

Reduction of salinity and hardness of water using copolymerized biopolymers

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Abstract

In this study two adsorbents were systematically synthesized through grafting using different biomaterials to target specific pollutants. Ethyl acrylate was grafted to guar gum using potassium persulfate as initiator to form the guar gum-graft-poly(ethylacrylate) (GG-g-PEA) for the reduction of the hardness of solutions; while the polyacrylamide (PAM) was grafted on the backbone of chitosan to form chitosan-g-polyacrylamide (C-g-PAM) for the reduction of salinity of solutions. The adsorbents were characterized to confirm their properties using scanning electron microscope (SEM) and they were tested for the removal of calcium and magnesium, and sulfate respectively from solutions. The results show that the grafting process was successful for both GG-g-PEA and C-g-PAM formation. Both adsorbents showed good removal potential of the respective pollutant, and their adsorption behaviour was predicted by kinetic and isotherm models. It was observed that GG-g-PEA did not exhibit exactly the same behaviour for the removal of calcium and magnesium; as the adsorption capacity predicted by the pseudo second order kinetic model for the adsorption of Ca ($q_e = 32.87$ mg/g) was relatively high compared to Mg ($q_e = 30.45$ mg/g). The removal of sulfate by C-g-PAM fitted the Langmuir model ($q_m = 277.78$ mg/g) and the pseudo-second order kinetic model ($q_e = 128.21$ mg/g).

The study has shown that improvement of the properties of biopolymers through grafting could allow their application in the reduction of hardness and salinity of water.

Key words: Grafting, copolymer, adsorption, water hardness and salinity

Introduction

Effluents from acid mine drainage or activities such as coal preparation as well as other anthropogenic activities often contain high concentration of sulphate, calcium, sodium, magnesium and chlorides. Mines, smelters, kraft pulp, paper mills, textile mills and tanneries are some of the major sources of sulphates discharged into environmental water; metallurgical roasting processes and combustion of fossil fuels produce atmospheric sulphur dioxide which is converted to dilute sulphuric acid and falls as acid rain contributing to the sulphate content of surface water. Calcium and magnesium are naturally abundant in soils or rocks and become available in water through the weathering/dissolution of exposed ore, waste rock and tailings (Banks et al. 1997; Schmiermund et al. 1997; Mendez-Ortiz et al. 2007). It has been found that these dissolved ions in combination have a negative effect on the aquatic life and balance of its ecosystem. Sulphate may cause health problem to human only if it occurs at high concentrations in drinking water; vulnerable people such as children, transients and elderly are considered as the subpopulation more sensitive to the cathartic effects of exposure to high concentrations of sulphate, because of the potential high risk of dehydration from diarrhoea that may be caused by high levels of sulphate in drinking water (US EPA 1999a, b). Magnesium is reported to have a more toxic effect on the aquatic life than calcium (van Dam et al. 2009). However, these contaminants have been neglected because of the lower effect on human being. Common practices for the removal of sulphate and calcium, mainly consist of the use of coagulation/flocculation processes or reverse osmosis which are either ineffective, costly or result in toxic byproducts. Adsorption is a better alternative to remove such pollutants from water, giving the opportunity to recover and control the pollutant while regenerating the adsorbent. Biopolymers are suitable adsorbent for the fact that they

are widely available and are biodegradable. Among these, agricultural wastes, organic polymeric resins, polysaccharide such as chitin and starch, and their derivatives (cyclodextrin and chitosan) (Robinson et al. 2002; Synowiecki and Al-Khateeb 2003; Bailey et al. 1999; Yuryev et al. 2002; Babel and Kurniawan 2003; Varma et al. 2004; Crini and Morcellet 2002). Intrinsic properties of biopolymers such as high reactivity due to the presence of chemical reactive groups, physico-chemical characteristics, chemical stability, renewability and biodegradability make them very attractive adsorbents (Ciesielski et al. 2003; Polaczek et al. 2000; Fosso-Kankeu et al. 2011, 2015, 2016). Cross-linking agents can be used to improve the performance of biopolymers as adsorbents through enhancement of their mechanical properties and their stability in acid solutions (Chiou et al. 2004); example of cross-linking reagents include ethylene glycon diglycidyl ether, epichlorohydrin, formaldehyde, glutaraldehyde, glyoxal and isocyanates (Crini and Badot 2008). In this study two adsorbents were systematically synthesized through grafting using different biomaterials to target specific pollutants, namely calcium and magnesium (hardness) as well as sulphate (salinity).

Methods

Reagents

Guar gum (GG), de-acetylated chitosan (high molecular weight) and sodium sulfate were purchased from Sigma-Aldrich (SA). Ethyl acrylate, acrylamide and potassium peroxydisulfate were purchased from Merck Chemical Co. Ltd., and calcium nitrate, acetone, magnesium chloride and ammonium ceric nitrate were purchased from ACE Pty. Ltd.

Synthesis of copolymers

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

Guar gum was dissolved in 15 mL of distilled water using a magnetic stirrer. The solution was stirred for 10 minutes in a 600 mL beaker. To this 3 mL of ethyl acrylate (0.17 M) was added to the GG solution and was stirred for 10 minutes. Potassium persulfate (0.0035 M) was added to the reaction mixture and solution was stirred for another 5 minutes. The reaction mixture was irradiated in a domestic microwave (Hisense microwave grill, 900 MW, microwave frequency 2450MHz) at a known microwave power (60%, 80%, and 100%) for a definite time (1 min, 2 min and 3 min) period. 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 hours to dissolve the homopolymer. The GG-g-PEA samples were then dried in an oven for 24 hours at 40°C to a constant weight. The samples were then crushed using a pestle and mortar and the polymer was weighed. The copolymer at optimum microwave power and time was used in adsorption experiments. The microwave power was varied from 60% to 100% in increments of 20%. The exposure time was varied from 1 min to 3 min in increments of 1 min.

Synthesis of chitosan-g-polyacrylamide (C-g-PAM)

The grafting of the PAM onto the chitosan backbone was done using the ceric ammonium initiation method (Yuan et al. 2010). 100 mL of a 1% acetic acid solution was prepared in a 250 mL Erlenmeyer flask, into which, 0.4 g of chitosan was added and shaken at 100 rpm for 30 minutes. The same weight of ceric ammonium nitrate was added with a pre-determined amount of PAM and the mixture was allowed to react for 3 hours. After the 3 hours, the mixture was precipitated in acetone and the white, jelly like copolymer was washed with more acetone two more times, to remove any homopolymer. All the copolymer was added into a single beaker and this was dried in a vacuum oven at 50°C for 24 hours.

Characterization of synthesized copolymers

SEM analysis was done to identify the compound morphology. The model used was a FEI Quanta 200 ESEM Scanning Electron Microscope, integrated with an Oxford Inca 400 energy dispersive x-ray spectrometer.

Adsorption experiments

Removal of calcium and magnesium

The synthesized guar gum-graft-poly(ethylacrylate) (GG-g-PEA) copolymer was evaluated for the removal of Mg^{2+} and Ca^{2+} from aqueous solutions and conditions of adsorption parameters were optimized. Different adsorption parameters were changed while keeping the others constant. The adsorption experiments were carried out in a temperature controlled incubator shaker set at a speed of 200 rpm, keeping temperature constant at 30 °C for 2 h and 30 min. The adsorption of Mg^{2+} and Ca^{2+} was investigated at various time intervals (5, 20, 40 and 60 mins) while keeping constant the other parameters: the concentration was fixed at 50 mg/L, total volume of solution was 25 mL and an adsorbent dosage of 25 mg was used. The effect of initial metal ion concentration was also investigated. The concentration of the metal ions in solution ranged from 25-100 mg/L. The suspensions were centrifuged at a speed of 4000 rpm for 10 min. The supernatant was then transferred into glass vials for analysis. Control experiments revealed that no sorption occurred on glassware.

Removal of sulphate

The adsorption experiment was carried out in a batch system. Sodium sulphate was added to 100 mL of de-ionized water and shaken lightly until the sulphates were dissolved. Chitosan-g-polyacrylamide (C-g-PAM) copolymer was then added and allowed to adsorb the sulphates before a small sample of the solution was removed and centrifuged. 1 mL of the centrifuged liquid was mixed with 10 mL of a 1% nitric acid solution and sent for ICP-OES analysis to find the concentration of sulphur still present in the water. For the tests, four different parameters were tested, one at a time with the others kept constant.

The parameters tested included the copolymer concentration (0.1 g/100 mL, 0.2 g/100 mL, 0.3 g/100 mL, 0.4 g/100 mL), sulphates concentration (500 mg/L, 1000 mg/L, 2000 mg/L, 3000 mg/L) and adsorption time (15 min, 30 min, 60 min, 90 min). One parameter was varied while the others were kept constants.

Isotherms and kinetics models

The adsorption affinity of the copolymer adsorbent for the removal of the adsorbate was evaluated using the Langmuir and Freundlich isotherms. The Langmuir isotherm model assumes monolayer adsorption in single solute systems with its linear form given by (Fosso-Kankeu et al. 2011; Mittal et al. 2013; Fosso-Kankeu et al. 2015):

$$\frac{C_e}{q_e} = \frac{1}{k \cdot q_m} + \frac{C_e}{q_m} \quad (1)$$

The Freundlich model is not restricted to monolayer adsorption and it can be applied in heterogeneous systems where its linear form can be expressed by:

$$\log q_e = \log k_f + \frac{1}{n} \cdot \log C_e \quad (2)$$

In the isotherm models C_e is the concentration of adsorbate at equilibrium in (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium in (mg/g), q_m is the adsorption capacity in (mg/g), k is a Langmuir constant related to energy released during adsorption in (L/mg), k_f is the Freundlich adsorption capacity parameter in (mg/g) and n is the intensity of adsorption.

To aid in identifying the adsorption rate the pseudo first- and second order models are used (Patil and Nayak 2011; Fosso-Kankeu et al. 2011; Mittal et al. 2013; Fosso-Kankeu et al. 2015). The pseudo first- and second-order kinetic models are given by:

$$\log(q_e - q_t) = \log q_e - k_1 \cdot \frac{t}{2.303} \quad (3)$$

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

where: q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium in (mg/g), q_t is the amount of adsorbate adsorbed at time t in (mg/g), k_1 is the first order rate constant in (min^{-1}), k_2 is the second order rate constant in ($\text{g}/\text{mg}\cdot\text{min}^{-1}$) and t is the time in (min).

Results and discussion

Physicochemical characteristics of copolymers

Morphology of copolymers

Guar gum (GG) and GG-g-PEA

The surface morphology of guar gum (GG) and GG-g-PEA was studied by using a scanning electron microscope to investigate the grafting of PEA onto GG. It can be seen from Figure 1a that the fibrous nature of the guar gum particles and it suggests that the biopolymer is amorphous by nature. The grafted copolymers particle size is significantly higher than GG, which is evidence that Ethyl acrylate was grafted successfully onto GG and the particles also differ in shape.

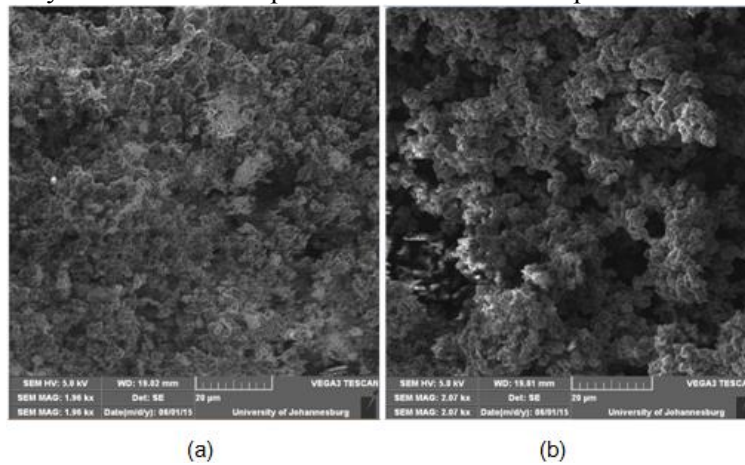


Figure 1 SEM micrograph of guar gum (a) and GG-g-PEA (b)

Chitosan and C-g-PAM

The SEM images in Figures 2a and b show the pure chitosan and C-g-PAM at 800x magnification, respectively. The main difference that indicates successful grafting is the tiny dots and particles on the surface of the copolymer which is where the PAM was grafted to the chitosan backbone. These images compare very well with other SEM images from literature (Shanmugapriya et al. 2011; Patil and Nayak 2011).

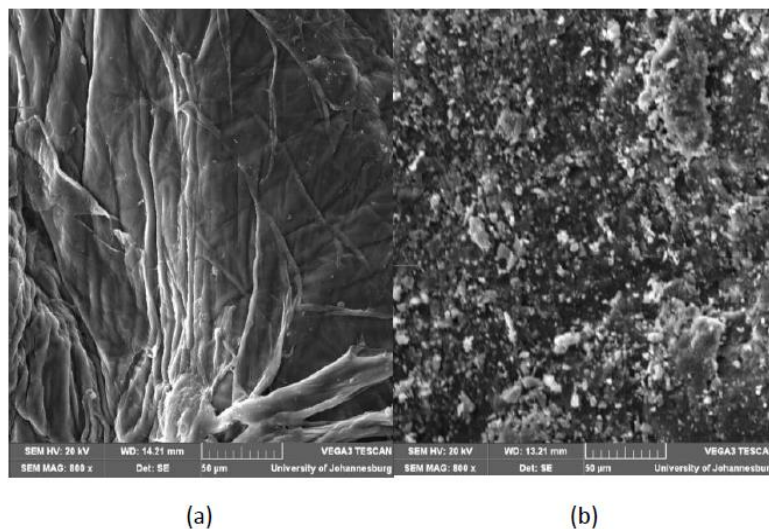


Figure 2 SEM micrograph of pure chitosan (a) and C-g-PAM (b)

Adsorption isotherm study

Langmuir model

The Langmuir graph was made by plotting C_e/q_e vs. C_e where the slope = $1/q_m$ and the intercept = $1/K_L q_m$.

Removal of Ca(II) and Mg(II)

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 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, summarised in Table 1, 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 and 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.

Removal of SO_4^{2-}

From the Langmuir plot of the adsorption of sulphate the adsorption parameters were obtained; the value of q_m was 277.78 (mg/g) and K_L was 0.00349. The R^2 value was relatively close to unity, implying that the adsorption occurs mainly on the monolayer surface.

Freundlich model

Removal of Ca(II) and Mg(II)

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 (Mittal et al. 2013). The constants such as K_f , $1/n$ and R^2 are listed in Table 1. The Freundlich constants were calculated from the slope and y-intercept from a linear plot of $\log q_e$ vs. $\log C_e$. It is observed that the values of the coefficient of determination 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. 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 adsorbent for a given adsorbate also increases. The value of the exponent, $1/n$ gives us an indication of the favourability of adsorption. 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, this indicates that the adsorption process is favourable over the whole range of concentrations studied and if the values of $1/n$ are bigger than 1.0 then this indicates that the adsorption process is favourable at higher concentrations but not favourable for lower concentration (Fosso-Kankeu et al. 2015, 2016).

Removal of SO_4^{2-}

The Freundlich isotherm graph, plotted as $\log q_e$ vs. $\log C_e$, had a much worse fit with the very low R^2 value indicating the poor fit. Thus the values that could be calculated from this method will be disregarded.

Table 1 Calculated parameters for the adsorption isotherm models

Isotherms	Parameters	Ca(II)	Mg(II)	SO4
Langmuir	q_e			277.8
	b	No fit	No fit	0.0035
	R^2			0.9
Freundlich	$1/n$	4.288	3.26	
	K_f	0.0029	0.00019	No fit
	R^2	0.914	0.9553	

Adsorption kinetics study

Pseudo-First order

Removal of Ca(II) and Mg(II)

The pseudo first order model was applied for the kinetic study of the adsorption of Ca(II) and Mg(II) onto GG-g-PEA. The plot of $\log(q_e - q_t)$ vs t allowed to determine the kinetics parameters (Table 2) of the pseudo first order for both Mg(II) and Ca(II) adsorption. The adsorption data for Ca(II) does fit with the pseudo first order model and is indicated by the value of R^2 (0.9860), the adsorption data of Mg(II) does not fit the pseudo first order model and is indicated by the 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).

Removal of SO_4^{2-}

The value (6.803) of the coefficient of determination from the plot of $\log(q_e - q_t)$ vs t for the pseudo first order, was relatively low and therefore not suitable to predict the adsorption behaviour for the removal of sulphate.

Pseudo-Second order

The pseudo second order model was also applied for the kinetic study of the adsorption of Ca(II) and Mg(II) onto GG-g-PEA. The model fits well with the adsorption data of Ca(II) and Mg(II) and is indicated by the values of R^2 (Table 3). The kinetic parameters of this model are tabulated in Table 3. The R^2 values for the adsorption of Ca(II) and Mg(II) are 1 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 (Mittal et al. 2013; Fosso-Kankeu et al., 2014). The adsorption capacity of GG-g-PEA is relatively high for both metals and it is $q_e = 32.87$ and $q_e = 30.45$ for Ca(II) and Mg(II) respectively. Metal ions with higher atomic weight can generate 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 (Fosso-Kankeu et al. 2011; Fosso-Kankeu and Waanders 2014).

Removal of SO_4^{2-}

The values from the time tests were used to plot the pseudo-second order graph, by plotting t/q_t vs. t . The graph has a R^2 value closer to unity which indicates the suitability of the model to predict the adsorption behaviour of the copolymer and thus the K_2 value of -0.00092 (g/mg min) and q_e value of 128.21 (mg/g) were calculated.

Table 2 *Calculated parameters of the adsorption kinetics*

Kinetic Model	Parameters	Ca(II)	Mg(II)	SO_4^{2-}
Pseudo first order	K_1	0.05	0.047	
	q_e	17.53	19.88	No fit
	R 2	0.986	0.879	
Pseudo second order	K_2	0.268	0.3835	-0.009
	q_e	32.87	30.45	128.21
	R 2	1	1	0.98

Conclusions

The GG-g-PEA and C-g-PAM were successfully synthesized in this study as shown by the SEM results. The application of the synthesized adsorbents for the reduction of the hardness and salinity of water, showed that their capacity could be easily predicted using the pseudo-second order kinetic model. It was therefore deduced that the GG-g-PEA had higher affinity for Ca(II) than Mg(II) while

C-g-PAM exhibited a relatively high adsorption capacity for SO_4^{2-} . The developed adsorbents can therefore be considered to remediate surface water pollution.

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