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Diffusion coefficients of *Grewia* spp. biopolymers in water

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Diffusion coefficients of biopolymers extracted from *Grewia* spp. barks in water were studied under various physicochemical conditions. Extractions were carried out on barks of 3 cm in length at different pH (5-9), temperature (25-50°C) and ionic strength (10^{-3}-10^{-2}M), using $CaCl_2$ and NaCl as background electrolytes. Factorial experimental plan design was used and diffusion coefficients were determined using second law of Fick equation, with linear and logarithmic approximation. Obtained results show that diffusion coefficients of *Grewia* spp. biopolymers are in the range of 9.78458E-06±1.6462E-08 cm^2/min, and are not significantly influenced by the pH, the ionic strength and the temperature. Maximum diffusion was obtained with $CaCl_2$ at high ionic strength. Both linear and logarithmic approximations were found to be suitable for diffusion coefficients and were dependent on the background electrolyte used.

Key words: Biopolymers, diffusion coefficient, *Grewia*.

INTRODUCTION

Different plants extracts have been used or tested as biopolymers for coagulation; *Moringa oleifera, Strychnos potatorum, Jatropha curcas sabdariffa, Curcuma angustifolia* (Pritchard et al., 2010**)**, *Phaseolus vulgaris* and *Grewia. Grewia* spp. is a flowering plant from the family of *tiliacées* that grows in the shade of nearby rocks and reeds, native to warm tropical regions of Africa, Asia and Australia (Emeje et al., 2008). It is used as a thickener, stabilizer in food process and in some cases it may act as a coagulant /flocculant (Ndi et al., 2013).

In water clarification processes, studies on efficient bio-

polymers for coagulation purposes are widespread due to the environmental impact of those coagulants (Chun-Yang, 2010). Biopolymers can be extracted from different parts of the plant including barks, leaves and roots but, when powders are used, fine particles are released, increasing the suspended material and the turbidity of the suspension, and may act as a support for bacterial growth (Kebreab et al., 2005). Therefore, purification of extracted biopolymers is often required. Unfortunately, these methods include a combination of lyophilisation, chromatography and dialysis, which are complex

Table 1. Factors range.

Factor	Values
pH	5- 9
Salt concentration (M)	0.001- 0.01
Temperature (°C)	25-50

Table 2. Complete factorial design matrix.

Run	pH	Ionic strength	Temperature
1	-1	-1	-1
2	1	-1	-1
3	-1	1	-1
4	1	1	-1
5	-1	-1	1
6	1	-1	1
7	-1	1	1
8	1	1	1

and expensive for implementation in rural areas of developing countries (Kebreab et al., 2005). Thus, looking for an optimum in the extraction of biopolymers with fewer amounts of fines released is of great importance for coagulation purposes. Using barks instead of powders as coagulant/flocculant may increase the settling velocity of flocs, reducing considerably the amount of fines released in the suspension, and further accelerate the clarification step.

During flocculation, the required amount of coagulant or flocculant for good clarification purpose is directly linked to the initial water quality. Thus, knowledge of biopolymer concentration in the suspension is of great importance for coagulation process. When barks are soaked in water, biopolymers are released from the bark to the suspension. This extraction process can be improved by agitation of the suspension, but in a house hold scale it is generally done without any agitation, as it is easily carried out, leading to natural diffusion of biopolymers from the bark to the suspension. As natural diffusion is a mass transfer process, induced by gradient concentration, there's need to evaluate the amount of biopolymers released within the contact period time of the bark in the liquid. This can be done knowing diffusion coefficients.

Diffusion coefficient is a key parameter of mass transfer process and describes how fast the amount of released biopolymers in the suspension is. Diffusion coefficient although generally assumed as constant depends on many parameters like ionic strength, pH, temperature and bark concentration (Giovana et al., 2011).

Diffusion coefficients are well determined by direct methods including technique of fluorescence recovery after photo bleaching (FRAP) which has been refined through the use of a laser scanning confocal microscope (LSCM) or by indirect methods like spectroscopy, chromatography and mass balance in the system (Matthew et al., 2000). When indirect methods are used, plotting the amount of biopolymer released as a function of the concentration as described by the second law of Fick equation gives the diffusion coefficient. Approximation of the Fick equation commonly used is linear and logarithmic ones which were found to be suitable for biopolymers diffusion in water system. The linear model corresponds to the earlier part of the slope of the diffusion process while logarithmic is mainly used when the required time for extraction is high (Poirot, 2007).

The aim of this study is therefore to evaluate diffusion coefficients of *Grewia* spp. biopolymers and to find suitable models describing it under different physicochemical conditions.

MATERIALS AND METHODS

Biological material

Grewia spp. was collected from Mokolo, a town located in the far Northern region of Cameroon. *Grewia* spp. barks of 3 cm length were used as biological material for biopolymer extraction. They were dried at 45°C using a forced convection dryer (CKA2000AUF) for 24 h, allowed to cool in a desiccator, and kept in sealed plastic bags prior to their use. The thickness (L) of *Grewia* spp. bark used was obtained by measuring the average size of 100 barks selected randomly.

Characterization

FTIR analyses were carried out before and after biopolymer extraction.

Polymer extraction

Polymer extraction was carried out in batch mode without any mechanical stirring of the solution, with distilled water of pH (5-9) adjusted using 1 M hydrochloric acid (Sherman Chemicals limited) or 1 M NaOH solutions (Prolabo), and ionic strength (0-0.01 M) adjusted using NaCl (Jeulin) and $CaCl_2$ (Jeulin) salts. Conductivities were monitored using conductimeter (HI 8733, HANNA Instrument) and biopolymer mass was determined after each extraction by drying in an oven (Memmert) at 105°C and weighing the resulting extract on a mass balance of 10^{-3} precision (Gibertini).

Extraction kinetics were done with a ratio of barks mass (5, 10 and 20 g) over extraction solvent volume of 250 mL.

Experimental design

Complete factorial design was used. Selected factors are presented in Table 1. The experimental matrix is described in Table 2, and the diffusion coefficient was defined as the response.

Diffusion coefficients determination

Diffusion coefficients were derived from the slopes of the following equations (Aghfir et al., 2008; Claudia et al., 2009). Taking into
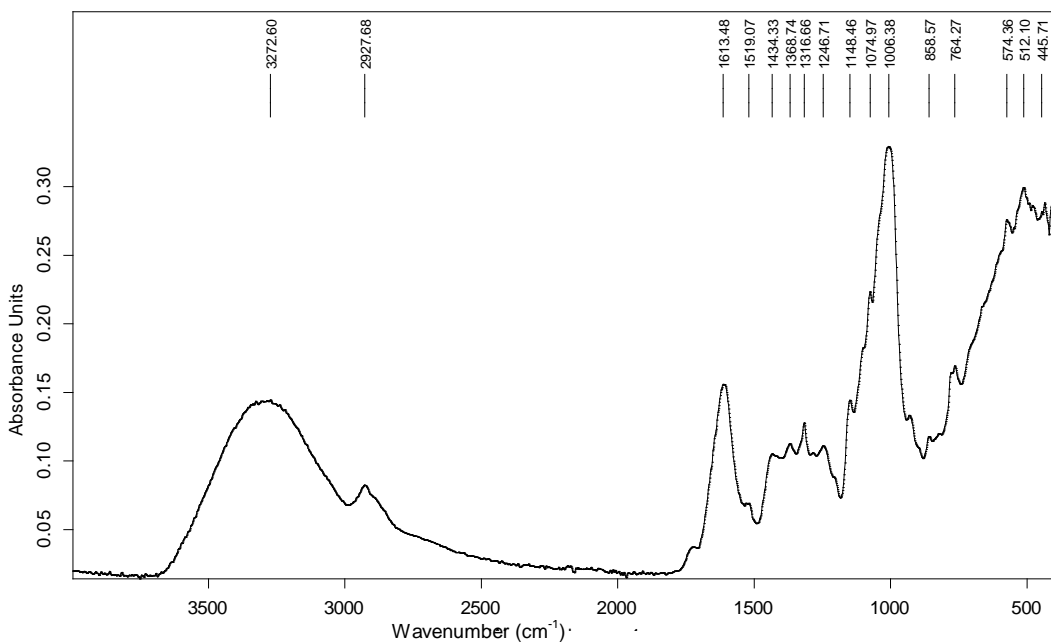
Figure 1. The FT-IR spectroscopic spectrum of the powders of *Grewia* unextracted.

consideration the hypothesis that:

1. The particles have the shape of a plate;
2. Uniform initial distribution of moisture;
3. Simplification of the movement of moisture by diffusion;
4. Negligible contracting;
5. Constant coefficient of diffusion.

The diffusion coefficient can be calculated by using the following equations for the two models:

$\frac{M_t}{M_\infty} = \frac{4}{L}\left(\frac{D_m \cdot t}{\pi}\right)^{\frac{1}{2}}$ Equation1 (for the linear approximation),

$Ln\left(1 - \frac{M_t}{M_\infty}\right) = Ln\left(\frac{8}{\pi^2}\right) - \left(\frac{\pi^2 D_m \cdot t}{4L^2}\right)$ Equation 2   (for the logarithmic approximation).

Where M_t is the mass of polymers at the moment t, M_∞ is the mass of polymers at infinite time, L is the thickness of the barks, t the time and D_m the multidirectional diffusion coefficient. The obtained quadratic equation was expressed as:

Diffusion coefficient = C_{ST} + C_A*A + C_B*B + C_C*C+ C_{AB} *A*B + C_{AC}*A*C - C_{BC} *B*C

Where, C_X denotes the coefficient factor related to the factor X studied.

RESULTS AND DISCUSSION

Characterization of *Grewia* spp.

The FT-IR spectroscopic spectra of the powders of *Grewia* unextracted and extracted are presented in the

Figures 1 and 2, respectively. The main difference between these two spectra is at the level of the intensities of the peaks.

The spectra exhibit the typical bands and peak characteristic of polysaccharides. The broad band occurring at 3272.60 cm^{-1}, results from the presence of hydroxyl (-OH) group. The peak obtained at 2927.68 cm^{-1} results from stretching modes of the C-H bonds of methyl group (-CH₃). Natural gum usually contains fractions of sugar acid units which would usually impart a weakly anionic character to the gum macromolecule (Wang et al., 2003).

Absorption bands around 1618 and 1430 cm^{-1} are typical of carboxylate group of the galacturonic acid residues (Figueiro et al., 2004). The peak obtained at 1519.07 cm^{-1} is typical of carboxylic group. The peak obtained at 1074.97cm^{-1} result from the presence C-O-C group. The peaks obtained at 1720.23 and 1607.16 cm^{-1} results from the presence of C=O group. The wave numbers between 800 and 1200 cm^{-1} represents the finger print region for carbohydrates (Fillipove, 1992).

Physicochemical effects on released G*rewia* spp. biopolymers

Figure 3 presents the effect of bark mass/water solution ratio (5/250, 10/250 and 20/250) on biopolymer extraction over time on the ratio of biopolymer mass (EP) recovered over the initial mass of the bark introduced (BM). As shown, less than 4% of the bark mass is released in the
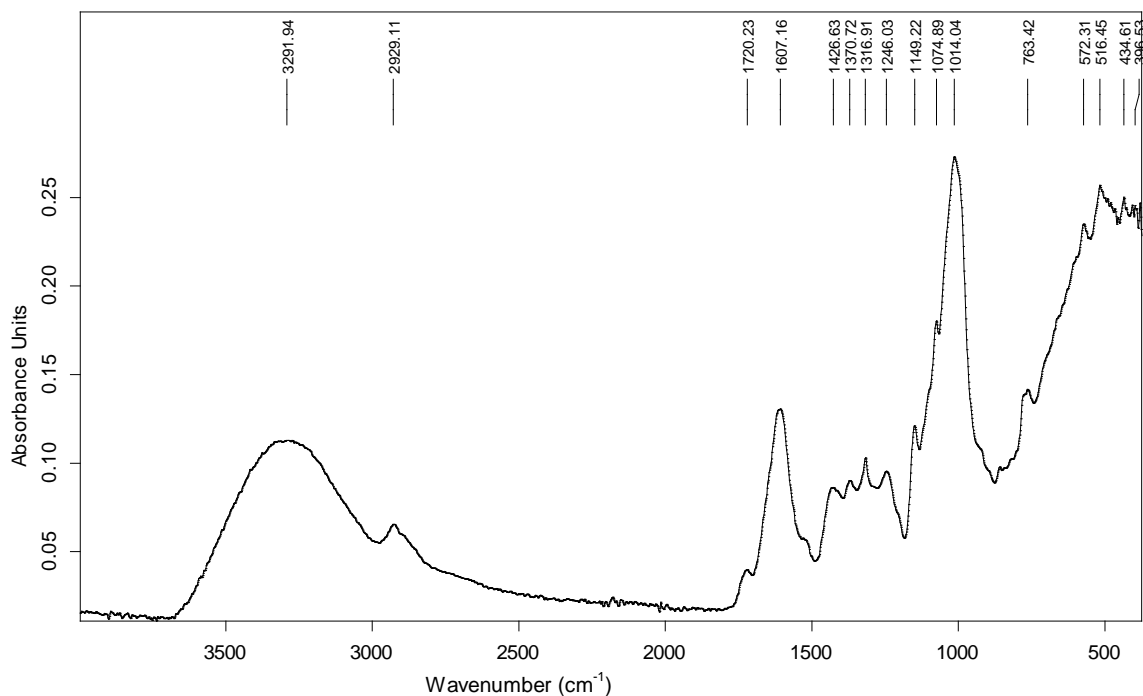
Figure 2. The FT-IR spectroscopic spectrum of the powders of *Grewia* extracted.
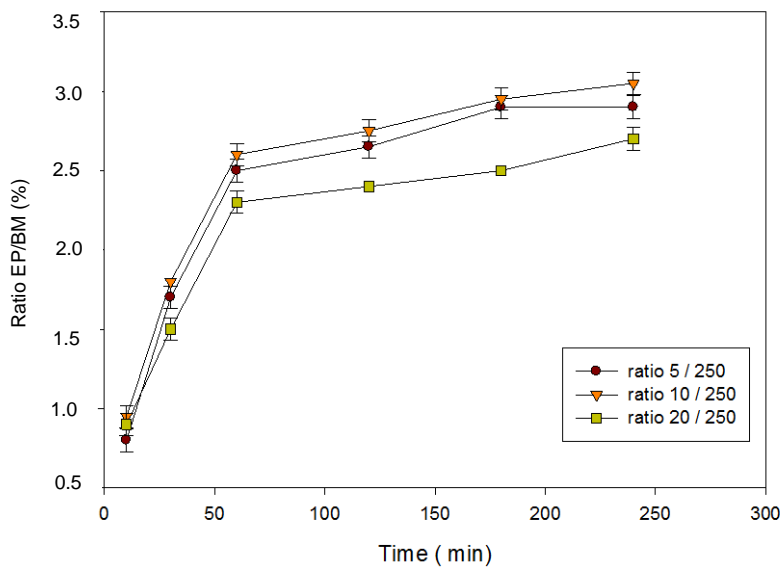

Figure 3. Kinetics of biopolymer extraction for different bark mass/water solution ratio.

suspension during batch operations whatever the ratio. From 0 to 60 min, rapid transfer of biopolymer from the bark to the suspension is observed. Further, the biopolymer is still recovered, but at a low rate. When 20 g of bark is introduced in 250 mL of suspension, the amount of polymer recovered slightly decreases. Polymer extraction in dilute solutions is coherent with other works related to polymer transfer. Reduction of the amount of polymer when bark ratio increases is due to the well-known resistance of transport due to the gradient of

Table 3. Factors coefficients and interactions for modeling of diffusion coefficient with NaCl for linear and logarithmic model, using complete factorial design plan.

Term	Linear model with NaCl		Logarithmic model with NaCl	
	coefficient	Probability	Coefficient	Probability
A:PH	2.93E-8	> 0.05	6.61E-7	> 0.05
B:FI	1.19E-6	> 0.05	1.26E-5	> 0.05
C:TEMP	3.99E-6	> 0.05	5.09E-5	> 0.05
AB	2.98E-8	> 0.05	-3.31E-6	> 0.05
AC	1.65E-7	> 0.05	3.31E-6	> 0.05
BC	4.44E-7	> 0.05	6.61E-7	> 0.05
Constant	1.02E-5		1.36E-4	

Table 4. Factors coefficients and interactions for modeling of diffusion coefficient with $CaCl_2$ for linear and logarithmic model, using complete factorial design plan.

Term	Linear model with $CaCl_2$		Logarithmic model with $CaCl_2$	
	Coefficient	Probability	Coefficient	Probability
A:PH	3.62E-7	> 0.05	3.31E-6	> 0.05
B:FI	2.27E-6	> 0.05	9.92E-6	> 0.05
C:TEMP	3.52E-6	> 0.05	4.69E-5	> 0.05
AB	1.65E-7	> 0.05	4.63E-6	> 0.05
AC	1.96E-7	> 0.05	-3.31E-6	> 0.05
BC	-8.78E-8	> 0.05	6.61E-7	> 0.05
Constant	1.07E-05		1.43E-4	

concentration in the solution which becomes low and then reduces the transfer of the polymer inside the suspension.

Modeling diffusion coefficients of *Grewia* spp.

Using complete factorial design followed with linear and logarithmic approximation, coefficients of factors involved in the extraction process and quadratic interactions are presented in Table 3 for diffusion with NaCl salt and in Table 4 for diffusion with $CaCl_2$ salt.

The obtained quadratic equation with NaCl was expressed as:

Linear model
Diffusion coefficient = 1.02E-5- 2.93E-8*A+1.19E-6*B+3.99E-6*C+ 2.98E-8*A*B + 1.65E-7*A*C + 4.44E-7*B*C

Logarithmic model
Diffusion coefficient = 1.36E-4+6.61E-7*A+1.26E-5*B+5.09E-5*C-3.31E-6*A*B+3.31E-6*A*C+1.98E-6*B*C

The obtained quadratic equation with $CaCl_2$ was expressed as:

Linear model
Coefficient diffusion = 1.07E-05+3.62E-7*A+2.27E-6*B+3.52E-6*C+1.65E-7*A*B+1.96E-7*A*C- 8.78E-8*B*C

Logarithmic model
Coefficient de diffusion = 1.43E-4+3.31E-6*A+9.92E-6*B+4.69E-5*C+4.63E-6*A*B-3.31E-6*A*C+ 6.61E-7*B*C

Tables 3 and 4 present the coefficients of parameters involved in the quadratic equation resulting from the factorial design plan. The observed probability of all the factors was found to be greater than 0.05, showing that at a probability of 95%, these factors did not have a great influence on the diffusion coefficient.

Table 5 presents the values of statistic parameter used to validate the model. Since the values obtained R^2, AADM, B_f is near the values expected, the mathematical model obtained is considered as valid.

But by taking into account the parameters of validation of the model, one notes that the model logarithmic model

Table 5. Validation of the models.

Parameter	Expected values	CaCl$_2$		NaCl	
		linear model	logarithm model	Linear model	logarithm model
R^2	1	0.989	0.999	0.995	0.988
AADM	0	0.030	0.005	0.000	0.040
Bf	1	1.000	0.999	1.000	1.002
A$f1$	1	1.030	1.005	1.000	1.041
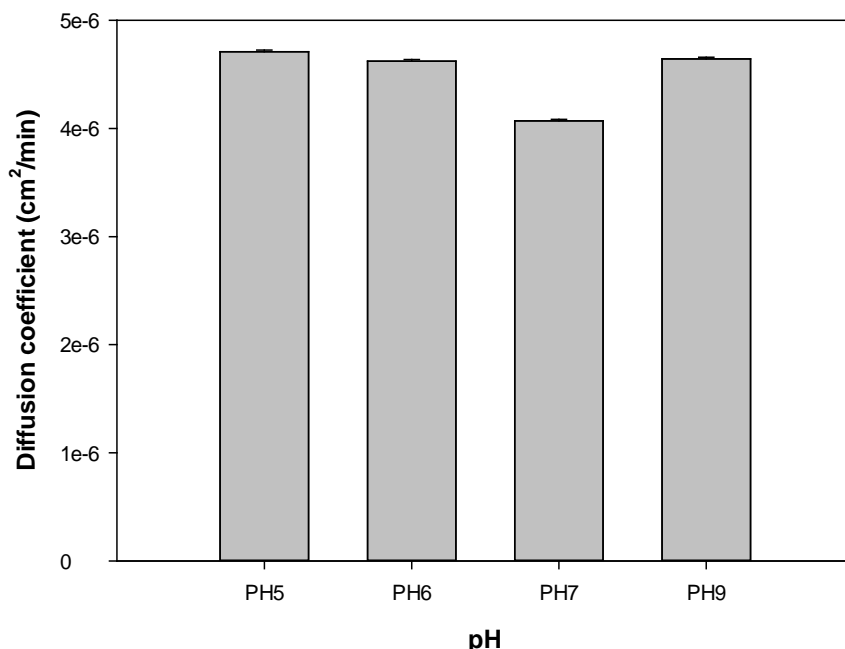
Figure 4. Biopolymers diffusion coefficients with the pH.

presents itself as an explanation of the interaction between the various factors of the extraction of polymers of *Grewia* in the presence of CaCl$_2$, whereas the linear model presents itself rather better than the extraction in the presence of NaCl.

Figure 4 presents the pH effect on extraction ratio on polymer removal and extraction time on polymer mass recovered over the mass of the bark as shown for a ratio bark/volume equal to 10/250. At the beginning of the diffusion of polymers into the solution (from 0 to 60 min), less influence of pH on polymer transfer is observed. Net pH influence is found after 120 min of extraction, and the lowest extraction ratio is obtained at pH 7, while the highest one is obtained at pH 6.

Plants polymers are mainly polysaccharides. They possess a high tendency to associate, caused by the abundance in hydroxyl or amino groups present in the macromolecules that easily undergo hydrogen bonding, and are very sensitive to pH variations. In acidic solutions, protonation of carboxylic and amino groups will increase electrostatic repulsion and solubilize the polymer, increasing its diffusivity (Nandhini and Abhilash, 2010; Lawrence et al., 2006). This behavior is also observed at high pH (9), but in this case, deprotonation is involved. At neutral pH 7, hydrogen bonds existing inside the polymers will increase the size of polymer which will result in a decrease of polymer diffusivity.

Figure 5 presents the effect of salts and salt concentration on polymer. Without any salt, the released amount of polymer is low (2.5 %) and increases with the type of salt and the concentration. As ionic strength increases, the solubility of the polymers increases as predicted by the salting in theory (Djamen, 2011). The solubilisation will induce a rapid diffusion of the polymer in the medium. In this particular case, traction is more pronounced with Ca than Na salts. These differences could be explained by the ionic conformation of the different salts used; Ca ions of greater ionic radius than
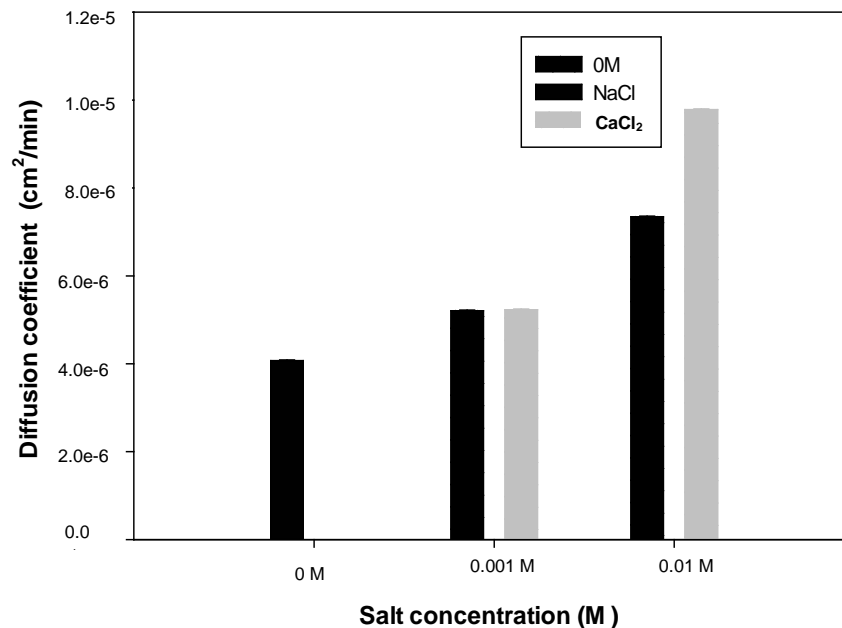
Figure 5. Effect of salts on diffusion coefficient.

Na ones release their solvation water more quickly, thus increasing the solubility of polymers and in fine the diffusion coefficient (Djamen, 2011).

From the above results it is obvious that physicochemical properties of the solution greatly affect the yield of polymer extraction.

Conclusion

The principal objective of this work was to determine the diffusion coefficient of polymers of *Grewia* spp. under various operating conditions. The results show that the polymers of *Grewia* spp. diffuse more quickly in the salt solutions and is effective at high temperatures than in distilled water; with diffusion coefficients of 9,78458e-06±1,646e-08, 7,3456e-06±1,746e-08 and 4,07001e-06±1,55077e-08 cm^2/min, respectively with CaCl$_2$, NaCl and distilled water. These results also show that the diffusion coefficients of *Grewia* spp. polymers in the presence of CaCl$_2$ are higher than those obtained in the presence of NaCl, and that it is not preferable to extract polymers from *Grewia* spp. with neutral pH. According to the type of salt, one can make use of either the linear model or the model logarithmic curve for the expression of the interaction between the parameters of extraction.

Conflict of interests

The authors have not declared any conflict of interests.

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