FLOCCULATION PROPERTY OF NEW WATER-SOLUBLE CELLULOSE-ACRYLAMIDE DERIVATIVES ELABORATED IN ALKALI MEDIUM

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Abstract. In the last few years, science and technology have made remarkable discoveries in the field of bio-renewable materials. In this context, polysaccharide based biopolymers present themselves as a high potential source of innovation. Due to its availability and biodegradability, Cellulose, the polymer belonging to the polysaccharide family, has a great interest today. Indeed, it is considered to be one of the most common organic polymers and an almost eternal source of raw material for the growing demand of eco-friendly materials. The objective of this work is to propose the elaboration of new water-soluble cellulose-acrylamide derivatives destined to the application as new bio-based flocculants for colloidal solution of $Fe(OH)_3$. However, the new cellulose based floculants, cellulose acrylamide (Cac) and hydroxyethyl cellulose acrylamide (HECac), were elaborated in alkali medium. Since, the structural characterization showed that the reached degree of the substitution (DS) is close to 0.6 and to 1.3 for Cac and HECac, respectively. In addition, the effect of the reaction time was studied, and the results showed that its prolongation affects strongly the flocculation properties of the polymers. Indeed, the saponified amide groups to the carboxylates have been achieved at most 50% when the time of the reaction exceeds 1.5 h. Moreover, the flocculation behavior of Cac and HECac indicates that the flocculation efficiency increased with increasing in the saponification rate, which indicating that the carboxylate form increases the surface negative charge density of the polymers, where the electrostatic interaction governs the flocculation phenomenon between water-soluble cellulose-acrylamide derivatives (Cac and HECac) and $Fe(OH)_3$ colloidal solution.

1. Introduction

Polymers derived from biomass can be grouped into two main families, polymers derived directly from living organisms and polymers synthesized from renewable

resources. Since, polysaccharides, proteins or lignin family polymers are found in the first category. The second category comprises polymers formed from the polymerization of naturally occurring monomers (Privas, 2013).The current global trend to promote the production and use of sustainable and biodegradable materials from natural resources has sparked interest in new high value-added cellulose products. Besides the cellulose is one of the affordable materials available for the preparation of various functional materials (Hokkanen et al., 2013). The cellulose is a linear condensation polymer consisting of the an hydroglucose units linked together by β-1,4-glycosidic bonds (Bledzki & Gassan, 1999). Each AGU contains three hydroxyl groups including 2 secondary alcohol functions (in position C_2 and C_3) and a primary alcohol attached to carbone at the position 6 (C_6). However, the hydroxyl groups are situated in an equatorial position with respect to the plane of the AGU cycle (Mazza, 2009).

The hydroxyl groups of the cellulose are involved in inter and intramolecular hydrogen bonds, which allows the appearance of a high crystalline order. Whereas, the engendered crystalline order defines the polymorphism types characterizes cellulose. However, cellulose can exist in at least five allomorphic forms; *Cellulose I* (native cellulose) is the form the most found in nature from almost every source, the polymorphism type I was divided into two forms (Iα and Iβ) with a slight change, which can be found alongside each other in statistically variable proportions (Baker et al., 2000). Cellulose may occur in other crystal structures denoted cellulose II, III and IV. Among these crystal structures, denoted cellulose II is the most stable structure of technical relevance. This structure can be formed from cellulose I by treatment with an aqueous solution of sodium hydroxide or when native cellulose is regenerated from solutions of semi-stable derivatives (Roy et al., 2009).

The high density of the hydrogen bonds in the cellulose constitutes the major obstacle of its use as a base polymer at the industrial level. In fact, at the structural level, the hydrogen bonds create a high stability for cellulose, which limits its solubility in almost all the usual solvents. Thus, its thermal degradation before its melting temperature drives away any thermal process of its modification. In this context, several solvents systems were already studied and discussed for the functionalization of the cellulose, where some systems have shown a high efficiency in solving the problem of solubility, but they are avoided because of their toxicity and their high toxicity. Moreover, the aqueous systems as well as NaOH/Urea/ H_2O and NaOH/thiourea/ H_2O have showed an acceptance of the scientific community for its environmental aspect. In addition, the introduction of the new functionalities in the cellulose structure can broaden the surface of its applications, but also the degree of substitution (DS) is a parameter determining of the physicochemical properties of materials (solubility, surface tension, thermal stability, dimensional stability, etc.).

In recent years, cellulose continued to build the new environmentally friendly industrial base. Indeed, cellulosic derivatives have frankly all the industrial sectors started by the pharmaceutical industry to the plastic, functional and smart materials. However, the incorporation of the cationic or the anionic entities offers to the cellulose its application as a bioflocculent in coagulation-flocculation eco-friendly technologies. Wherever, it appears more and more as not only a clarifying agent in clarification process but also as a powerful adsorbent competing with other polymers used in coagulation/flocculation processes for water purification (Bolto & Gregory, 2007).The optimization of the flocculation process will depend on the conditions that may be inherent to the liquid phase (pH, ionic strength, nature of the ions, temperature, etc) or

the particles to be separated (nature, size, surface charges, etc) (Achour & Guesbaya, 2005).

In the present work, new water-soluble cellulose-acrylamide derivatives (cellulose acrylamide (Cac) and Hydroxyethyl cellulose acrylamide (HECac)) were elaborated in alkali medium. The result products were destined to the application as new bio-based flocculants for colloidal solution of $Fe(OH)_3$. However, the structural characterization showed that the reached degree of the substitution (DS) is close to 0.6 and to 1.3 for Cac and HECac, respectively. Since, the effect of the reaction time was studied, and the results showed that its prolongation affects strongly the flocculation properties of the polymers. Indeed, the saponified amide groups to the carboxylates have been achieved at most 50% when the time of the reaction exceeds 1.5 h. Moreover, the flocculation behavior of Cac and HECac indicates that the flocculation efficiency increased with increasing in the saponification rate, which indicating that the carboxylate form increases the surface negative charge density of the polymers, where the electrostatic interaction governs the flocculation phenomenon between water-soluble cellulose-acrylamide derivatives (Cac and HECac) and $Fe(OH)_3$ solution.

2.   Experimental:

Materials

Cellulose powder and HEC were purchased from HIMEDIA and SIGMA Company, respectively. Acrylamide (C_3H_5NO), NaOH were obtained from Aldrich Company. All chemicals used in the experiments were of analytical grade and were used without further purification.

Methods

The FTIR spectra were recorded using a *Shimadzu IRAffinity-1 FTIR* spectrophotometer, where the samples were dispersed in KBr pellets. For each sample, the data were collected from 4000 to 400 cm^{-1} with a resolution of 2 cm^{-1} and an accumulation of 32 scans. The crystallinity of the Cellulose, HEC, Cac and HECac samples was investigated by *EQUINOX 200 Diffractometer* operating using Cu K_α radiation ($k_\alpha = 1.5418$ A), voltage of 40 kV and operation current of 30 mA. All patterns were performed in the range $2\theta \approx 5$–$40°$, pitch $0.05°/s$. The transmittance of clarified zone is measured on a *Shimadzu- spectrophotometer* using the quartz tanks.

2g of Cellulose and 2g of HEC were dissolved in aqueous NaOH/urea and NaOH (1N) solutions, respectively; to obtain a clear solution, then 2.6g and 1.85 g of acrylamide was added, respectively. Then, the mixture was stirred for 1h30 and 3 hours at 60 ° C. The obtained solution was neutralized by HCl aqueous and precipitated with ethanol, filtered under vacuum and dried to obtain (Cac and HECac).

Determination of DS

Determination of DS_{COO^-}

0.5 g of Cac and HECac samples were solvated in deionized water and were acidified by HCl solution at a pH≈2, and then were recovered by precipitation in ethanol. Moreover, the acidified Cac and HECac were dissolved in 20 ml of NaOH (0.1N) solution, and then the alkali solution was titrated by HCl (0.1N) using phenolphthalein as color indicator. The DS_{COO^-} was calculated according to the (1):

$$DS_{COO-} = \frac{n_{COO-}}{n_{NH2}} DS_{NH2} \qquad (1)$$

Determination of DS_{NH2}

The DS_{NH2} was determined using a typical dosage of liberated ammonia in aqueous alkali solution. The NH_3 liberated was trapped in saturated boric acid solution and titrated by HCl solution. However, 0.4 g of Cac and HECac samples were dissolved in 20 ml of NaOH (4N) solution, followed by liberation of NH_3 resulted from the saponification of grafted amide to carboxylate form during 16 h under stirring until the total saponification, and the saponification rate was flowed by FTIR. The ammonia liberated was tapped in saturated boric acid solution and titrated by HCl (0.1N) solution using Tashiro indicator as color indicator (Figure1).The DS_{NH2} was calculated according to the (2):

$$DS_{NH2} = \frac{n_{NH2} M_{monom\ \grave{e}re}}{1 - Mac\left[n_{COO-} + n_{NH2}\right]} \qquad (2)$$
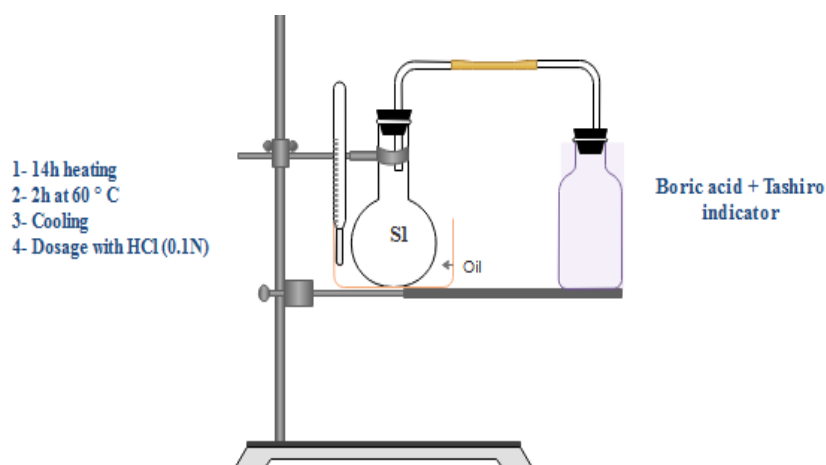

Figure 1. Determination of DS_{NH2}

Flocculation of colloidal ferric hydroxide ($Fe(OH)_3$)

$Fe(OH)_3$ was chosen as a model to evaluate the flocculation properties of Cac and HECac samples. The preparation consists in having a saturated solution of the iron chloride which will be added drop-wise to the boiling water until the obtaining of the colloidal $Fe(OH)_3$ system. Different concentrations of Cac and HECac samples (10-200 µl) have been added in 5 ml of colloidal $Fe(OH)_3$ solution. The transmittance of clear part has been measured by spectrophotometer UV visat 600 nm.

3. Results and discussion

The elaboration ofwater-soluble cellulose-acrylamide derivatives (Cac and HECac) was occurred out in alkali medium using the system NaOH/urea/H_2O and NaOH solution, respectively Figure 2. The solvation is carried out at a low temperature in order to increase the mobility of hydroxyl protons to ensure the hydrodynamic volume increase of the cellulose and the inter-chain insertion of solvent. However, proton mobility causes the continuous swelling of the cellulosic aggregates to the state of explosion under the action of solvent. The catalytic action of NaOH allows the

weakness of the H-O bond in the structure cellulosic which causes the easy removal of acid proton. The saponification of amide groups to carboxylate, which is accompanied by an evolution of ammoniac, is often considered in an alkaline medium, to better characterize Cac and HECac we have studied the saponification rate of amides to carboxylates.
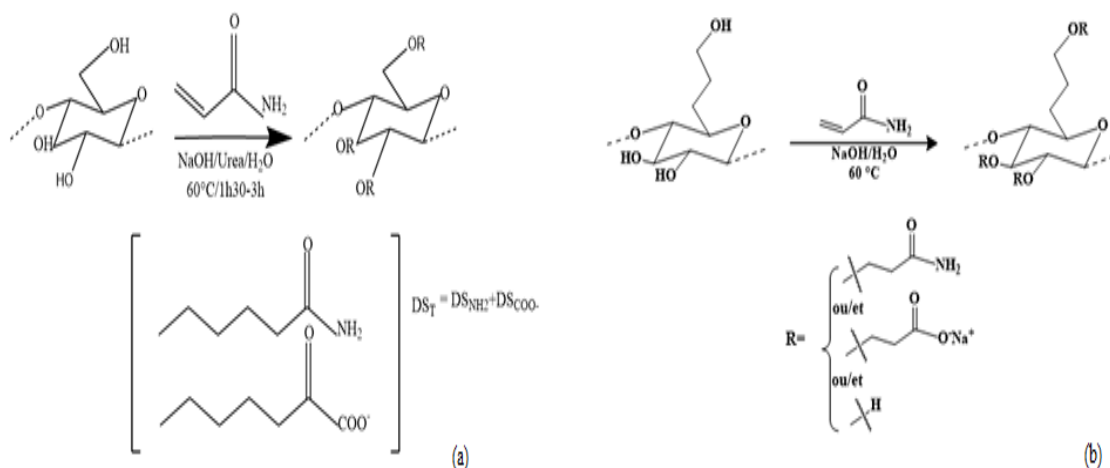

Figure 2. Schematic reactions of the elaboration of (a) Cac and (b) HECac

Effect of reaction times

DS results shown in Table 1 of Cac, HECac samples, the reaction time was maintained for 1.5 hours and 3 hours, respectively. At the same time, the DS of samples of Cac1h30, Cac3h and HECac 1h30, HECac3h was 0.56, 0.63, 1.28, and 1.32 respectively. It can be seen that with the increase of the reaction time, the DS and the C / N increase clearly over time, which implies the phenomenon of saponification of the amide function to carboxylate under the action of NaOH.

Table 1. Effect of reaction time on DS values

	Cac 1h30	Cac 3h	HECac 1h30	HECac 3h
DS_{COO^-}	0.26	0.23	0.64	0.77
DS_{NH2}	0.30	0.40	0.64	0.55
DS_{TOT}	0.56	0.63	1.28	1.32
C/N	0.53	0.57	1.00	1.40
DH (%)	46	36	50	55

Structural analysis of Cac and HECac

FTIR

The FTIR spectra of acrylamide, cellulose and Cac1h30 and Cac3h are shown in Figure 3(a) and 3(b). On the acrylamide spectrum, we clearly see the two strong localized absorption bands at 3354 cm^{-1} and 3186 cm^{-1} characteristic of the symmetric and asymmetric elongation of the NH bond of the primary amine group, thus the absorption band at 1614 cm^{-1} was attributed to the vibrations of the C=C bond. The FTIR spectrum of cellulose showed the wide and strong band at 3346 cm^{-1} which due to the asymmetric elongation vibrations of the OH group, and is confirmed by the

absorption band corresponding to the deformation of OH group at 1371 cm^{-1}. The glucose structure is proven by the characteristic C-O-C absorption band of pyranose rings at 1060 cm^{-1}. The 1637 cm^{-1} band corresponds to the bending mode of the naturally absorbed water within the cellulosic structure (Sun et al., 2004) (Sun, Sun, Zhao, & Sun, 2004).

The absence of the absorption band characteristic of the elongation of C=C at 1614 cm^{-1} on the spectrum of Cac1h30 is a strong indication of grafting of acrylamide on the cellulosic backbone. Also, a spread of the band around 3440 cm^{-1} demonstrated the superposition of the bands of OH and that of NH. In addition, the Cac1h30 spectrum shows the appearance of the new absorption bands attributed to the grafted acrylamide group. Indeed, the new bung detected at 1645 cm^{-1} and 1575 cm^{-1} was assigned to the C=O vibrations of the primary amide group and carboxylate, respectively. The appearance of the carboxylate functions on the FTIR spectra is due to the saponification of the amide group grafted under the action of the base NaOH (Sun et al., 2004)
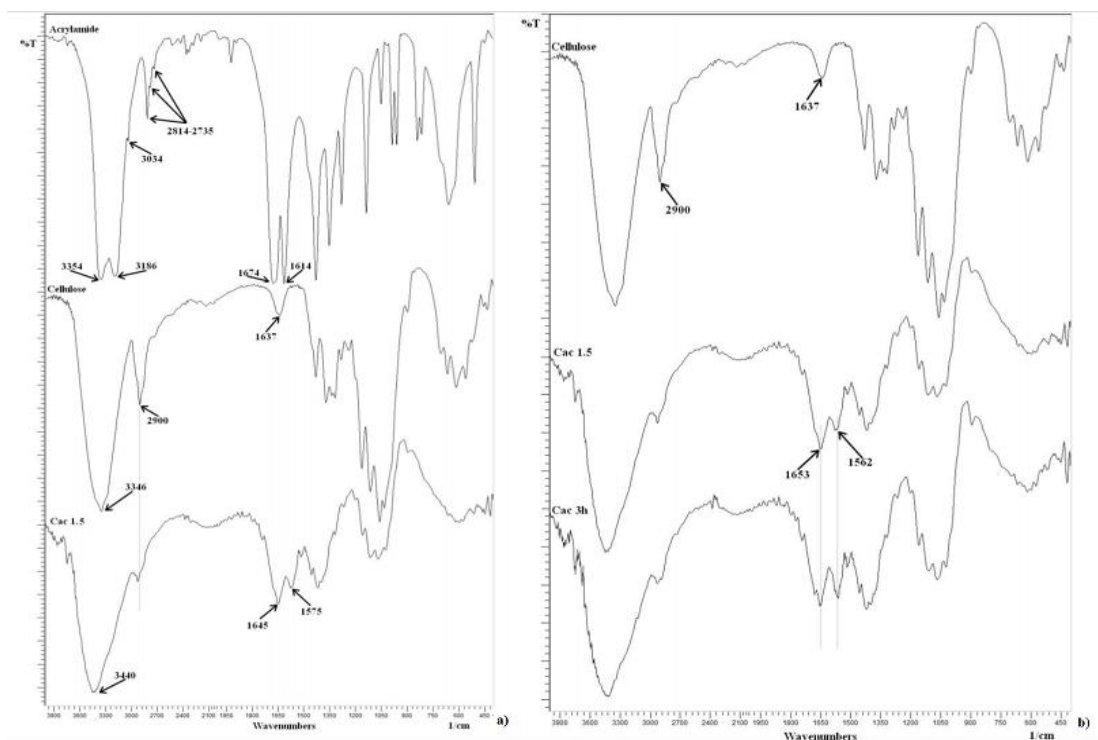

Figure 3. FTIR spectra of (a) Acrylamide, Cellulose and Cac 1h30 and (b) cellulose, Cac 1h30, Cac 3h

Increasing the reaction time from 1h30 to 3h a weak effect on the grafting rate was noted, the DS increases from 0.55 to 0.69 for cellulose grafted acrylamide (Cac). The same for HEC, a slight variation of DS value between HECac1h30 and HECac3h. However, the reaction time has a remarkable effect on saponification phenomenon where the ratio carboxylate/amide (C/N)was increasing about 50% from HECac1h30 (C/N=1.00) to HECac3h (C/N=1.40).

The FTIR spectra of acrylamide, HEC and HECac were shown on Fig. 3a and 3b. The adsorption band characteristic of the elongations of the bonded O-H is localized around 3400cm^{-1} and that of 2920 and 2881cm^{-1} are attributed to the vibrations of C-H. On the HEC spectrum, the deformations of the hydroxyl groups of naturally absorbed

water are localized around 1640 cm^{-1} (El Barkany et al., 2017). The bung at 1670 cm^{-1} on the HECac spectrum corresponds to C=O carbonyl elongations. The positivity of the reaction is proved by the apparition of C=C elongations at 1614 cm^{-1}, and the appearance of the two characteristic peaks of the amide function at 1670 cm^{-1} and around 1570 cm^{-1}. In addition, the deformation of the absorption bond around 3390 cm^{-1} indicates the superposition of the two OH and NH$_2$ bands at 3415 cm^{-1} and 3270 cm^{-1}, respectively (Jayakumar et al., 2000).

The experimental results grouped in table 1 indicates that the reaction time, practically, has no effect on the value of DS$_{tot}$ of HECac which remains close to 1.3, whereas DS$_{COO-}$ (HECac3h) is 3/2 of DS$_{COO-}$ (HECac1h30) which indicates that after reaching the limit value of DS$_{tot}$, which divides in 50% of DSi, the saponification reaction continues even after the stop of grafting. This result is supplemented by the results of the FTIR spectroscopic analyzes. Indeed, the transformation of the amide functions to the carboxylates is proved by the decrease of the width of the absorption band at 3400 cm^{-1} indicating the disappearance of -NH which turns into COONa.
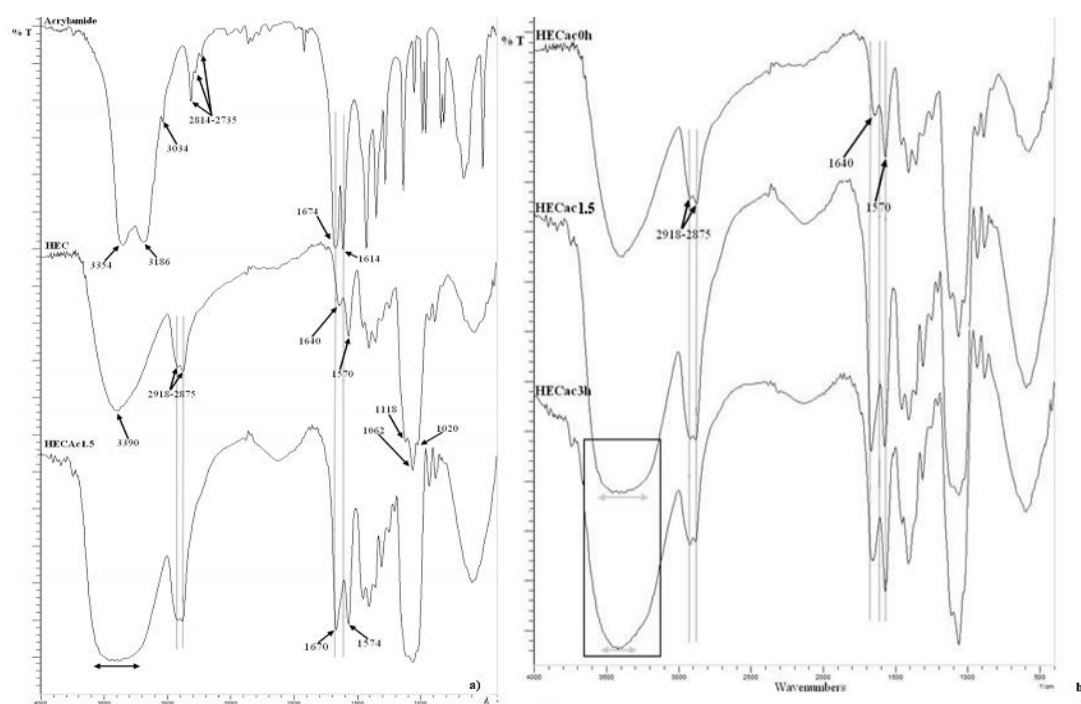

Figure 4. FTIR spectra of (a) acrylamide, HEC and HECac1h30 and (b) HEC, HECac 1h30 and HECac 3h

Similarly, the increase in the intensity of the absorption band at 1570 cm^{-1} corresponding to the carboxylates with decreasing in that of amide characteristic band (CO at 1670 cm^{-1}) at DS$_{tot}$ constant is a strong indication of occurrence of the saponification reaction.

X-ray diffraction

Figure 4a shows the diffractograms of acrylamide, cellulose and Cac 3h. The acrylamide diffractogram showed a high crystalline character due to the formation of hydrogen bonds between the mobile protons of nitrogen and oxygen of the carbonyl function. The cellulosic crystalline structure showed five peaks at Bragg angles 2θ;

14.87°, 16.23°, 20.46°, 22.42°, and 34.56° attributed to reticular plans planes of the Miller indices (hkl); (101), (021), (002) and (040), respectively. This indicates that the starting cellulose is of type I polymorphism. After the modification, the Cac diffractogram indicates a destruction of the orders of the reagents where the disappearance of the characteristic peaks of acrylamide and of cellulosic polymorphism. The suppression of the crystalline order is due to hydrogen bonds the intercalation removing of cellulosic chains and acrylamide grafted entities. On the other hand the substitution of the cellulosic hydroxyl eliminates the second intramolecular fraction of the density of the hydrogen bonds where the amorphous character is more developed in Cac than the cellulose (Guo et al., 2013). In addition, knowing that the amorphous appearance increases the accessibility of solvent to the polymer mass, the decrease in the crystallinity of Cac is a positive parameter for the good solubility in water.

The X-ray diffraction pattern of Cac3h shows the appearance of the new peaks indicating the formation of the new ordered areas. This new crystallinity is formed through the inter-chain physical interactions of hydrogen bond and electrostatic bonds between the amide and carboxylate groups.
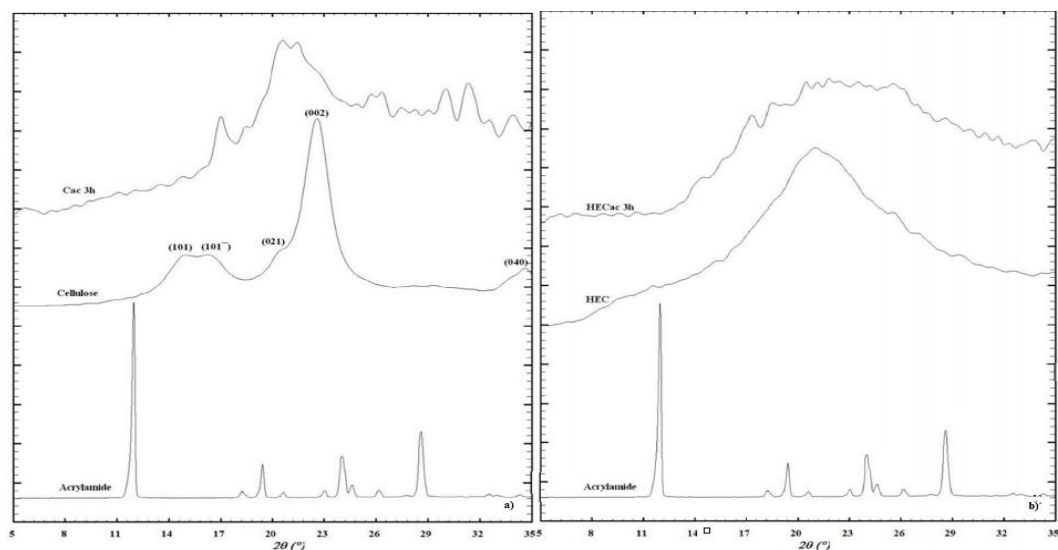

Figure 5. XRD patterns of (a) Acrylamide, Cellulose and Cac 3h and (b) acrylamide, HEC and HECac 3h

The analysis of the crystal order of HEC before and after modification (HECac) was shown in Figure 4b, and it shows that the crystalline order of acrylamide has completely disappeared, whereas the polymeric matrix keeps practically its amorphous appearance even after modification. On the diffractogram of HECac3, the onset of such a crystalline order was observed but negligible in front of the amorphous character, we suggest that the increase of DS beyond 1.3 can increase the density of hydrogen bonds and consequently develop a certain supra molecular order.

Flocculation of colloidalFe(OH)3 solution

The flocculation of colloidal $Fe(OH)_3$ solution by synthesized products (HEC, HECac 3h, Cac 1h30 and Cac 3h) is illustrated in Fig 5. Indicating that the samples HECac and Cac with different DS values were efficient for the flocculation of $Fe(OH)_3$ colloid solution, and the maximum transmission value reached around 100% for HECac3h. Indicating that the introduction of charged carboxyl groups into the Cac or HECac can improve the flocculation efficiency of the samples by the neutralization of the charges. The cationic particles of $Fe(OH)_3$ colloid are attracted by electrolysis of the carboxyl groups of HECac and Cac which can be bound and fixed.
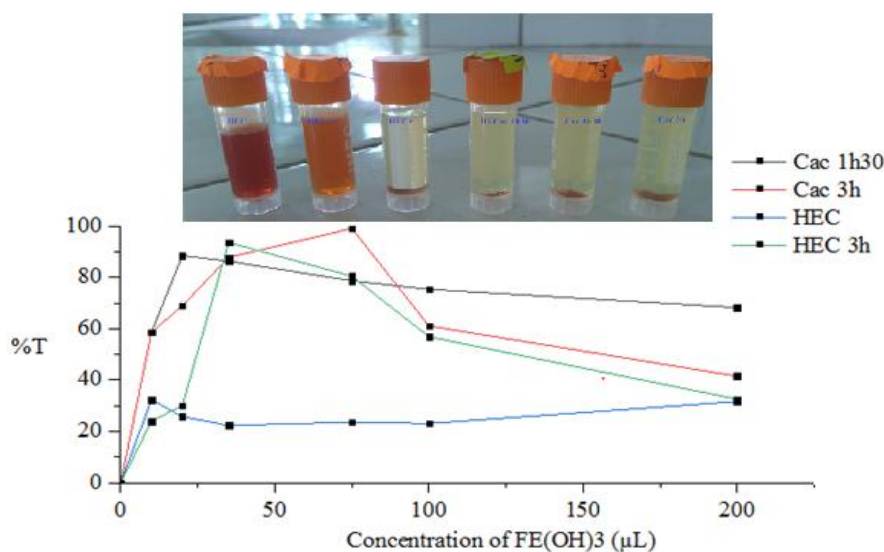

Figure 6. Spectral transmittance of colloidal $Fe(OH)_3$ solution flocculated by Cac 1h30, Cac 3h HEC and HECac 3h

When the carboxyl groups have completely neutralized the cationic charges, the transmittance reaches its maximum. However, when the optimum concentration interval is exceeded, the stabilization is effected by the electrostatic repulsion of $Fe(OH)_3$ colloid particles that has been already bounded to the samples and the transmittance decreases again. This is mainly due to a mechanism of neutralization of the charges.

The mechanism of the colloidal flocculation of Fe $(OH)_3$ with (HEC, HECac 3h, Cac 1h30 and Cac 3h can be explained by a combination of charge neutralization and bridging polymers. The neutralization of the charge is the index in the flocculation of Fe $(OH)_3$. The synthesized samples contain both functions ($-CONH_2$) and carboxyl groups ($-COO-$). Due to an electrostatic interaction with carboxyl groups and a hydrogen bond The absorbed Cac and HECac polymers tend to form loops and extend at a distance from the surface of the particles in the aqueous phase, hence the concentration plays a significant role because when the concentration is increased [10 μL-200 μL], the transmittance of the clarified zone is clearly noted, but at a concentration of approximately 75 μL and beyond this value (100 μL and 200 μL) the transmittance decreases, which explains why a saturation of absorption. By the combination of charge

neutralization and polymer bridging, the samples are effective flocculants for the Fe (OH)$_3$ colloid.

We can say that in view of the non-toxicity and biodegradability of the synthesized products based on cellulose, it can be considered as a promising flocculent with excellent flocculating properties for the industrial processes.

4.   Conclusion

New water-soluble cellulose-acrylamide derivatives (Cac and HECac) were successfully elaborated in aqueous alkali medium. The samples were characterized by FTIR and XRD, and the results showed that the modification engendered some modification in structure order, which attributed to the decrease in the density hydrogen bonds. The sample series of Cac 1h30, Cac 3h and HECac 1h30, HECac 3h showed that the DS values ranging between 0.56, 0.63, 1.28 and 1.32 respectively. As the reaction time increases, the DS and C/N values increase as well as the carboxyl group content. The flocculation results proved that, by the combination of the neutralization of the filler and the polymers, the samples are effective flocculants for the Fe(OH)3 colloid. Moreover, the flocculation behavior of Cac and HECac indicates that the flocculation efficiency increased with increasing in the saponification rate, which indicating that the carboxylate form increases the surface negative charge density of the polymers, where the electrostatic interaction governs the flocculation phenomenon between water-soluble cellulose-acrylamide derivatives (Cac and HECac) and Fe(OH)$_3$solution.

This study demonstrated that the synthesized products could potentially be used as a new, effective, non-toxic and biodegradable flocculent in the water treatment field.

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