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Copolymerization of ethyl acrylate onto guar gum for the adsorption of Mg(II) and Ca(II) ions

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ABSTRACT

In the present study, the copolymerization of ethyl acrylate and guar gum was induced by microwave irradiation in the presence of catalytic amount of the initiator potassium persulfate (KPS). The maximum percentage conversion was found to be 107.1% under microwave power of 900 MW after 3 min exposure. The copolymerized guar gum-graft-poly-ethyl acrylate (GG-g-PEA) was characterized using FTIR spectroscopy and SEM analysis. The effect of pH on the capacity of the GG-g-PEA copolymers to reduce the hardness of the water was investigated, leading to the effective removal of Ca(II) and Mg(II) ions from solutions at pH 8. The calculated values of the coefficient of determination (0.914–0.9553) for Ca(II) and Mg (II), respectively, showed that the equilibrium isotherm data followed the Freundlich isotherm model. The pseudo-second-order model was suitable for the modelling of the kinetic data, predicting adsorption capacities of 0.2680 g/mg/min for Ca(II) and 0.3835 g/mg/min for Mg(II), respectively. The synthesized GG-g-PEA adsorbent could therefore be recommended for the reduction in the water's hardness.

Keywords: Copolymerization; Water pollution; Adsorption affinity; Light metals

1. Introduction

Much has been achieved since the industrial revolution; the manufacturing process is more effective and productive, science is much more advanced and has made lives more convenient. Water pollution from the disposal of heavy metals into the water bodies, however, continues to be a big concern globally.

The wastewater containing the heavy metal ions comes from many sources such as fertilizer manufacturers, metal plating operations, mining operations, battery manufacturing processes, the production of paint and pigments and the ceramic and glass industries which are just a few to be mentioned [1–3].

Heavy metal ions present in the water are not biodegradable, cannot be metabolised or be decomposed, thus accumulation and distribution of these metals occur in the environment [4,5]. It is necessary to develop various technologies that are efficient for the removal of these pollutants from the discharge water. The technologies that are used to remove such pollutants include biological treatments, membrane processes, advanced oxidation processes, chemical precipitation and electrochemical techniques, reverse osmosis, ion exchange and adsorption techniques [6].

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Some of these processes are often associated with problems such as a high operational cost and the inability of these processes to remove the heavy metals to acceptable levels. Thus, the adsorption process is one of the most promising techniques for removing heavy metals from water [7]. Adsorption is generally preferred because of its low cost, high efficiency, easy handling and the availability of different sorbents. A number of adsorbents that have been used include activated carbon, zeolites, clays and agricultural residues. The major disadvantages of these adsorbents are that they have low adsorption capacities because of their weak interactions with the metal ions and difficulty of separation and regeneration of some of the adsorbents from the water treated [8].

The use of natural polymers for metal adsorption has received attention due to their low cost, biodegradability, easy availability and non-toxicity. These polymers have certain drawbacks such as uncontrollable hydration, microbial contamination and limited solubility in water. These properties are altered by hybridization of the natural polymers with synthetic polymers. The attachment of synthetic polymers to natural polymers produces new materials which could have the desirable properties such as an improved stability, solubility and their adsorbing capacity after the synthetic vinyl modification. The technique used to obtain these new desirable materials is through graft copolymerization [9].

Graft copolymerization is a method used for changing the physiochemical properties of natural and synthetic polymers without drastically altering its properties. Graft polymers are copolymers that have a linear backbone of one of the elements of the copolymer and further consisting of random distributed branches of the other elements of the copolymer. Grafting is a convenient technique used for tailoring the material properties for specific uses [10]. Guar gum (GG) is a naturally occurring galactomannan polysaccharide which has been attractive as adsorbent because of its high swelling capacity, it can be modified by grafting to improve its property [11–13].

Grafting is done using three different methods such as redox initiation, gamma-irradiation and microwave irradiation. Vinyl modification is necessary because it improves the flocculation characteristics, solubility and sorbing capacity. The vinyl monomers usually used in grafting for metal ion adsorption are acrylamide, N-tert-butylacrylamide, methylmethacrylate, acrylonitrile and methacrylamide. Grafting with ethyl acrylate is not frequently reported, while a graft polymer was successfully produced by Pandey and Mishra [9] through free radical polymerization of xanthan gum and ethyl acrylate in the presence of potassium peroxydisulphate. It is therefore important to investigate the potential of ethyl acrylate in the grafting of GG for metal adsorption.

Recent attention on conventional methods used for grafting has been diverted to the use of microwave irradiation and gamma irradiation due to the fact that they reduce the formation of homopolymers which decrease the yield and also contaminates the copolymer product [14]. The conventional procedures of grafting may also lead to the degradation of the polysaccharide backbone.

Grafting of biopolymeric materials using microwave irradiation has lately gained more attention. Polysaccharide grafting using microwave irradiation has several advantages when compared to conventional methods of grafting. Grafting using microwave irradiation can be performed in an open vessel with a reduced solvent content, unlike the conventional thermal grafting reaction where an inert atmosphere is needed. Microwave grafting reactions are more convenient and safer to operate and the use of chemicals is also reduced, which makes it more cost-effective. Furthermore, less reaction time is needed for grafting with a high batch-to-batch consistency [14].

In the present investigation, the focus is on the removal of calcium and magnesium ions from aqueous solutions using a copolymer of ethyl acrylate and GG synthesized by graft copolymerization with a microwave-assisted method.

2. Methodology

2.1. Characterization of adsorbents

GG, ethyl acrylate and potassium peroxysulphate used in this study were obtained from Sigma Aldrich. Fourier Transform Infrared Spectroscopy was used to analyse the structural changes that occurred during adsorption and an ATR-FTIR Perkin-Elmer spectrum 100 spectrometer was used with a resolution of 4 cm^{-1} and at a spectral range of 400–500 cm^{-1}. SEM analysis was done to identify the compound morphology with the aid of a model FEI Quanta 200 ESEM Scanning Electron Microscope, integrated with an Oxford Inca 400 energy dispersive X-ray spectrometer. The % conversion of the copolymer was calculated using the following equation:

$$\% \text{ conversion} = \frac{W_1}{W_0} \times 100 \tag{1}$$

where W_1 is the weight of the copolymer and W_0 is the weight of the original GG used.

2.2. Synthesis of guar gum-graft-poly(ethylacrylate) (GG-g-PEA)

The GG was dissolved in 15 mL distilled water using a magnetic stirrer in a 600 mL beaker and subsequently 3 mL of ethyl acrylate (0.17 M) was added and the resulting solution was stirred. Potassium persulfate (0.0035 M) was added to the reaction mixture and the solution was stirred and then the reaction mixture was irradiated in a domestic microwave oven (Hisense microwave grill, 900 MW, microwave frequency 2,450 MHz) at a known microwave power (60, 80, and 100%) for a definite time (1, 2, and 3 min). After exposure, the reaction mixture was allowed to cool down to room temperature and was precipitated with an excess amount of acetone. The copolymer was then washed with acetone. The grafted copolymer samples were then placed in a Soxhlet apparatus for 3 h to dissolve the homopolymer. The guar gum-graft-poly-ethyl acrylate (GG-g-PEA) samples were then dried in an oven for 24 h at 40˚C to obtain a constant weight. The samples were then crushed using a pestle and mortar and the copolymer was weighed. The copolymer produced at optimum microwave power and time was used in the adsorption experiments (Table 1).

Table 1
Percentage conversion to copolymer following optimization of microwave power and exposure time

Microwave power (%)	Exposure time (min)	% Conversion
60 (540 MW)	1	11.76
	2	37.25
	3	45.88
80 (720 W)	1	43.53
	2	46.07
	3	95.49
100 (900 MW)	1	68.04
	2	82.74
	3	107.1

2.3. Preparation of metal stock solutions

Calcium solution preparation: A calcium stock solution with a concentration of 1,000 ppm was prepared. This was achieved by dissolving a given mass of the analytical grade salt of $Ca(NO_3)_2$ in 1 L of distilled water. The solution was stirred well to make sure that all the salt dissolved in the distilled water.

Magnesium solution preparation: A magnesium stock solution with a concentration of 1,000 ppm was prepared. This was achieved by dissolving a given mass of the analytical grade salt of $MgCl_2$ in 1 L of distilled water. The solution was stirred well to make sure that all the salt dissolved in 1 L distilled water.

2.3. Adsorption experiments

The copolymer was used for the removal of Mg(II) and Ca(II) from aqueous solutions and the adsorption parameters were optimized. The adsorption experiments were carried out in a temperature controlled incubator shaker set at a speed of 200 rpm, keeping the temperature constant at 30˚C for two and a half hour. The pH was varied from pH 2 to pH 8 with an increment in 2 pH units. The pH was adjusted using sulphuric acid or sodium hydroxide (1 M). The concentration of metal ions was fixed at 50 mg/L; the total volume of the solution was 25 mL and an adsorbent dosage of 25 mg was used. The adsorbent dosage was varied from 10 to 70 mg in increments of 20 to study the effect of adsorbent dosage on the removal of Ca(II) and Mg(II). The effect of the initial metal ion concentration was also investigated where the concentration of the metal ions in the solution ranged from 25 to 100 mg/L. The suspensions were centrifuged at a speed of 4,000 rpm for 10 min. The supernatant was then transferred into glass vials for analysis. The metal content of the supernatant was analysed using an ICP-OES (ICP Expert II, Agilent Technologies 720 ICP-OES) spectrometer. Control experiments revealed that no sorption occurred on the glassware. The adsorption capacity of the copolymer was calculated with the aid of the equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where q_e is the equilibrium adsorption concentration of the adsorbate per unit mass of the adsorbent (mg/g), C_0 is the initial concentration of the adsorbate in the solution (mg/L), m is the mass of the copolymer used (g) and V is the volume of the solution (L).

2.4. Isotherm and kinetic models

The Langmuir and Freundlich isotherms were used to determine the adsorption affinity of the copolymer for magnesium and calcium. The linear expression for the Langmuir model is given by the equation below [15,16]:

$$\frac{C_e}{q_e} = \frac{1}{q_m k} + \frac{C_e}{q_m} \tag{3}$$

where q_e is the equilibrium adsorption concentration of the adsorbate per unit mass of the adsorbent (mg/g), q_m is the maximum adsorption capacity of the copolymer (mg/g), C_e is the equilibrium concentration of adsorbate left in the solution (mg/L) and k is the Langmuir constant related to the adsorption energy.

The linear expression for the Freundlich model is given below [15,16]:

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \tag{4}$$

where q_e is the equilibrium adsorption concentration of the adsorbate per unit mass of the adsorbent (mg/g), C_e is the equilibrium concentration of adsorbate left in the solution (mg/L), K_F and $1/n$ are the Freundlich constants related to the adsorption capacity and intensity of adsorption.

3. Results and discussion

3.1. Characterization of the adsorbents

3.1.1. SEM analysis

The surface morphology of the GG and GG-g-PEA was studied using a scanning electron microscope to investigate the grafting of the PEA onto the GG. The fibrous nature of the GG particles can be seen in Fig. 1(a), suggesting that the biopolymer is amorphous by nature. The grafted copolymers particle size is significantly higher than that of the GG, which is an evidence of the physical transformation that has taken place during copolymerization [17].

3.1.2. FTIR analysis

The FTIR spectra of pure GG and GG-g-PEA are shown in Fig. 2, where a strong O–H stretching peak (3,344 cm^{-1}) and a small C–H stretching peak are visible at (2,899 cm^{-1}) [11]. On the FTIR spectrum of the GG-g-PEA (Fig. 2), an increase of the intensity at 1,730 cm^{-1} (ester –C=O group) can be seen in addition to the O–H stretching at 3,367 cm^{-1} and the C–H stretching vibrations at 1,647 cm^{-1}, confirming the grafting of the EA onto the GG [17].

The spectrum of the adsorbent loaded with Ca(II) is shown in Fig. 3 and it has some significant changes compared to the spectrum of the GG-g-PEA. In the Ca (II)-loaded copolymer both the O–H stretching peaks and the carbonyl stretching peak have shifted to a lower frequency compared to the peaks of the copolymer (2,927 cm^{-1} and 1,730 cm^{-1}) indicating a complexation between the ester and hydroxyl groups and the calcium species [18].

The spectrum of the adsorbent loaded with Mg (II) is shown in Fig. 4, indicating that there are some significant changes compared to the spectrum of the GG-g-PEA. In the Mg-loaded copolymer, both the O–H stretching peaks and the carbonyl stretching peak have shifted to a lower frequency compared to the peaks of the copolymer (3,367 cm^{-1} and 1,730 cm^{-1}) indicating a complexation between the ester and hydroxyl groups and the magnesium species [17].

3.2. Uptake of metals from synthetic solutions

3.2.1. Effect of pH on Ca(II) and Mg(II) adsorption

The pH is one of the significant parameters that determine the removal efficiency of metals in the wastewater. Thus, the effect of pH on the adsorption of Ca(II) and Mg(II) is studied. The pH was varied from 2 to 8 with increments in 2 pH units. The parameters that were kept constants during the experiments were the amount of adsorbent (25 mg), concentration of the adsorbate (50 mg/L) and contact time (2 h 30 min).

The effect of pH on the adsorption of Mg(II) and Ca (II) is shown in Fig. 5. It is clear from the figure that the amount of adsorbed metal ions increases with an increase in the pH to an optimum value of pH 8 at which no significant amount of either Mg(II) nor Ca(II) is further removed. This variation of percentage adsorption is related to the surface charge of the adsorbent and the H^+ ions present in the solution. The surface of the adsorbent is primarily surrounded with hydronium ions at low pH values, which causes a decrease in the interaction between the metal ions i.e. Mg(II) and Ca(II) and the binding sites which is attributed to greater repulsive forces and therefore lower adsorption [15–19]. The competing effect of the hydrogen ions is decreased with an increase in the pH. Thus at higher pH values, the surface on the GG-g-PEA become more negative, which in turn increases the adsorption.

3.2.2. Adsorption isotherms

The Langmuir and Freundlich isotherms were used to fit adsorption data as they can be used to study the relationship between the adsorbed amount of metal per unit weight of adsorbent used and the equilibrium ion concentration remaining in the solution.

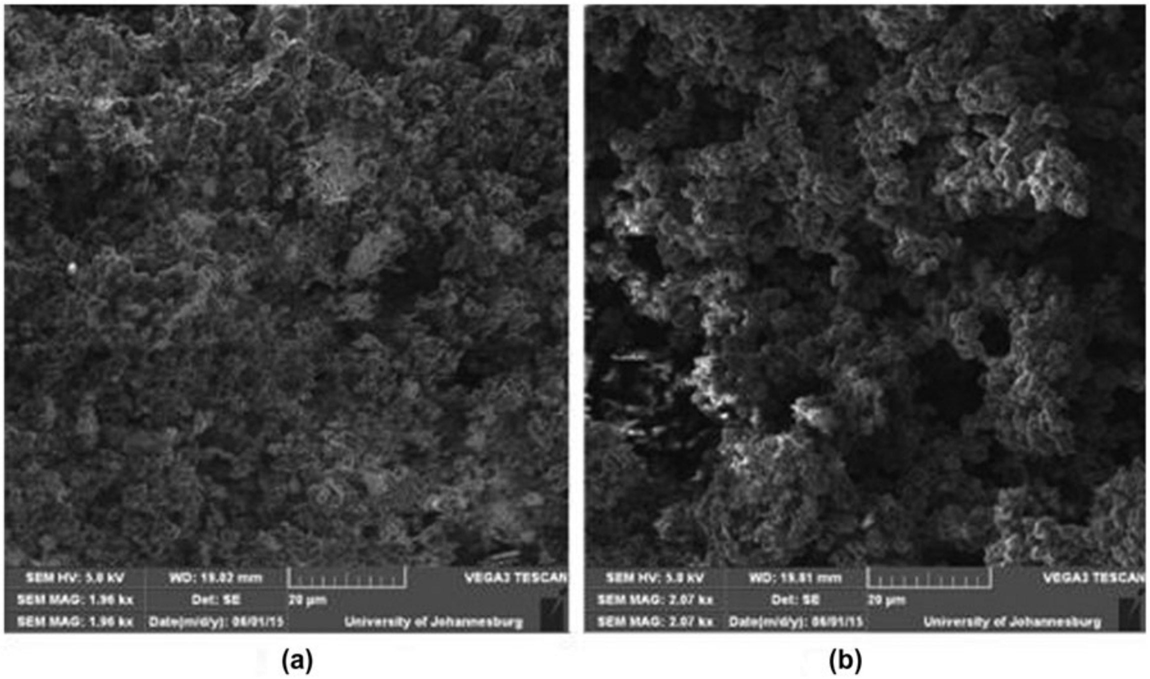

Fig. 1. SEM micrograph of GG (a) and GG-g-PEA (b).

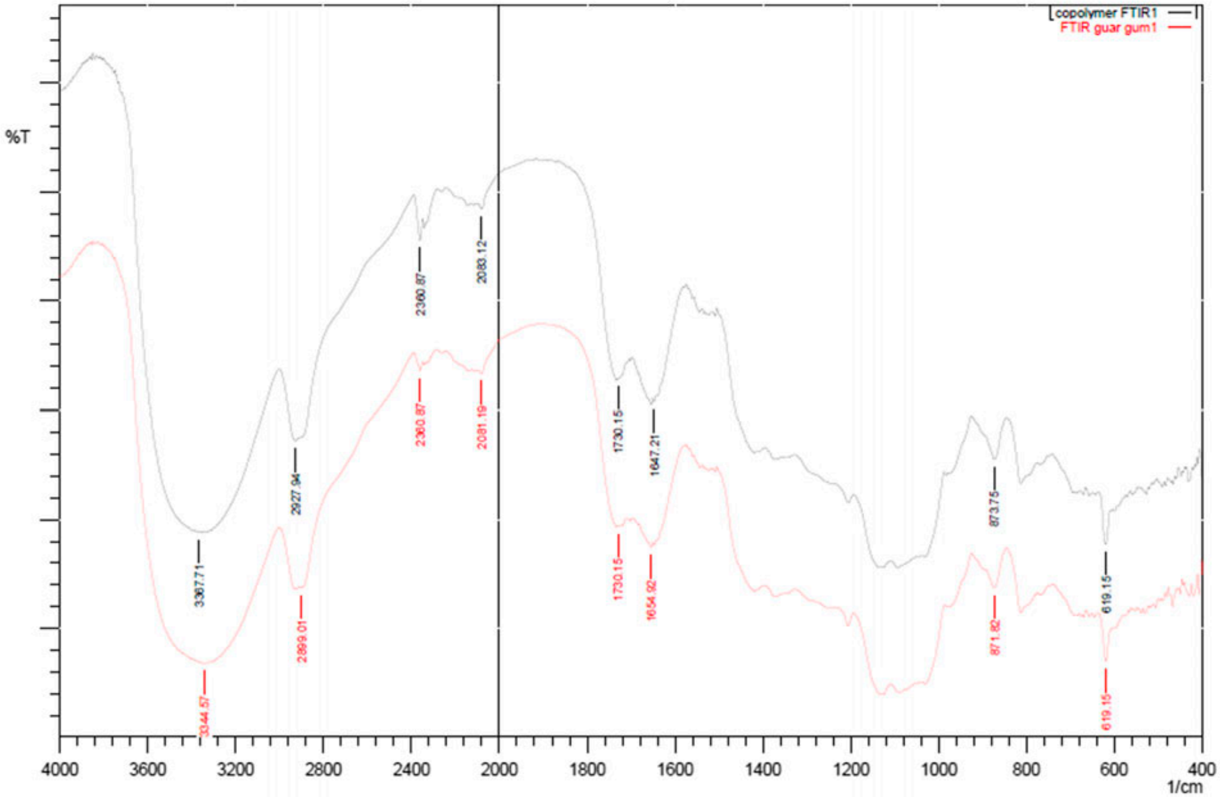

Fig. 2. FTIR spectrum of GG and GG-g-PEA.

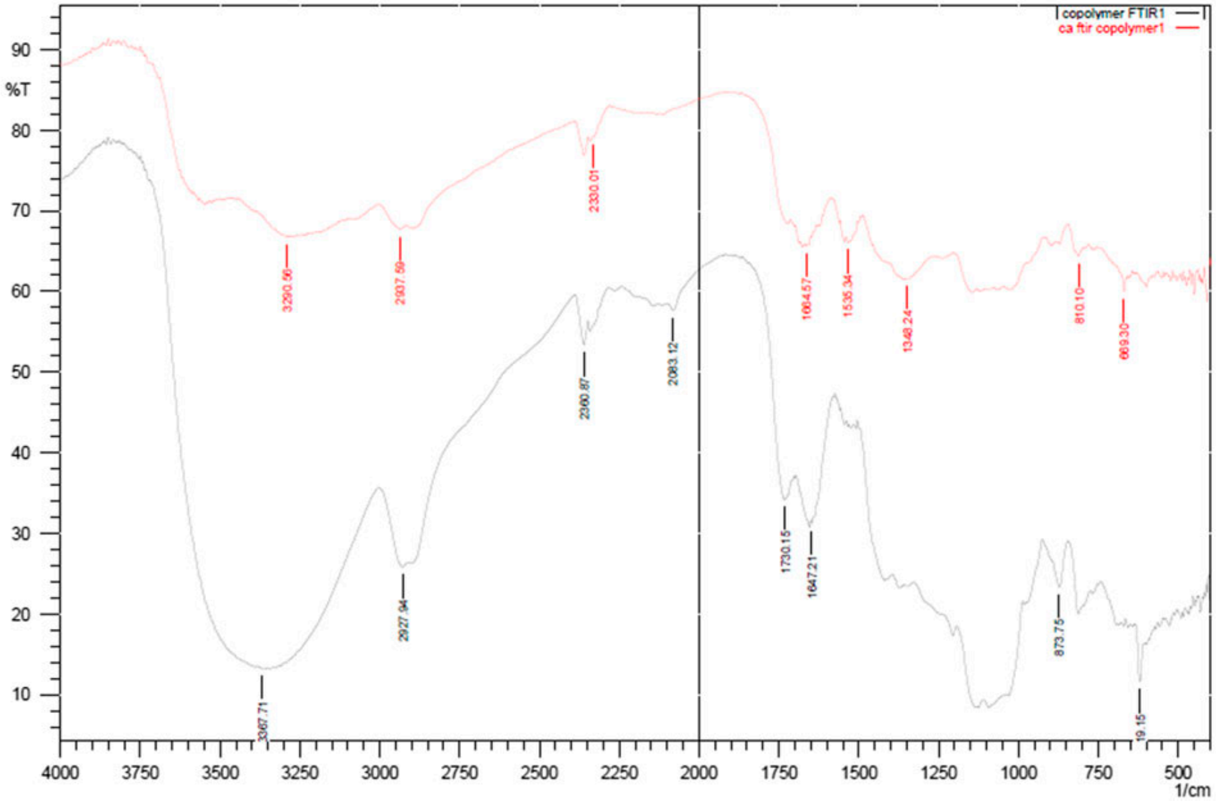

Fig. 3. FTIR spectrum of GG-g-PEA and copolymer with adsorbed Ca(II).

3.2.2.1. Langmuir isotherm model. The Langmuir isotherm is valid when monolayer adsorption is assumed due to a finite number of sites available on the surface of the adsorbent. The linear relation of the Langmuir model (Fig. 6) is used to calculate the maximum adsorption capacity (q_m mg/g) and the Langmuir constant (k) using the slope and the y-intercept. According to the results, summarized in Table 2, this model does not fit the data for the adsorption of Ca (II) and Mg(II) as shown by the values of the coefficient of determination (R^2) which are relatively low (0.7276–0.8158 for the adsorption of Ca(II) and Mg(II), respectively). It implies that the Langmuir model is not suitable for the prediction of the adsorption behaviour; therefore, homogeneous binding does not take place.

3.2.2.2. Freundlich isotherm model. In this model, it is considered that heterogeneous adsorption takes place and that the adsorption capacity depends on the concentration of the copolymer. This type of model is usually used for solutions of low concentration of adsorbate [16] with the constants such as K_f, $1/n$ and R^2 listed in Table 2. The Freundlich constants were calculated from the slope and y-intercept from a linear plot of $\log q_e$ vs. $\log C_e$ (Fig. 7). It is observed that the values of the determination coefficient are close to unity (for the adsorption of Ca(II), $R^2 = 0.914$ and for the adsorption of Mg(II), $R^2 = 0.955$), implying that the Freundlich model is suitable for the prediction of the adsorption behaviour observed in this study. The value of K_f is a rough indicator of the adsorption capacity and $1/n$ is an indicator of the adsorption intensity. As the value of K_f increases, the adsorption capacity of the adsorbent for a given adsorbate also increases. The value of the exponent, $1/n$ gives an indication of the favourability of the adsorption process. It is observed that GG-g-PEA has a greater adsorption capacity for Ca(II). If the values of $1/n$ are less than 1.0, it indicates that the adsorption process is favourable over the whole range of concentrations studied and if the value of $1/n$ is bigger than 1.0 then it indicates that the adsorption process is favourable at higher concentrations but not favourable for lower concentration [16].

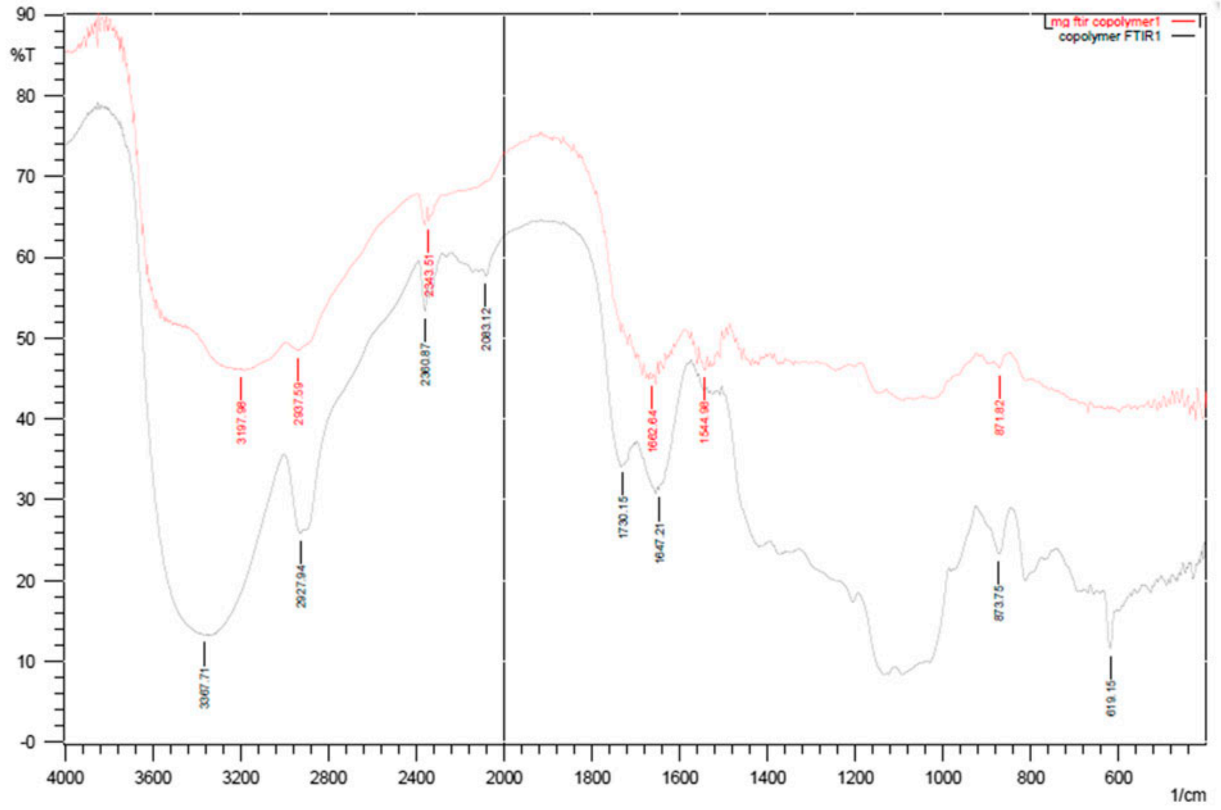

Fig. 4. FTIR spectrum of GG-g-PEA and copolymer with adsorbed Mg(II).

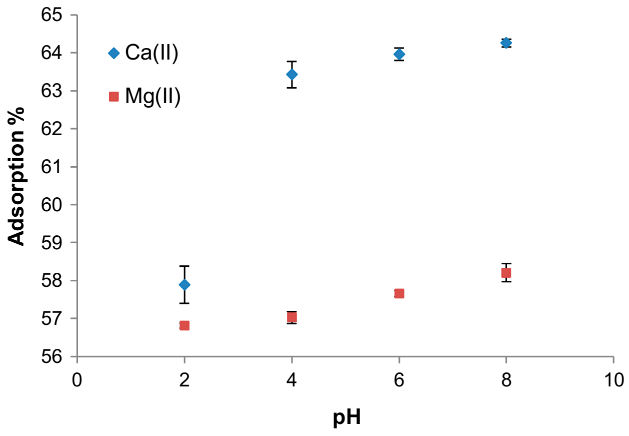

Fig. 5. Effect of pH on % adsorption of Ca(II) and Mg(II).

3.3. Adsorption kinetic studies

The purpose of the kinetic study was to determine the adsorption capacity of the copolymer for the removal of Ca(II) and Mg(II) from the synthetic solutions. The adsorption studies were carried out using an initial concentration of 50 mg/L of both Ca(II) and Mg(II) at different time periods (5–60 min) and keeping the other parameters such as pH of 7, adsorbent dosage of 25 mg and total solution volume of 25 mL, constant.

3.3.1. Pseudo-first-order

The pseudo-first-order model was applied for the kinetic study of the adsorption of Ca(II) and Mg(II) onto the GG-g-PEA. The plot of $\log(q_e - q_t)$ vs. t for the pseudo-first-order modelling of the adsorption of both Mg(II) and Ca(II) is given in Fig. 8. The adsorption data for Ca(II) does fit the pseudo-first-order model as shown by the value of R^2 (0.9860), but the adsorption data of Mg(II) does not fit the pseudo-first-order model given the lower value of R^2 (0.879). Thus, the pseudo-first-order kinetics can be used to describe the adsorption of Ca(II) but cannot be used to describe the adsorption of Mg(II).

3.3.2. Pseudo-second-order

The pseudo-second-order model was also applied for the kinetic study of the adsorption of Ca(II) and

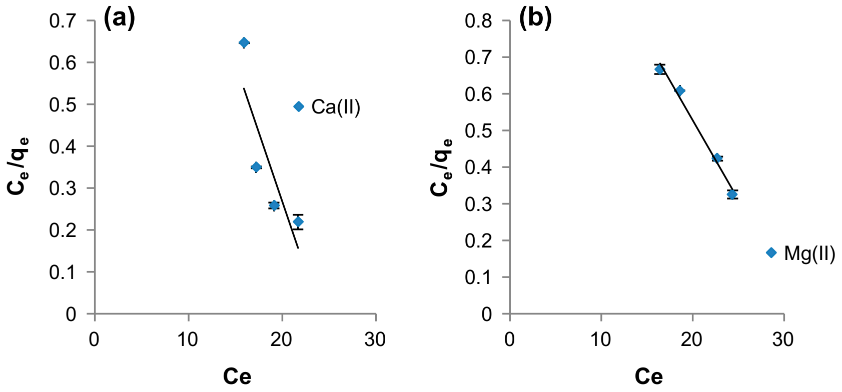

Fig. 6. Langmuir isotherm for: (a) Ca(II) adsorption and (b) Mg(II) adsorption.

Table 2
Isotherm parameters for the adsorption of Ca(II) and Mg(II)

Isotherms	Isotherm constants	Ca(II)	Mg(II)
Langmuir	q_e	na	na
	B	na	na
	R^2	0.7276	0.8158
Freundlich	$1/n$	4.288	3.260
	K_f	0.0029	0.00019
	R^2	0.914	0.9553

Note: na: Not available.

Mg(II) onto the GG-g-PEA. The plot of the pseudo-second-order models for the adsorption of the metals is shown in Fig. 9. The model fits both the adsorption data of Ca(II) and Mg(II), as indicated by the values of R^2 (Table 3). The R^2 values for the adsorption of Ca(II) and Mg(II) are one for both Ca(II) and Mg(II) which suggests that the pseudo-second-order rate model is an appropriate assumption, demonstrating that the adsorption occurs via a chemisorption process [20]. The adsorption capacity of GG-g-PEA is relatively high for both metals ($q_e = 32.87$ and $q_e = 30.45$ for Ca(II) and Mg(II), respectively) with the adsorption capacity higher for the removal of Ca(II). Although the electronegativity order established by Pauling [21] may suggest a higher adsorption affinity for Mg(II) than Ca(II) [Mg(II) > Ca(II)], the opposite trend observed in this study is likely due to the fact that the metal ions with a higher atomic weight can generate a higher momentum energy, which may promote the adsorption of the metal ion by increasing the probability of effective cohesion between the metal ion and the sorbent surface. It therefore ensues that a higher atomic weight leads to higher adsorption preference by the sorbent. This explains the preferential binding of Ca(II) on the copolymer compared to Mg(II) [22].

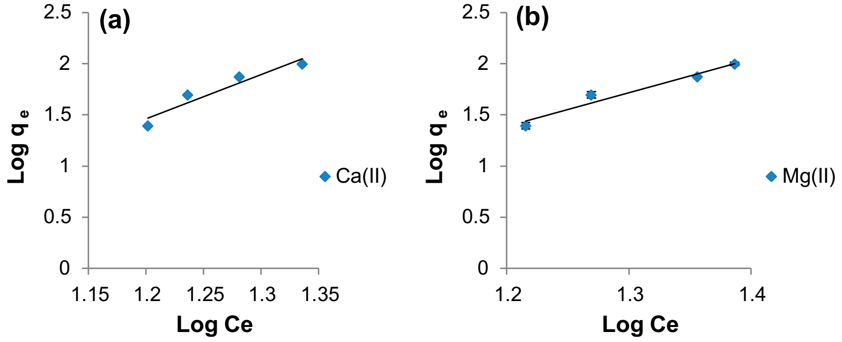

Fig. 7. Freundlich isotherm for: (a) Ca(II) adsorption and (b) Mg(II) adsorption.

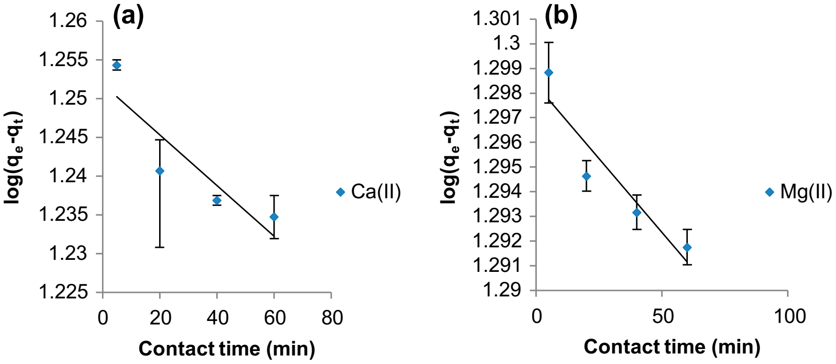

Fig. 8. Pseudo-first-order kinetic plots for: (a) Ca(II) adsorption and (b) Mg(II) adsorption.

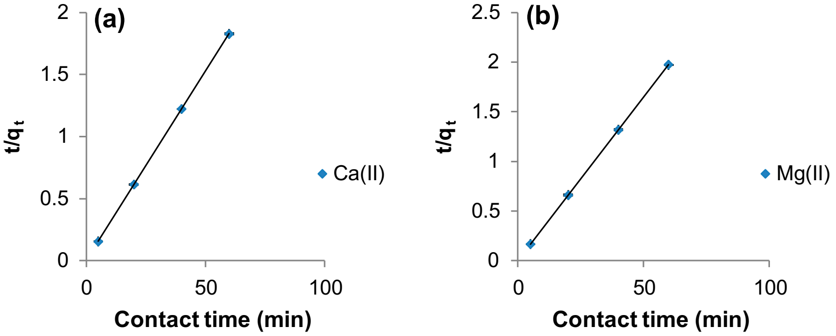

Fig. 9. Pseudo-second-order kinetic plots for: (a) Ca(II) adsorption and (b) Mg(II) adsorption.

Table 3
Kinetic parameters for the adsorption of Ca(II) and Mg(II)

Kinetic model	Kinetic parameters	Ca(II)	Mg(II)
Pseudo-first-order	K_1	0.0500	0.0470
	q_e	17.53	19.88
	R^2	0.9860	0.8790
Pseudo-second-order	K_2	0.2680	0.3835
	q_e	32.87	30.45
	R^2	1	1

4. Conclusion

Ethyl acrylate was successfully grafted on the backbone of GG using potassium peroxysulfate as initiator. The optimum conditions for the synthesis of the copolymer were at a microwave power of 900 W and an exposure time of 3 min. The copolymer with the highest yield and conversion was used in adsorption experiments.

The optimum process conditions were determined for efficient metal removal by means of adsorption using the copolymer. The effect of pH was investigated and better adsorption was achieved at the optimum pH of 8 and at the adsorbent dosage of 25 mg. The Langmuir isotherm model showed no fit for the adsorption of Ca(II) and Mg(II), while the pseudo-first-order model showed a perfect fit only for the adsorption of Ca(II) on the copolymer and was therefore not suitable for the comparative prediction of the adsorption of both metals. The Freundlich isotherm model was more suitable to determine the adsorption behaviour of the copolymer and implies heterogeneous binding of the metals onto the copolymer. The data also fitted the pseudo-second-order model for the prediction of the binding capacity; it was therefore found that the copolymer had a higher adsorption capacity for calcium compared to magnesium. This explains the preferential binding of Ca(II) onto the copolymer. FTIR analysis suggests that the ester and hydroxyl binding groups in the copolymer are the primary groups involved in the removal of the metals. Therefore, the copolymerization has resulted in the addition of binding groups on the existing natural polymer.

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