Carbohydrate Polymers 90 (2012) 370–379

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

# Microwave synthesized xanthan gum-g-poly(ethylacrylate): An efficient $Pb^{2+}$ ion binder

Sadanand Pandey, Shivani B. Mishra*

*Department of Chemical Technology, University of Johannesburg, P.O. Box 17011, Doornfontien 2028, Johannesburg, South Africa*

ARTICLE INFO

*Article history:*
Received 1 May 2012
Received in revised form 16 May 2012
Accepted 18 May 2012
Available online 27 May 2012

*Keywords:*
Microwave irradiation
Graft copolymerization
Adsorption isotherm

ABSTRACT

Microwave induced emulsion copolymerization of ethylacrylate and xanthan gum resulted in copolymer samples of different % grafting (%*G*). The synthesis was done in the presence of catalytic amount of KPS as an initiator and the adsorption behavior of the copolymer (360%*G*) was investigated by performing both the kinetics and equilibrium studies in batch conditions. The copolymer was characterized by different techniques. Several experimental parameters were varied to optimize the adsorption conditions. The most favorable pH for the adsorption was pH 5, and at this pH the adsorption data were modeled using Langmuir and Freundlich isotherms. On the basis of the Langmuir model, $Q_0$ was calculated to be 142.86 mg g$^{-1}$ for microwave synthesized copolymer (mwXG-g-PEA). The sorption by mwXG-g-PEA followed pseudo second-order kinetics where a linear plot of $t/(qt)$ versus $t$ was obtained, the correlation coefficient ($R^2$) and rate constant at 100 mg L$^{-1}$ Pb(II) being 0.994 and $3.013 \times 10^{-4}$ g/(mg min), respectively.

## 1. Introduction

Heavy metals are toxic to aquatic flora and fauna even in relatively low concentrations. Some metals can be assimilated, stored and concentrated by organisms (Mohan, Pittman, & Steele, 2006; Mohan & Singh, 2002). Heavy metals including cadmium, lead and zinc, are toxic at high concentrations and are priority pollutants observed in municipalities and specific industries throughout the United States (Kosarek, 1981; Wilson, Yang, Seo, & Marshall, 2006). Lead poisoning in human causes severe damage to the kidney, nervous system, reproductive system, liver and brain. Severe exposure to lead has been associated with sterility, abortion, stillbirths and neo-natal deaths (Goyer & Chisolon, 1972; Manahan, 1984). Process industries, such as acid battery manufacturing, metal plating and finishing, ammunition, tetraethyl lead manufacturing, ceramic and glass industries and environmental contaminated water are the major sources of lead pollution (Subramanian & Cooner, 1991).

Pb(II) dominates in acid while $PbOH^+$ predominates in most environmental pHs. The drinking water guideline recommended by World Health Organization (WHO) and American Water Works Association (AWWA) is 0.05 mg L$^{-1}$ (WHO, 1984). The maximum allowable lead in drinking water has been set at a concentration of 15 ppb by the U.S. Environmental Protection Agency (EPA, 2002).

Adsorption appears to be the most widely used for the removal of heavy metals ions to lowers from water which cannot be removed by other techniques. The adsorption capacity of adsorbent i.e. activated carbon are affected by metal ionic charge. (Mohan et al., 2006; Mohan & Singh, 2002). Many activated carbons are available commercially but very few of them are selective for heavy metals and are also expensive. Thus a search for inexpensive substitutes is underway. Improved, tailor-made, inexpensive and readily regenerated adsorbents are needed. In recent years, versatile methods for cleaning wastewater by employing cost effective and efficient adsorbents have been developed (Mittal & Gupta, 2010; Pandey & Mishra, 2011a, 2011b, 2011c; Singh, Kumari, Pandey, & Narain, 2009). Keeping this in view, the naturally occurring polysaccharides can be used as sorbents but their solubility in water limits their applications as an adsorbent. Their stability (Singh, 2005), solubility as well as their adsorbing capacity (Singh, Tripathi, Tiwari, & Sanghi, 2006) can be well modified through graft copolymerization with the vinyl monomers. Grafting can be done using redox initiators (Bai & Liu, 2007), $\gamma$-irradiation (Khan, Ahmad, & Kronfli, 2002) or using microwave irradiation (Singh & Tripathi, 2006).

One of the natural polymers that have drawn a great interest of researchers is xanthan gum. Behari, Pandey, Kumar, and Taunk (2001) reported the graft copolymerization of acrylamide onto xanthan gum initiated by the $Fe^{2+}/BrO_3^-$ redox system in aqueous medium under a nitrogen atmosphere. Polysaccharide based graft copolymer (xanthan gum-g-4-vinyl pyridine) was synthesized using potassium peroxymonosulphate/ascorbic acid redox initiator

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* Corresponding author. Tel.: +27 11 559 6163; fax: +27 11 559 6425.
*E-mail addresses:* Sadanand.au@gmail.com (S. Pandey), smishra@uj.ac.za (S.B. Mishra).

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http://dx.doi.org/10.1016/j.carbpol.2012.05.053

in inert atmosphere (Kumar, Singh, & Ahuja, 2009). Graft copolymerization of methacrylic acid onto xanthan gum by $Fe^{2+}/H_2O_2$ redox initiator (Kumar, Srivastava, & Behari, 2007) and graft copolymerization of acrylic acid onto xanthan gum using a potassium monopersulfate/$Fe^{2+}$ redox pair (Pandey, Banerjee, Taunk, & Behari, 2003) results in improvement of stability of xanthan gum. Recently, grafting of polyacrylamide (Kumar, Srivastava, & Behari, 2009) on xanthan gum was successfully done by employing microwave-assisted and ceric-induced graft copolymerization.

In this present article, we report the microwave assisted grafting reaction of (ethylacrylate) EA onto (xanthan gum) XG and investigate the effect of microwave power, exposure time, initiator concentration and monomer concentration on grafting. To the best of our knowledge, it is the first of its kind of study reported in the literature by microwave assisted grafting of EA onto XG. The metal ion adsorption capacity of the materials was investigated using the batch technique with $Pb^{2+}$ ions in aqueous solutions.

## 2. Materials and methods

### 2.1. Materials

LG (Model No. MS-283MC; 1200 W) domestic microwave oven having 2450 MHz microwave frequency and a power output from 0 to 1200 W with continuous adjustment was used for all the experiments. All the reactions were performed in open glass vessels and each time temperature of the reaction mixture (<100 °C) was measured by inserting thermometer into reaction vessel just after the microwave exposure. All the reagents used were of analytical grade. Double distilled deionized water (Merck) was used throughout the study. The aqueous solutions of lead nitrate was prepared by dissolving $Pb(NO_3)_2$ (Merck, South Africa) and respective acids in deionized distilled water. Xanthan gum from *Xanthomonas campestris* was supplied by Sigma, monomer ethylacrylate and potassium peroxydisulphate (KPS) was supplied by Merck, South Africa.

### 2.2. Analysis

The concentrations of Pb(II) solutions were determined by atomic absorption spectrophotometer at 217 nm using a slit width of 1 nm. Systronics Digital pH meter model 335 was used for pH measurements. The XRD measurements were carried out using X' Pert Pro MPD PANalytical powder diffractometer operating in the reflection mode with CuKα radiation. SEM analyses of the modify xanthan gum were performed using a JEOL JSM-5600 instrument (JEOL, Pleasanton, CA) operated at 20 mA with an accelerating voltage of 20 kV equipped with an EDS detector, for low resolution images. To avoid charging these samples were coated with carbon.

### 2.3. Method

#### 2.3.1. Graft copolymerization of xanthan gum under microwave irradiation

Xanthan gum (0.1 g) was dissolved in the minimum required amount of distilled water in a 150 mL open-necked flask. To this solution, calculated amounts of potassium peroxydisulfate (KPS) and ethylacrylate (EA) were added and the total volume was made up to 25 mL. The flask was exposed under fixed microwave power for a definite time period in a LG (Model No. MS-283MC, Made: Korea) domestic microwave oven with a microwave frequency of 2450 MHz. A power output from 0 to 900 W with continuous adjustment was used for all the experiments. After each exposure, the temperature of the reaction mixture was determined with a thermometer. Xanthan-graft-poly(ethylacrylate) was precipitated by pouring the reaction mixture into a large quantity of acetone, while the homopolymer remained in the solution. The precipitated copolymer was filtered and repeatedly washed with acetone to ensure the complete removal of the homopolymer from the precipitated copolymer. The copolymer samples thus obtained were then finally extracted with acetone in a Soxhlet apparatus for 4 h to dissolve all the homopolymer and the copolymer samples thus obtained were finally dried under vacuum at 50 °C for >24 h to a constant weight.

#### 2.3.2. Grafting using $K_2S_2O_8$ under thermostatic water bath (cXG-g-PEA)

To a solution of XG (100 mg in 25 mL) taken in a 150 mL reaction flask, ethylacrylate (0.17 M) were added on thermostated water bath (45 °C). After 30 min $K_2S_2O_8$ (0.035 M) was added and this time of addition of persulfate was taken as zero time (Pandey & Mishra, 2011a). Graft copolymerization was allowed for 1 h. Then the reaction product (cXG-g-PEA) was precipitated in acetone to obtain the elastic copolymer that was repeatedly extracted with acetone for the removal of adhered poly(ethylacrylate). The product was crushed finally to small flakes (0.5–1 mm) and dried. %*G* and %*E* were calculated to be 320% and 75.29%, respectively.

#### 2.3.3. Estimation of grafting parameter

The %grafting, % grafting efficiency, % conversion, and % homopolymer, was calculated using Eqs. (1)–(4) given by (Athawale & Lele, 1998).

$$\textit{percent grafting}\,(\%G) = \frac{W_1 - W_0}{W_0} \times 100 \quad (1)$$

$$\textit{percent efficiency}\,(\%GE) = \frac{W_1 - W_0}{W_2} \times 100 \quad (2)$$

$$\textit{percent conversion}\,(\%C) = \frac{W_1}{W_0} \times 100 \quad (3)$$

$$\textit{percent homopolymer}\ \ (\%H) = 100 - \%GE \quad (4)$$

### 2.4. Removal of Pb(II) by microwave synthesized copolymer (mwXG-g-PEA)

mwXG-g-PEA was evaluated for Pb(II) removal from the aqueous solution and the conditions for the adsorption were optimized. Different adsorption parameters were changed (one at time), keeping the others fixed. Under the optimum adsorption conditions for mwXG-g-PEA, adsorption of Pb(II) by cXG-g-PEA was also studied for comparison.

### 2.5. Adsorption batch experiments

Stock solutions of 1000 mg $L^{-1}$ of standardized Pb(II) were prepared from lead nitrate in distilled-deionized water. Adsorption experiments were carried out using the mwXG-g-PEA as adsorbent on a temperature controlled incubator shaker set at 120 rpm maintained at 35 °C for 240 min. A known amount of adsorbent was thoroughly mixed with 25 mL of respective Pb(II) solutions, whose concentrations and pH were previously known. pH of the reaction mixture was initially adjusted using either nitric acid or sodium hydroxide (1 M). After the flasks were shaken for the desired time, the suspensions were filtered through Whatman 0.45 mm filter paper and the filtrates after suitable dilutions, were analyzed for Pb(II) concentration using atomic absorption spectrophotometer at 217 nm using a slit width of 1 nm. Control experiments showed that no sorption occurred on either glassware or filtration systems. pH of the reaction mixture was adjusted using either hydrochloric acid or sodium hydroxide (1 M).

For optimizing the adsorption, one parameter was varied at a time keeping the others fixed. For pH studies, 25 mL of 100 mg $L^{-1}$

Pb(II) solutions was adjusted to various pH ranging from 1 to 7 and the optimum pH was determined using 50 mg adsorbent dose. Various doses of the adsorbent ranging from 10 to 100 mg were used for studying the effect of adsorbent dose on the adsorption of the Pb(II) at 100 mg L$^{-1}$ concentrations. The effect of temperature on the lead sorption was studied from 10 to 50 °C at 100 mg L$^{-1}$ Pb(II) concentration using 50 mg adsorbent dose. To study the effect of lead concentration, the range for different initial lead concentrations used were 100–700 mg L$^{-1}$ using 50 mg adsorbent dose at pH 5. In order to evaluate kinetic data, the agitation time was varied from 30 min to 240 min and the kinetic studies were performed at Pb(II) concentrations (at 100 mg L$^{-1}$) using 50 mg adsorbent dose at pH 5. Separate flasks were prepared for each time interval and only one flask was taken for desired time. Unless otherwise stated the experiments were carried out at 100 mg L$^{-1}$ Pb(II) concentration, 50 mg adsorbent dose, 25 mL working volume, 120 rpm and 240 min shaking time. After 240 min the mixtures were filtered and the amount of the adsorbed metal ions was determined using AAS.

## 3. Results and discussion

Poly(ethylacrylate) (PEA) was successfully grafted in good yield using persulfate redox initiator as well as by microwave induced grafting; however, at the same monomer concentration, higher %*G* could be achieved under microwave conditions indicating incorporation of more/larger PEA grafts. The optimum %*G* was obtained by exposing a reaction mixture (25 mL) containing ethylacrylate (EA) (0.17 M), KPS (0.0025 M) and XG (0.1 g) at 100% microwave power for 15 s (Table 1).

Grafting is being carried out in aqueous medium and the water, being polar absorbs microwave energy. This results in dielectric heating of the reaction medium. Microwaves are also reported to have the special effect of lowering of Gibbs energy of activation of the reactions (Galema, 1997). These two effects cause quick decomposition of peroxydisulfate into sulphate ion radicals. The resulting sulphate ion radicals interact with water to give free hydroxyl radicals. The primary free radicals (sulphate ion radicals and/or the hydroxyl radicals) combine with ethylacrylate to give monomer free radicals. Since homopolymerization is reported to be faster (Reyes, Rist, & Russell, 1966) than graft copolymerization, the growing homopolymer free radical abstracts hydrogen from the xanthan gum molecule to result in a macro radical to which more ethylacrylate moieties become attached to form a chain. This chain will grow until it combines with other such chain to give a graft copolymer. The stability of the hydroquinone radical results from delocalization of electron charge density throughout the aromatic structure thus addition of hydroquinone quenches the grafting. Since under identical reaction conditions, 0.0025 M persulfate could not initiate graft copolymerization in the conventional grafting method (on thermostatic water bath) even at 95 °C, some microwave effect can be assumed in the microwave-accelerated grafting procedures. The representative sample (sample with maximum %*G*) of mwXG-g-PEA was characterized using FTIR, XRD, and SEM analysis and was used for the adsorption experiments.

### 3.1. Characterization of the mwXG-g-PEA

The FTIR spectra of XG, PEA, mwXG-g-PEA and Pb loaded mwXG-g-PEA are been discuss in this article. IR spectrum of XG showed strong peak at 3417 cm$^{-1}$ due to O—H stretching vibration [27,31] and adsorption band at 2919 cm$^{-1}$ appeared due to C—H stretching of alkyl group [30,31]. On comparing the FTIR spectra of XG, PEA and mwXG-g-PEA (figure in supplementary file) a band at 3427 cm$^{-1}$ is

**Table 1**
(a) %*G* and %*E* as a function of change in microwave power and exposure time at EA (0.17 M), KPS (0.0025 M) and XG (0.1 g/25 mL), reaction volume 25 mL; (b) %*G* and %*E* as a function of KPS concentration at EA (0.17 M), XG (0.1 g/25 mL), at 900 W and 15 s; (c) %*G* and %*E* as a function of monomer concentration at KPS (0.0025 M), XG (0.1 g/25 mL), 900 W and 15 s; (d) %*G* and %*E* as a function of gum concentrations at monomer (0.17 M), KPS (0.0025 M), at 900 W and 15 s.

| (a) Microwave power (%) | Exposure (s) | Yield (mg) | %Grafting (%*G*) | %Efficiency (%*GE*) | %Conversion (%*C*) | %Homopolymer (%*H*) |
|---|---|---|---|---|---|---|
| 20 (240 W) | 5 | 240 | 140 | 32.94 | 56.47 | 67.05 |
| | 10 | 246 | 146 | 34.35 | 57.88 | 65.64 |
| | 15 | 258 | 158 | 37.17 | 60.70 | 62.82 |
| | 20 | 262 | 162 | 38.11 | 61.64 | 61.88 |
| 40 (480 W) | 5 | 252 | 152 | 35.76 | 59.29 | 64.23 |
| | 10 | 276 | 176 | 41.41 | 64.94 | 58.58 |
| | 15 | 315 | 215 | 50.58 | 74.11 | 49.41 |
| | 20 | 325 | 225 | 52.94 | 76.47 | 47.05 |
| 60 (720 W) | 5 | 270 | 170 | 40 | 63.52 | 60 |
| | 10 | 308 | 208 | 48.94 | 72.47 | 51.05 |
| | 15 | 324 | 224 | 52.70 | 76.23 | 47.29 |
| | 20 | 308 | 208 | 48.94 | 72.47 | 51.05 |
| 80 (960 W) | 5 | 287 | 187 | 44 | 67.52 | 56 |
| | 10 | 333 | 233 | 54.82 | 78.35 | 45.17 |
| | 15 | 360 | 260 | 61.17 | 84.70 | 38.82 |
| | 20 | 400 | 300 | 70.58 | 94.11 | 29.42 |
| 100 (1200 W) | 5 | 415 | 315 | 74.1 | 97.64 | 25.9 |
| | 10 | 438 | 338 | 79.5 | 103.05 | 20.5 |
| | 15 | 460 | 360 | 84.70 | 108.23 | 15.3 |
| | 20 | 452 | 352 | 82.82 | 106.35 | 17.18 |

| (b) [$K_2S_2O_8$ ($\times 10^3$ M)] | %*G* | %*GE* | %*C* | %*H* | (c) [EA] ($\times 10^2$ M) | %*G* | %*GE* | %*C* | %*H* | (d) XG (mg/25 mL) | %*G* | %*GE* | %*H* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1.0 | 242 | 56.94 | 80.47 | 43.06 | 11 | 216 | 78.54 | 114.9 | 21.46 | 50 | 286 | 67.29 | 32.71 |
| 1.5 | 260 | 61.17 | 84.70 | 38.83 | 13 | 260 | 80 | 110.76 | 20 | 100 | 360 | 84.70 | 15.3 |
| 2.0 | 300 | 70.58 | 94.11 | 29.42 | 15 | 310 | 82.66 | 109.33 | 17.34 | 150 | 343 | 80.70 | 19.3 |
| 2.5 | 360 | 84.70 | 108.2 | 15.30 | 17 | 360 | 84.70 | 108.23 | 15.3 | 200 | 308 | 72.47 | 27.53 |
| 3.0 | 340 | 80 | 103.5 | 20 | 19 | 346 | 72.84 | 93.89 | 27.16 | 250 | 277 | 65.17 | 34.83 |
| | | | | | | | | | | 300 | 180 | 42.35 | 57.65 |
| | | | | | | | | | | 350 | 60 | 14.11 | 85.88 |

due to O—H stretching vibration in the spectrum of XG and the band at 2934 $\text{cm}^{-1}$ is due to C—H stretching. In case of mwXG-g-PEA, it is observed that there is variation in intensity of C—H stretching vibration and shifting of peak from 2934 $\text{cm}^{-1}$ to 2984 $\text{cm}^{-1}$ and the most significance observation is the disappearance of O—H stretching vibration peak in case of mwXG-g-PEA, indicating the participation of hydroxyl groups in chemical reaction. The graft copolymerization is further confirmed by characteristic absorption bond of ester at 1722 $\text{cm}^{-1}$ due to —C=O stretching vibration and at 1155 $\text{cm}^{-1}$ due to —C—O stretching vibration of monomer molecules respectively. The FTIR of PEA and mwXG-g-PEA are similar because both contain same ester group. The appearance of additional peaks in spectrum of graft copolymer and disappearance of O—H stretching vibration peak in the spectrum of mwXG-g-PEA showed that grafting might have taken place on OH sites of XG. The IR spectrum of lead loaded adsorbent (Pb-mwXG-g-PEA) had significantly different spectrum than that of the mwXG-g-PEA. In the loaded copolymer, the O—H stretching and carbonyl stretching peaks are seen shifted to 3441 and 1726 $\text{cm}^{-1}$ respectively indicating complexation between the lead species and the hydroxyl and ester groups of the copolymer. After lead sorption, a change in position, shape and intensity of C—H stretching peak was also observed which further confirmed the loading of lead. Pb-mwXG-g-PEA showed significantly different adsorption pattern in the region of 650–1500 $\text{cm}^{-1}$ due to the incorporated lead species.

The XRD spectra showed the amorphous nature of XG (Kumar, Singh, et al., 2009; Pandey & Mishra, 2011b). On comparing the XRD spectra of XG and mwXG-g-PEA, in case of XG, there is no considerable peak of crystallinity. The XRD pattern for XG shows single amorphous structure as demonstrated by broad halo. The XRD of PEA shows the small amount crystallinity, while diffractogram of mwXG-g-PEA showed the crystalline nature with the characteristics peak of EA appearing at $2\theta$ 15°, 26°, 28°, 29° which is due to grafted PEA onto XG backbone. mwXG-g-PEA on lead loading (Pb-mwXG-g-PEA) lost its crystalline character and showed a broad hallow similar to the polymer. It was observed due to the adsorbed lead on to mwXG-g-PEA.

Surface morphology of mwXG-g-PEA was studied using scanning electron microscopy to investigate the grafting of PEA onto XG. It is clearly seen (Figure in supporting file) that fibrous nature of XG particles that suggest the amorphous nature of the biopolymer (Pandey & Mishra, 2011c). The SEM images of grafted copolymer show that grafting of EA onto XG brings about the change in the shape and size of the particles. Further it can be observed that particles of mwXG-g-PEA are bigger in size than ungrafted XG and it look to be aggregated.

The SEM picture showed that graft copolymer before and after Pb(II) loading had significantly different morphologies which evidenced lead loading onto graft copolymer. The mwXG-g-PEA had an aggregated cluster like appearance while in Pb loaded copolymer a small deposition of lead are seen on the graft copolymer surface (figure in supporting file). The lead adsorption on the mwXG-g-PEA was further confirmed by the help of EDX spectra. The EDX spectra of the lead loaded mwXG-g-PEA indicated significant Pb(II) sorption by the grafted copolymer (figure not produced).

### 3.2. Optimization of Pb(II) removal

Adsorption conditions were optimized by varying various adsorption parameters, one parameter at a time keeping the others fixed (Fig. 1).

#### 3.2.1. Effect of initial pH on lead adsorption

The acidity of solution (pH) is one of the most important parameters controlling uptake of heavy metals from aqueous solutions. The initial pH of the solutions was varied from 1 to 7 with an increment of 1 pH unit. In this group of experiments, the amount of adsorbent (0.05 g), the concentration of adsorbate Pb(II) (100 $\text{mg L}^{-1}$), and contact time (4 h) were kept constant. The effect of changing pH on Pb(II) sorption by mwXG-g-PEA is shown in Fig. 2a. It was observed that percentage sorption onto mwXG-g-PEA is maximum at pH 5.0 same as the other reported adsorbents (Chen & Wang, 2007) whose maximum adsorption capacity is at pH 5.

In this work, the effect of pH on lead adsorption is shown in Fig. 1a. As indicated in this figure, the equilibrium adsorption quantity of Pb (II) on two adsorbents significantly increases with increased pH from 4 to 5, whereas there is a minor influence on lead adsorption capacity for pH less than 4. With a further increase in pH from 5 to 7 for mwXG-g-PEA, however, the equilibrium adsorption capacity decreases slightly. In contrast, the equilibrium adsorption capacity of XG is maintained at about the same level at pH from 5 to 7. For the system with pH beyond 7 adsorption was not determined because the formation of $\text{Pb(OH)}_3{}^-$ negative ions and $\text{Pb(OH)}_2$ precipitation had a significant effect on the adsorption of lead ions (Li, Bai, & Liu, 2005). For both XG and mwXG-g-PEA the maximum adsorption equilibrium is found at about pH 5. The results also indicate that mwXG-g-PEA is more sensitive to pH on adsorption of lead relative to XG because the lead adsorption on mwXG-g-PEA is mainly attributed to the electrostatic interaction (Issabayeva, Aroua, & Sulaiman, 2006) which can be confirmed from the fact that the final equilibrium pH of the reaction mixture of mwXG-g-PEA is always lower than initial pH. A rise in pH not only enhances the dissociation of acidic functional groups on mwXG-g-PEA surface but also causes the loss of the outer hydration sheaths of the metal ions and subsequent formation of $\text{Pb(OH)}^+$ and $\text{Pb}^{2+}$ ions (Netzer & Hughee, 1984). Consequently, these variations related to solution pH considerably enhance electrostatic interaction between lead ions and the adsorbent and thus increase adsorption capacity of mwXG-g-PEA. In conclusion, pH 5 was selected as an optimum value for conducting further adsorption experiments according to influence of solution pH on lead adsorption.

#### 3.2.2. Effect of %G

The experimental results demonstrating the effect of %*G* on the sorption of Pb(II) by mwXG-g-PEA is shown in Fig. 1b. With increase in %*G* from 146 to 360%, adsorption increases from 60 to 76.5% at fixed adsorbent dose of 50 mg, pH 5.0, Pb(II) 100 $\text{mg L}^{-1}$, temperature 30 °C, 100 rpm, and time 4 h. The increase in adsorption is due to increase in adsorbing sites on poly(ethylacrylate) grafts with increase in %*G*.

#### 3.2.3. Effect of initial concentration of Pb(II)

The experimental results demonstrating the effect of initial concentration of $\text{Pb}^{2+}$ on the adsorption of Pb(II) by mwXG-g-PEA is shown in Fig. 1c. With the increase in the initial concentration of Pb(II) from 100 to 700 $\text{mg L}^{-1}$, using 50 mg adsorbent dose at pH 5.0, the percentage adsorption of Pb(II) decreases from 76.5 to 35%. At higher initial Pb(II) concentration, ratio of available adsorbing site in the adsorbent (which is fixed) and the available Pb(II) decreases which results in a decrease in percentage adsorption

#### 3.2.4. Effect of adsorbent dose

The experimental results demonstrating the effect of adsorbent dose on the adsorption of Pb(II) by mwXG-g-PEA is shown in Fig. 1d. The percentage adsorption of Pb(II) increases from 18 to 77.4% by increasing the adsorbent dose from 10 mg/25 mL to 100 mg/25 mL at initial adsorbate concentration 100 $\text{mg L}^{-1}$. This is because at higher dose of adsorbent more adsorption sites are available due to increased surface area.

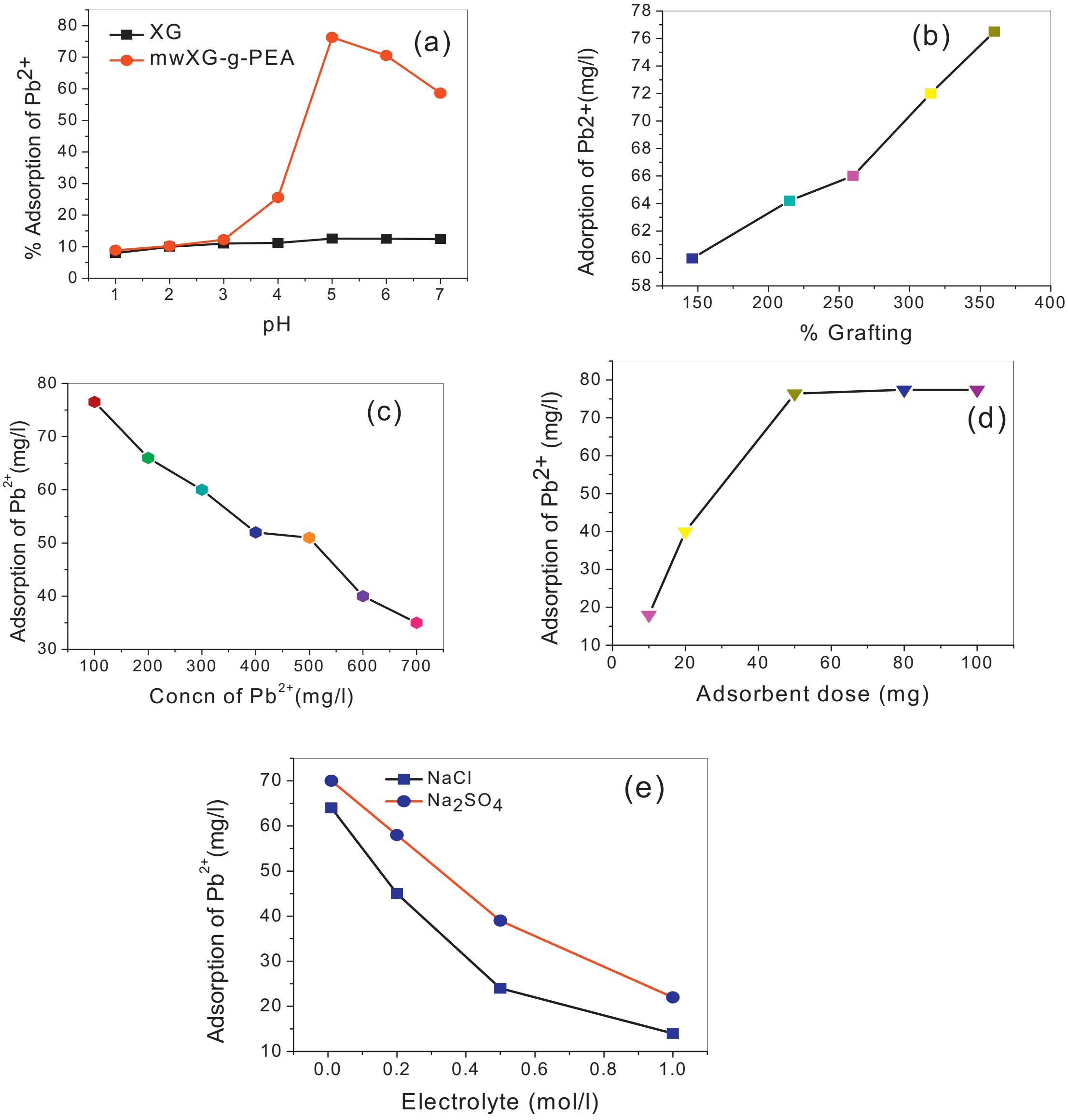

**Fig. 1.** (a) Effect of pH; (b) %Adsorption vs. %G at fixed concentration of Pb(II) (100 ppm), pH 5.0, adsorbent dose (50 mg), batch volume (25 mL), contact time (4 h), rpm (100) at 35 °C; (c) %Adsorption vs. $Pb^{2+}$ concentration at fixed adsorbent dose (50 mg), pH 5.0, batch volume (25 mL), contact time (4 h), rpm (100) at 35 °C; (d) %Adsorption vs. adsorbent dose at fixed Pb(II) concentration (100 ppm) pH 5.0, batch volume (25 mL), contact time (4 h), rpm (100) at 35 °C; (e) %Adsorption vs. electrolyte concentration adsorbent dose (50 mg), Pb(II) (100 ppm) pH 5.0, batch volume (25 mL), contact time (4 h), rpm (100) at 35 °C.

#### 3.2.5. *Effect of electrolyte*

The experimental results demonstrating the effect of electrolyte (NaCl and $Na_2SO_4$) on the adsorption of Pb(II) by mwXG-g-PEA is shown in Fig. 1e. With increase in concentration of both NaCl and $Na_2SO_4$ from 0.01 to 1.0 M, adsorption decreases from 64 to 14 and 70 to 22%, respectively. Lowering of adsorption in the presence of electrolytes can be explained on the basis of competition of the $Pb^{2+}$ with other ionic species furnished by the electrolytes.

### 3.3. *Adsorption isotherm studies*

Adsorption data were fitted to the Langmuir and Freundlich isotherms. The Langmuir isotherm is valid for monolayer sorption due to a surface of a finite number of identical sites and expressed in the linear form as under (Eq. (5)):

$$\frac{C_e}{q_e} = \frac{1}{(bQ_0)} + \frac{C_e}{Q_0} \tag{5}$$

where $C_e$ is the equilibrium concentration (mg $L^{-1}$) and $q_e$ the amount adsorbed at equilibrium (mg $g^{-1}$). The Langmuir constants $Q_0$ (mg $g^{-1}$) represent the monolayer adsorption capacity and $b$ (L $mg^{-1}$) relates the heat of adsorption.

The essential feature of the Langmuir adsorption can be expressed by means of $R_L$, a dimensionless constant referred to as separation factor or equilibrium parameter for predicting whether an adsorption system is favorable or unfavorable. $R_L$ is calculated using the following equation:

$$R_L = \frac{1}{1 + bC_0} \tag{6}$$

where $C_0$ is the initial Pb(II) concentration (mg $L^{-1}$). If $R_L$ values lies between 0 and 1, the adsorption is favorable.

The Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption and is expressed in linear form as given in Eq. (7):

$$\ln q_e = \ln K_f + (1|n) \ln C_e \tag{7}$$

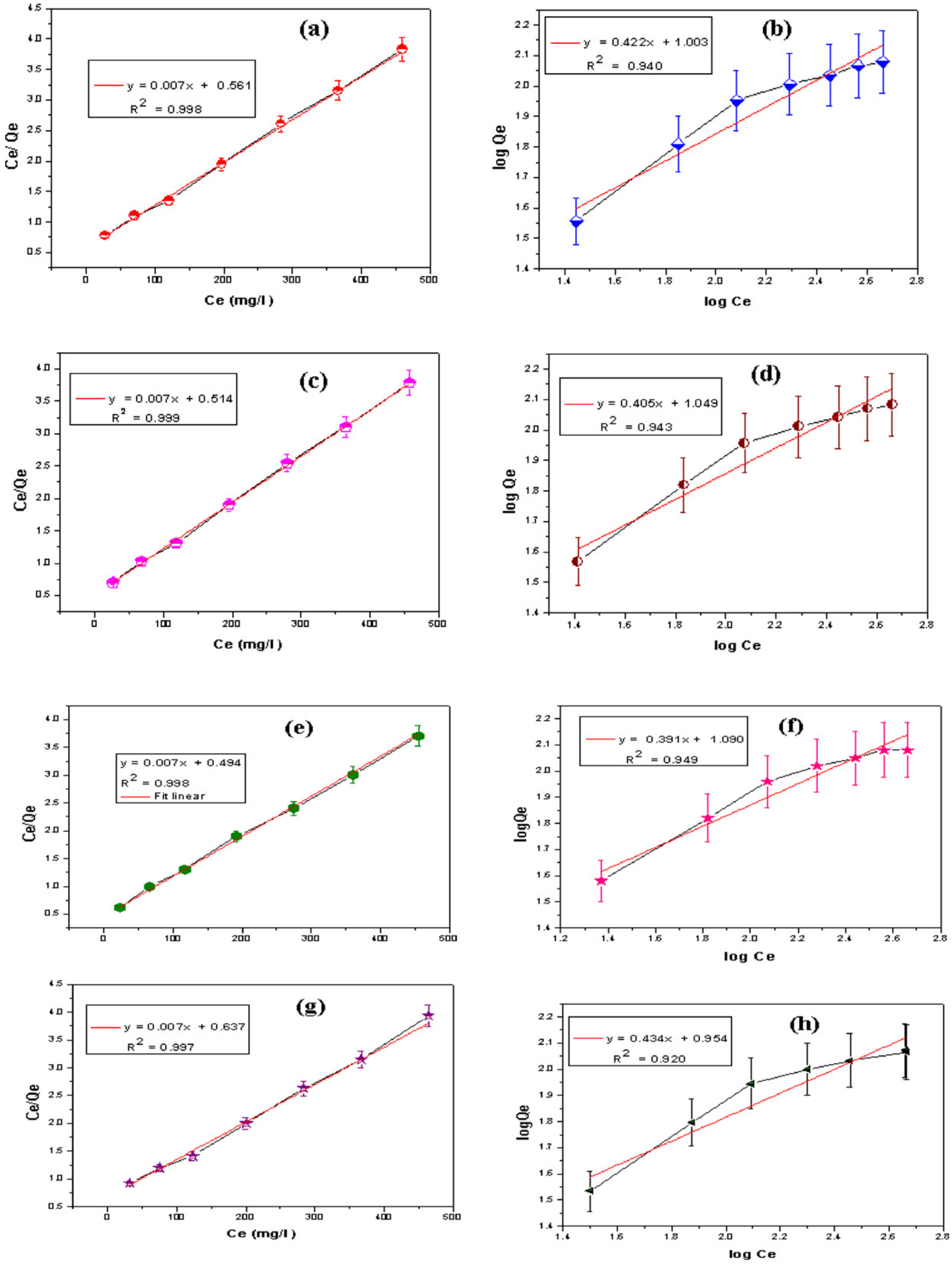

**Fig. 2.** Langmuir adsorption isotherm and Freundlich adsorption isotherm of Pb(II) adsorption by mwXG-g-PEA (a, b) at 15 °C; (c, d) at 25 °C; (e, f) at 35 °C and (g, h) at 45 °C respectively with ±5% error bar.

where $K_f$ (mg g$^{-1}$), is roughly an indicator of the adsorption capacity and 1/$n$ is the adsorption intensity.

In general, as the $K_f$ value increases the adsorption capacity of adsorbent for a given adsorbate increases. The magnitude of the exponent, 1/$n$ gives an indication of the favorability of adsorption. As the values of $n > 1$ represents favorable adsorption condition. Values of $K_f$ and $n$ are calculated from the intercept and slope of the plot (Fig. 2) and are listed in Table 2a. The $R^2$ value for Freundlich

**Table 2**
(a) Constants for Langmuir and Freundlich isotherms for Pb (II) adsorption by mwXG-g-PEA; (b) pseudo-second-order, second-order, Lagergren first-order models for Pb (II) adsorption of Pb (II) ions by mwXG-g-PEA; (c) thermodynamic parameters for Pb (II) adsorption by mwXG-g-PEA.

(a)

| Temperature (°C) | Langmuir isotherm | | | | Freundlich isotherm | | |
|---|---|---|---|---|---|---|---|
| | $Q_0$ | $b$ (L mg$^{-1}$) ± SD | $R_L$ | $R^2$ | $n$ | $K_f$ | $R^2$ |
| 15 | 142.86 | 0.01248 ± 0.00090 | 0.4448 | 0.998 | 2.369 | 10.67 | 0.940 |
| 25 | 142.86 | 0.01362 ± 0.00086 | 0.4234 | 0.999 | 2.469 | 11.19 | 0.943 |
| 35 | 142.86 | 0.01417 ± 0.00088 | 0.4137 | 0.998 | 2.556 | 12.30 | 0.949 |
| 45 | 142.86 | 0.01099 ± 0.00089 | 0.4764 | 0.997 | 2.304 | 8.99 | 0.920 |

(b)

| Pb(II) (mg L$^{-1}$) | Lagergren | | Pseudo second order | | Second order | |
|---|---|---|---|---|---|---|
| | $R^2$ | $K_L$ (min$^{-1}$) | $R^2$ | $K'$ (g mg$^{-1}$ min$^{-1}$) | $R^2$ | $K_2$ (g mg$^{-1}$ min$^{-1}$) |
| 100 | 0.904 | $0.898 \times 10^{-4}$ | 0.994 | $3.013 \times 10^{-4}$ | 0.980 | $2.7 \times 10^{-4}$ |

(c)

| Temp (K) | $\Delta G$ (kJ mol$^{-1}$) | $\Delta H$ (kJ mol$^{-1}$) | $\Delta S$ (J mol$^{-1}$) |
|---|---|---|---|
| 288 | −2.6248 | +41.685 | +153.85 |
| 298 | −2.8100 | | +149.31 |
| 308 | −2.9483 | | +144.91 |
| 318 | −2.7522 | | +139.73 |

isotherm is lower than Langmuir isotherm. The value of Freundlich exponent $n$ is the range of $n > 1$, indicating a favorable adsorption (Treybal, 1968).

Equilibrium adsorption data of both the microwave as well as conventionally synthesized copolymer could be modeled satisfactorily to both the Langmuir and Freundlich isotherms. The isotherm studies for mwXG-g-PEA were performed at different temperature intervals and are shown in Fig. 2. Isotherm studies for cXG-g-PEA were also performed at 15, 25, 35 and 45 °C for comparison; however, adsorption isotherms graph of the cXG-g-PEA are not shown. The equilibrium data fitted to Langmuir model better than Freundlich model indicating unilayer adsorption. From Langmuir isotherms (at 15 °C, 25 °C, 35 °C and 45 °C) $Q_0$ was calculated to be 142.86 mg g$^{-1}$ in case of mwXG-g-PEA and 120.6 mg g$^{-1}$ in case of cXG-g-PEA indicating that the adsorbent had a very high capacity to remove Pb(II) ions from the solution (Fig. 2a and b) and the removal of lead is comparatively more in mwXG-g-PEA than cXG-g-PEA, and increase in temperature does not alter the $Q_0$, while the Langmuir constants increase. The comparative chart of different adsorbents used for lead removal is mentioned in Table 3. The Langmuir and Freundlich isotherms at 15 °C, 25 °C, 35 °C and 45 °C are shown in Fig. 2a–h. The value of Langmuir constant $b$ also increased with temperature there by suggesting that the Pb(II) exhibited higher affinity for the grafted material at higher temperature than at lower temperature. An $n$ value greater than unity indicated that the biosorption of Pb(II) onto the grafted material was favorable. The parameter $R_L$ indicates the nature of shape of the isotherm. The value of $R_L$ in the present investigation has been found to be 0.4448, 0.4234, 0.4137, and 0.4764 at 15 °C, 25 °C, 35 °C and 45 °C respectively showing that the adsorption of Pb(II) on grafted material is favorable at the temperature studied.

The sorption capacity of the synthesized mwXG-g-PEA for Pb(II) was compared to that of several adsorbents as reported in the literature. In this study, the sorption capacity of the mwXG-g-PEA for Pb(II) was the highest among all the sorbents examined.

### 3.4. *Sorption kinetics*

The sorption kinetics study was performed to know the extent of time for the removal of Pb (II) from the solution, adsorption studies were carried out at initial Pb (II) concentration of 100 mg L$^{-1}$ at different time intervals (30–240 min) keeping the other parameter to be constant such as pH 5, adsorbent dose 50 mg, temperature 35 °C. Measurements of ppm of Pb (II) adsorption as a function of time are shown in Fig. 3. As it was discussed earlier that the increase in adsorption with dose can be attributed to increased surface and the number of more binding sites for adsorption. Furthermore, time taken to reach apparent equilibrium was reduced at the higher doses of adsorbents. For mwXG-g-PEA, sorption of Pb (II) attained a maximum after 240 min and thereafter was almost constant up to the studied time of 480 min. The removal of Pb (II) by mwXG-g-PEA ranged from 30 ppm to 76.5 ppm at adsorbent doses of 0.05 g/25 mL with time range from 30 min to 240 min. Therefore, it can be concluded that the rate of Pb (II) binding with adsorbent was greater in the initial stages, then gradually decreased and remained almost constant after an optimum period.

**Table 3**
Adsorption capacities of Pb(II) of different adsorbents.

| Adsorbent material | Adsorption capacity (mg g$^{-1}$) | Reference |
|---|---|---|
| Marine green macro alga | 28.72 | Pavasant et al. (2006) |
| Barley straw | 15.2 | Conrad and Hansen (2007) |
| Rice husk | 4.0 | Conrad and Hansen (2007) |
| Powdered waste sludge | 82 | Conrad and Hansen (2007) |
| Hazelnut shell | 1.78 | Conrad and Hansen (2007) |
| *Syzygium cumini L.* | 32.47 | King, Rakesh, Beenalahari, Prasanna Kumar, and Prasad (2007) |
| CG-g-PMMA | 126.58 | Singh, Tiwari, Sharma, and Sanghi (2007) |
| mwXG-g-PEA | 142.86 | Present study |

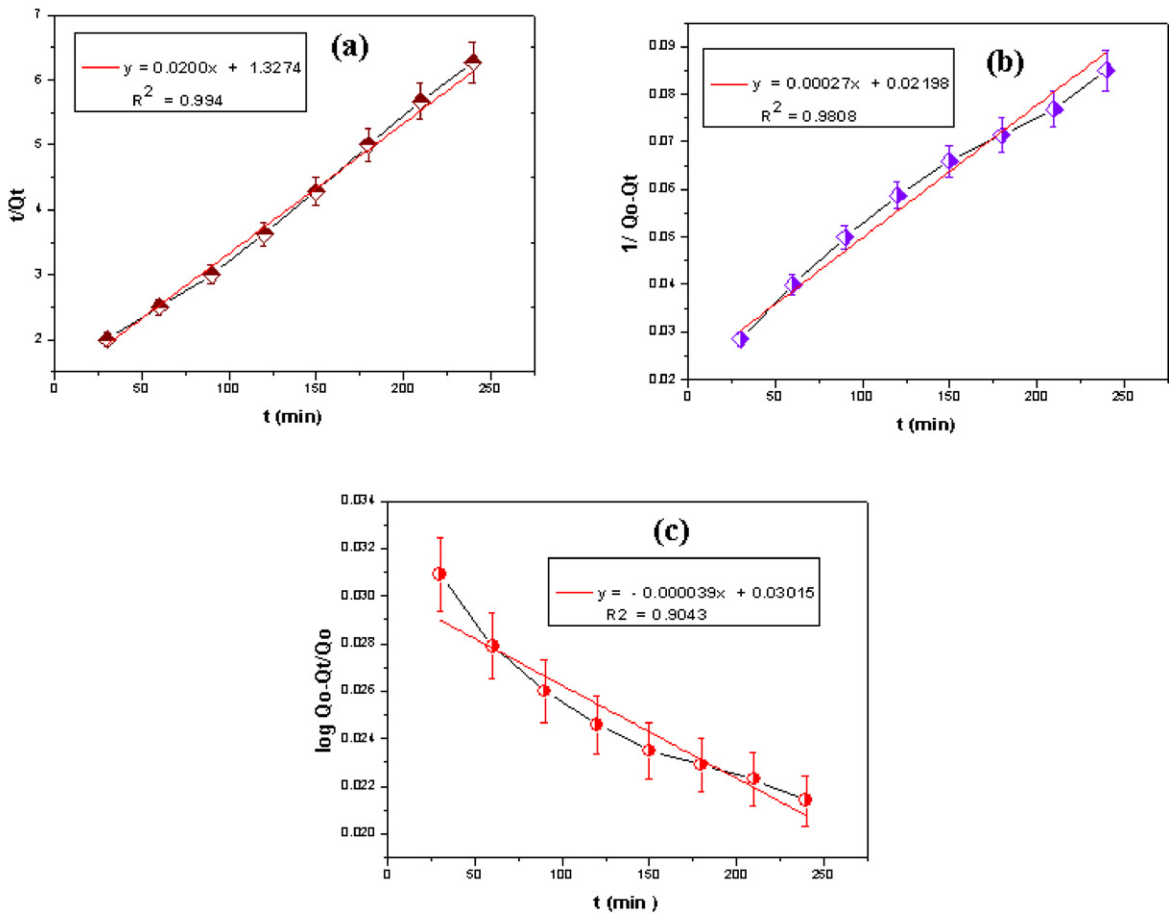

**Fig. 3.** (a) Pseudo-second-order, (b) second order and (c) Lagergren first order plot of lead adsorption by mwXG-g-PEA at pH 5.0, adsorbent dose (50 mg), Pb(II) concentration (100 ppm), batch volume (25 mL), contact time (4 h), rpm (100) at 35 °C with ±5% error bar.

The first rapid increase in binding capacity is due to the presence of number of vacant site available at the initial time interval, as a result there was an increased concentration gradient between adsorbate in solution and adsorbate in the adsorbent (Kavitha & Namasivayam, 2007). Generally, when adsorption involves a surface reaction process, the initial adsorption is rapid. Then, a slower adsorption would follow as the available adsorption site gradually decreases.

Kinetics (Sankararamakrishnan, Dixit, Iyengar, & Sanghi, 2006) of the adsorption was modeled by the first order Lagergren equation, the pseudo-second-order equation and the second-order rate equation shown below as Eqs. (8)–(10), respectively (Fig. 3a–c).

$$log(q_e - q_t) = log\, q_e - \frac{K_L}{2.303}t \tag{8}$$

$$\frac{1}{q_t} = \frac{1}{K' q_e^2} + \frac{t}{q_e} \tag{9}$$

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + K_2 t \tag{10}$$

where $K_L$ is the Lagergren rate constant of adsorption ($min^{-1}$); $K'$ the pseudo-second-order rate constant of adsorption ($g\,mg^{-1}\,min^{-1}$) and $K_2$ the second-order rate constant ($g\,mg^{-1}\,min^{-1}$); $q_e$ and $q_t$ are the amounts of metal ion sorbed ($mg\,g^{-1}$) at equilibrium and at time $t$, respectively.

Kinetic data of Pb(II) adsorption by the composite fitted best in to pseudo second order kinetic model as reported for other grafted biopolymeric material (Namasivayam & Rangananthan, 1993), where linear plot of $t/qt$ vs $t$ was obtained; the correlation coefficient ($R^2$) and rate constant were 0.994 and rate $3.013 \times 10^{-4}$, respectively at 100 ppm Pb(II) concentration. These results suggest that the adsorption kinetics is not diffusion controlled but is chemisorptions. Rate constants and $R^2$ values for the different kinetic models for the adsorption have been compared in Table 2b.

### 3.5. Adsorption thermodynamics

The values of thermodynamic parameters are relevant for the practical application of adsorption process. Isotherm data related to adsorption of Pb(II) on to the mwXG-g-PEA at 15 °C, 25 °C, 35 °C and at 45 °C were analyzed to obtain the values of thermodynamic parameters. Change in free energy ($\Delta G$), enthalpy ($\Delta H$) and entropy ($\Delta S$) for the adsorption process was calculated using Eqs. (11) and (12) (Rajgopal, Kathikeyan, Kumar, & Miranda, 2006) and computed values are listed in Table 2c.

$$\Delta G = \Delta H - T\,\Delta S \tag{11}$$

$$\frac{\ln b_2}{\ln b_1} = \frac{-\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{12}$$

where $\Delta G$ is the change in Gibbs free energy ($J\,mol^{-1}$); $R$ universal gas constant ($8.314\,J\,K^{-1}\,mol^{-1}$), $T$, $T_1$ and $T_2$ temperatures (K); $\Delta H$ change in enthalpy ($J\,mol^{-1}$); $b_1$ and $b_2$ are Langmuir constants at temperatures $T_1$ and $T_2$, respectively; $\Delta S$ is the change in entropy ($J\,mol^{-1}\,K^{-1}$).

Negative values of $\Delta G$ indicated that the adsorption process was favorable and spontaneous in nature. It may be noted that with the increase in temperature from 15 to 35 °C the value of $\Delta G$ decreased from $-2.6248\,\mathrm{kJ\,mol^{-1}}$ to $-2.9483\,\mathrm{kJ\,mol^{-1}}$ Thus adsorption of Pb(II) onto the mwXG-g-PEA was increased at higher temperature. The positive value of enthalpy change ($\Delta H$) confirmed the endothermic nature of the adsorption process. Positive values of $\Delta S$ suggested good affinity of the metal ion toward the adsorbent and increased randomness at the solid–solution interface during the fixation of the metal ion on the active site of the adsorbent.

### 3.6. Desorption

Desorption was carried out with 1 N, HCl, NaOH, $H_2SO_4$, and EDTA, where HCl though most efficient in removing Pb(II) from the 100 mg L$^{-1}$ solution. In acidic medium, the protons in solution replaces the metal ions on the graft copolymer, while the apparent poor recovery observed in basic media such as NaOH, may be due to the coordinating ligands being deprotonated, hence bound-metal ions finds it difficult to be detached from the copolymer. To optimize desorption with HCl, 0.5–1 N HCl was used where a maximum 76.92% desorption could be achieved with 1 N HCl. The material desorbed from first cycle in the second cycle could adsorb only 74.20% Pb(II) which was desorbed up to 64.24% in the second desorption cycle. In third cycle this desorbed polymer could adsorb 70.4% Pb(II), which could be desorbed up to 60.2%. The material in the fourth cycle could adsorb 64.2% followed by desorption up to 55.42% only. The material in the last fifth cycle could adsorb 54.8% followed by desorption up to 42.4% only. Complete desorption was not possible, perhaps due to the involvement of non electrostatic forces between the copolymer and the lead ions.

## 4. Conclusion

Chemical modification of the xanthan gum by microwave irradiation with ester group increased the adsorption capacity to more than four times compare to the xanthan gum. Adsorption followed Langmuir isotherm model. Adsorbent–adsorbate kinetics exhibited pseudo second-order. The prepared adsorbent was found to be much more efficient than the other commercially available absorbent reported so far. The mwXG-g-PEA could be an excellent adsorbent for the removal and recovery of lead ions from aqueous solution. This method is very promising compared to other conventional and generally more expensive processes.

## Acknowledgements

The author is thankful to the University of Johannesburg, Johannesburg and National Research Foundation (NRF), South Africa for its generous financial support and for providing instrumental facilities.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2012.05.053.

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