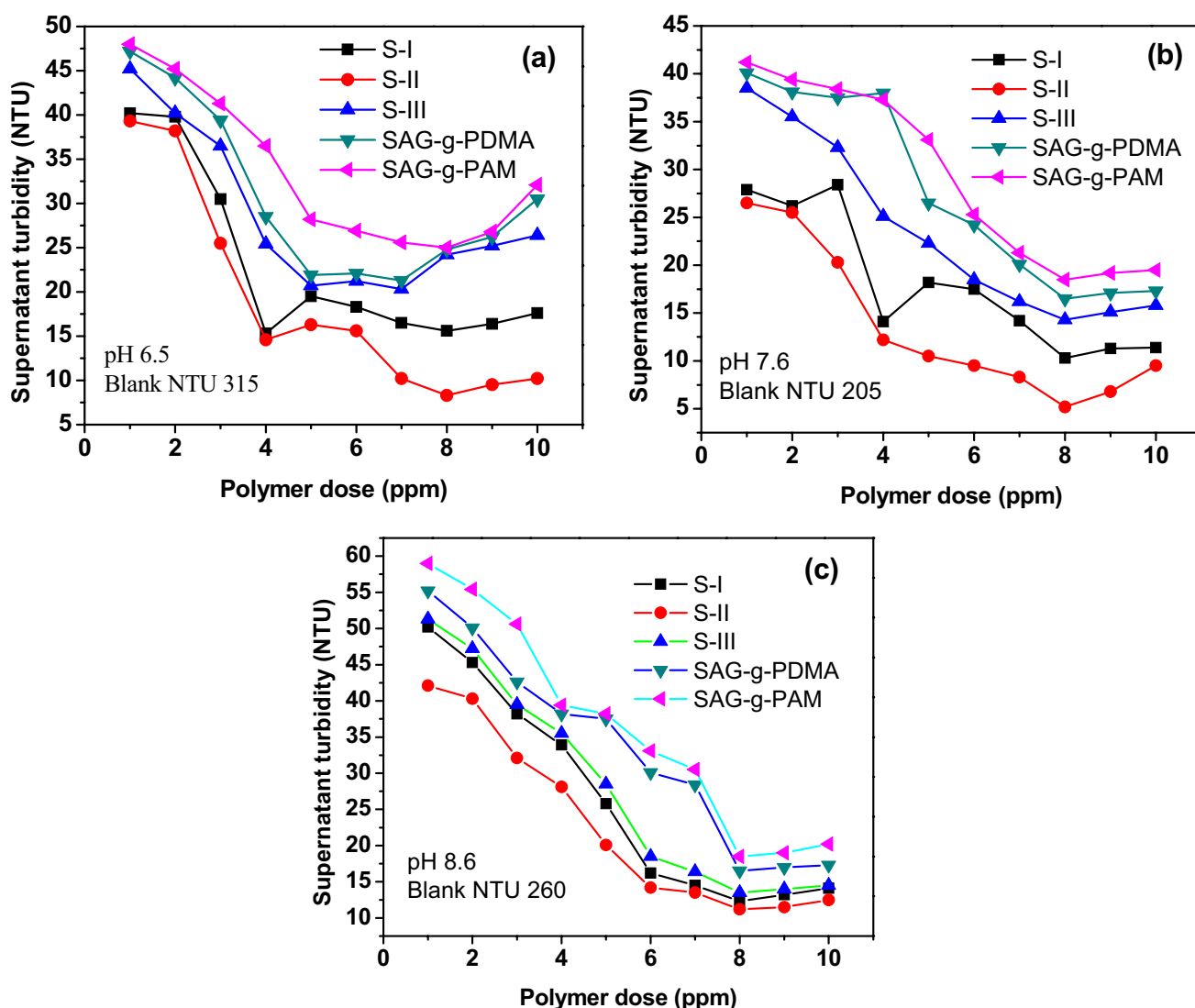


**Fig. 8** Selectivity of Pb(II) ion adsorption by the graft copolymer S-III in comparison to other metal ions

These results showed that the synthesized graft copolymer (S-III) has higher recognition power than the other competitor metal ions.

### Flocculation Studies

The flocculation performances of all the five graft copolymers were evaluated in 0.25 wt% iron ore slime, 1.0 wt% silica and 1.0 wt% kaolin clay suspensions. The results are shown in Fig. 9. It is obvious from the figure that the flocculation performances follows the order SAG-g-*poly*(NMA-co-DMA) > SAG-g-*poly*(AM-co-DMA) > SAG-*poly*(AM-co-NMA) > SAG-g-PDMA > SAG-g-PAM. The explanation comes in the following way; polymer bridging is the major flocculation mechanism for neutral



**Fig. 9** Comparison of the flocculation performances of SAG-g-PAM, SAG-g-PDMA, S-I, S-II and S-III in **a** 0.25 wt% iron ore slime, **b** 1.0 wt% kaolin clay and **c** 1.0 wt% silica suspensions

(unchanged) flocculants. For the effective bridging to occur the polymer chains should have greater flexibility [25] so that they have easy approachability to the contaminant particles in the colloidal particles. It is postulated that [26, 27] because of greater approachability of the dangling grafted chains present in the graft copolymers, graft copolymers showed better flocculation performance over linear polymers. In PAM chains extensive intramolecular hydrogen bonding occurs between the  $>C=O$  group of one  $-CONH_2$  unit with the  $-NH_2$  group of other. As a result of hydrogen bonding the *poly*(acrylamide) chains become rigid and helical [28] there by lose their flexibility and hence bridging becomes less efficient. In PDMA chains no such hydrogen bonding is possible, which makes the PDMA chains more flexible over PAM chains. Thus the graft copolymer containing PDMA chains showed better flocculation performances in all the three solid suspensions used. In SAG-*g-poly*(NMA-co-DMA), there remain PNMA and PDMA chains containing  $-NHMe$  and  $-NMe_2$  groups respectively. The volume of amide grouping having  $-NMe_2$  groups are larger than  $-NH_2$  groups (present in PAM chains), so strong steric repulsion between adjacently placed  $-CONMe_2$  and  $-CONHMe$  groupings further increases the flexibility of the dangling grafted chains. As a result of increasing flexibility of the grafted *poly*(NMA-co-DMA) chains intense bridging among the colloidal particles occurs resulting greatest flocculation performances of SAG-*g-poly*(NMA-co-DMA). Thus the flocculation performances of the graft copolymer having grafted synthetic polymer chains containing co-monomeric unit increases considerably than that containing grafted chains bearing single monomeric unit.

## Conclusion

SAG-*g*-PAM, SAG-*g*-PDMA, SAG-*g-poly*(AM-co-DMA), SAG-*g-poly*(NMA-co-DMA) and SAG-*g-poly*(AM-co-NMA) were successfully prepared by solution polymerization technique in water medium using potassium peroxydisulfate as the initiator. All the graft copolymers were used for the Pb(II) removal and flocculation studies and a comparative study were also made. For Pb(II) removal properties the maximum Pb(II) adsorption occurs at pH 4.5, time 120 min, temperature 35 °C and polymer dose 0.048 g (12 ml) in all the five graft copolymers. The Pb(II) ion removal abilities by the graft copolymers follow the order S-III > SAG-*g*-PAM > S-II > SAG-*g*-PDMA > S-I. For the flocculation performances of the graft copolymers follows the order S-II > S-III > S-I > SAG-*g*-PDMA > SAG-*g*-PAM. For Pb(II) adsorption, steric crowding near the coordination site onto the graft copolymer is important. Higher the crowding lower will be the adsorption characteristics but for flocculation the presence of co-monomeric unit in the

grafted chain is important. The flocculation performances of the graft copolymer having grafted synthetic polymeric chains containing co-monomeric unit increases considerably than that having grafted chain bearing single monomeric unit.

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## References

1. Kumar PS (2013) Environ Prog Sustain Energy 33:55–64
2. Wang I, Zhang J, Ahaio R, Li Y, Zhang C (2010) Bioresour Technol 101:5808–5814
3. Deblonde T, Cossu-Leguille C, Hantemann P (2011) Int J Hyg Environ Health 214:442–448
4. Knoig TN, Shulami S, Rytwo G (2012) Appl Clay Sci 67–68:119–124
5. Balasubramanian R, Perumal SV, Vijayaraghavan K (2009) Ind Eng Chem Res 48:2093–2099
6. King P, Rakesh N, Beenalahari S, Kumar Y, Prasad VSRK (2007) J Hazard Mater 142:340–347
7. Keles E, Ozer AK, Yoruk S (2010) Desalination 253:124–128
8. Santhy K, Selvapathy P (2004) Sep Sci Technol 39:3331–3351
9. Rivas BL, Pereira ED, Moreno-Villoslada I (2003) Prog Polym Sci 28:173–208
10. Rivas RL, Villoslada-moreno I (1998) Macromol Chem Phys 199:1153–1160
11. Kolya H, Tripathy T (2013) Int J Biomacromol 62:557–564
12. Sasmal D, Singh RP, Tripathy T (2015) Colloid Surface A 482:575–584
13. Kolya H, Tripathy T (2015) Polym Int 64:1336–1351
14. Luo X, Liu L, Deng F, Luo S (2013) J Mater Chem A 1:8280–8286
15. Kanwal F, Rehman R, Anwar J, Saeed M (2013) Asian J Chem 25:2399–2404
16. Bratby J (1980) Coagulation and Flocculation, Chap. 8. Uplands Press, Clayden
17. Girma KB, Lorenz V, Blaurock S, Edelman FT (2005) Coord Chem Rev 249:1283–1293
18. Clayden J, Greeves N, Warren S, Wothers P (2001) Organic chemistry. Oxford University Press, Oxford, p 293
19. Crini G, Peinday NH, Gimbert F, Robert C (2007) Sep Purif Technol 53:97–110
20. Langmuir I (1918) J Am Chem Soc 40(9):1361–1403
21. Mackay G (1982) J Chem Technol Biotechnol 32(7–12):759–772
22. Gueu S, Yao B, Adouby K, Ado G (2007) Int J Environ Sci Technol 4:11–17
23. M. A. K. Hanafish, Ibrahim SC, M. Z. A. Yahya (2006) J Appl Sci Res 2:1169–1174
24. Gupta VK, Ali I (2004) J Colloid Interface Sci 271:321–328
25. Dickinson E, Erikson I (1991) Adv Colloid Interface Sci, 34:1–2
26. R. P. Singh, Advance turbulent drag reducing and flocculating materials based on polysaccharides (1995), in: P. N. Prasad, J. E. Mark, T. J. Fai (Eds). Polymers and other advance materials, emerging technologies business opportunities. Plenum Press, New York, pp 227–249
27. Brostow W, Pal S, Singh RP (2007) Mater Lett 61:4381–4384
28. Kulicke WM, Knievrske R, Klein J (1982) Prog Polym Sci 8:373–468