Available online at www.sciencedirect.com
ScienceDirect
Journal of Environmental Sciences 2010, 22(10) 1539–1543
JOURNAL OF ENVIRONMENTAL SCIENCES
ISSN 1001-0742
CN 11-2629/X
www.jesc.ac.cn

Experimental evaluation of eco-friendly flocculants prepared from date palm rachis

Ramzi Khiari*, Sonia Dridi-Dhaouadi, Chadlia Aguir, Mohamed Farouk Mhenni

Research Unity of Applied Chemistry & Environment, Department of Chemistry, Faculty of Sciences of Monastir 5019, Tunisia.
E-mail: khiari_ramzi2000@yahoo.fr

Received 02 October 2009; revised 18 December 2009; accepted 21 December 2009

Abstract

Sodium carboxymethylcellulose (CMCNa) is an anionic water soluble polyelectrolyte widely used in many industrial sectors including food, textiles, papers, adhesives, paints, pharmaceuticals, cosmetics and mineral processing. CMCNa was produced by chemical modification of cellulose, and represents many advantages: natural, renewable, non-toxic and biodegradable. In this study, different kinds of CMCNa, prepared from an agricultural waste date palm rachis, were tested as eco-friendly flocculants for drinking water treatment and their performances as flocculants in turbidity removal enhancement were assessed. The prepared materials were characterized by the degree of substitution (DS) and polymerisation (DP). The study of the effect of some experimental parameters on the coagulation-flocculation performance, using the prepared materials combined with aluminium sulphate (as coagulant), showed that the best conditions for turbidity treatment were given for pH 8, coagulant dose 20 mg/L, flocculant concentration of 100 mg/L and stirring velocity (during the flocculation step) of 30 r/min. Under the optimum conditions, the turbidity removal using CMCNa, prepared from raw material, was about 95%. A comparison study between the flocculation performance of a commercial anionic flocculant (A_{100}PWG: polyacrylamide) and that of the prepared CMCNa showed that the performance of the waste-based flocculant with a DS of 1.17 and a DP of 480 was 10% better than that achieved by the commercial one.

Key words: carboxymethylcellulose; flocculants; date palm rachis; flocculation process

DOI: 10.1016/S1001-0742(09)60286-2

Introduction

Coagulation/flocculation in water treatment has been found to be a cost-effective, easy to handle and energy saving operation in various industrial applications (Abdel-Shafy and Abdel-Basier, 1991; Bromley et al., 2002, Tatsi et al., 2003). The process is extensively used for the removal of colour and turbidity from water. Unfortunately, it has a major drawback when used to supply drinking water since the toxicity of the chemicals must be taken into account. Some researchers focused their attention on the flocculation step by using natural and eco-friendly flocculating agents to reduce the toxicity and the treatment costs (Grau, 1991; Bromley et al., 2002, Anuradha and Malvika, 2006).

Date palm is one of the most cultivated palms in the arid and semi-arid regions of the world. According to statistic result from the Tunisian Ministry of Agriculture (2003), Tunisia has more than 4 million date palms, which occupy 32 thousand ha. After the date fruit harvesting, large quantities of date palm rachis wastes accumulate every year in Tunisia and this abundant renewable resource should find rational ways of valorisation. Date palm rachis contains a high ratio of cellulose (Khiari et al., 2010) (Table 1) which can be valorized to produce cellulosic derivatives.

In the present study, different kinds of sodium carboxymethylcellulose (CMCNa) were prepared from date palm rachis and tested as flocculants. These prepared materials were mainly characterized by substitution degree (DS) and polymerisation degree (DP).

Several studies have reported the synthesis of carboxymethylcellulose (CMC) using starting materials from various vegetable plants (Yokota, 1985; Lin et al., 1990; Baar et al., 1994; Heinze et al., 1994; Barai et al., 1997; Kauper et al., 1998; Mann et al., 1998; Olaru et al., 1998; Heinze and Pfeiffer, 1999; Hidayati et al., 2000; Togrul and Arslan, 2003; Aguir and M'henni, 2006). CMC is used in many fields such as textile (Botdrof and Soap, 1962), paper (Barber, 1961), agro-food applications (Botdrof and Soap, 1962), adhesive (Barba et al., 2002), cosmetic and pharmaceutical (Olaru et al., 1998) industries.

In the present article, the effects of some flocculation parameters (such as, pH, mixing speed, concentration) combined by a step of coagulation were studied. The performances of three different CMCNa prepared from date palm rachis were compared with a commercial flocculating counterpart (polyacrylamides A_{100}PWG) which is

* Corresponding author. E-mail: khiari_ramzi2000@yahoo.fr

Table 1 Chemical composition of raw date palm rachis

	Value (%)	Method
Cold water solubility	4.86	T207 cm-08
Hot water solubility	8.12	T207 cm-08
Alcohol-toluene solubility	6.30	T204 cm-07
1% Sodium hydroxide solubility	20.78	T212 om-07
Ash	7.58	T211 om-07
Klason lignin	27.22	T222 om-06
Holocellulose	74.88	Wise et al., 1946
α-Cellulose	62.13	T203 cm-99
Kappa number	6.97	T236 om-06

commonly used in water treatment in Tunisia. Our basic idea is to substitute the raw material in the production of the flocculant by the waste to decrease the cost of flocculant.

1 Materials and methods

1.1 Materials

1.1.1 Water characteristics

The water used in this study was natural surface water charged with suspended particles. The physicochemical characteristics of the studied water were determined including pH, solid materials (by centrifugation at 4000 r/min for 10 min), conductivity (conductivimeter Jenway 4510, UK) and turbididity (turbidimeter Aqualytic Al 1000, Jenway, UK). The results are as follows: pH 6; total suspended solid (TSS) 345 mg/L; conductivity 2150 μS/cm; turbidity 33 NTU.

1.1.2 Characteristics of flocculant

Four kinds of CMCNa (QR1, QR2, QE1 and QE2) were prepared from the date palm rachis as shown in Fig. 1.

These materials were characterized by some physicochemical properties (Table 2). DS was determined using a titration method (Tapio et al., 1994) and DP was estimated according to the NFT 06-037 standard method which consists in measuring the intrinsic viscosity (η) of the chosen polymer in cupriethylene-diamine solution using a capillary viscosimeter (Oswald-type viscosimeter, Schott, Germany). The measured viscosities were then used to calculate the polymer DP by Marc-Houwinck relationship (Eq. (1)):

$$[\eta] = K\,\mathrm{DP}^{\alpha} \tag{1}$$

where, K and α are two constants valid for a given polymer in a given solvent and at a given temperature.

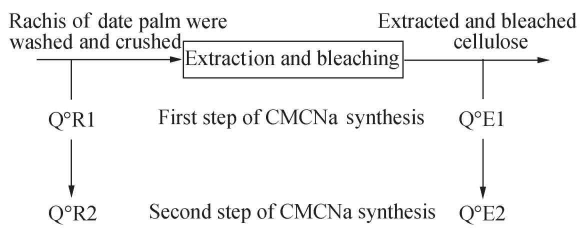

Fig. 1 Different steps of CMCNa preparation.

Table 2 Characteristics of prepared CMCNa from date palm rachis

	Extracted and bleached cellulose	QR1	QE1	QR2	QE2
DP*	1467	1040	400	480	240
DS	0	0.98	1.25	1.17	1.86

* Estimated values of DP.

It is worthy to mention that the two Marc-Houwinck constants are applied for cellulose macromolecules, which are quite different from those corresponding to CMCNa counterparts, especially for high DS.

Table 2 summarizes the characteristics related to four CMCNa samples used as flocculants. It showed that QR1 (DS = 0.98; DP = 1040) was partially soluble in water and therefore considered as an unsuitable sample for flocculation tests. QR2 (DS = 1.17; DP = 480) was then chosen as an example for Jar test.

A commercial anionic flocculant (A_{100}PWG) combined with aluminium sulphate (as coagulant) was compared with CMCNa prepared in the present study.

1.2 Methods

1.2.1 Jar tests

Jar tests were carried out with special flocculating equipment (Floculateur W10408, Fisher Bioblock, Germany), to evaluate the flocculation performance of the prepared CMCNa. The Jar tests were batch experiments involving three successive steps, namely: (1) rapid mixing coagulation (200 r/min for 4 min) in which 4 mL of a coagulant solution (500 mg aluminium sulphate per litre) was added to 100 mL of water; (2) slow mixing flocculation stage (30–70 r/min for 15 min), in which a fixed quantity of the flocculating agent (6–14 mg) was added into the solution; and (3) solid/liquid separation in which the water was left for half an hour for sedimentation.

The flocculating equipment allowed four beakers to be agitated simultaneously at the same stirring velocity (from 0 to 250 r/min). After sedimentation, the supernatant was analyzed in terms of percentage of turbidity abatement (Abat):

$$\mathrm{Abat} = \frac{\mathrm{Tur}_0 - \mathrm{Tur}_f}{\mathrm{Tur}_0} \times 100\% \tag{2}$$

where, Tur_0 and Tur_f are the water turbidity before and after coagulation-flocculation treatment, respectively.

1.2.2 Effect of pH on coagulation-flocculation process

The pH study was done for the prepared CMCNa flocculant QR2 since the coagulation-flocculation process is pH dependent (Ismail, 1978; Abdel-Shafy et al., 1987, 1991; Tatsi et al., 2003; Anuradha and Malvika, 2006). Before rapid mixing coagulation, the pH value of seven water samples were adjusted to 1.92, 2.67, 6.12, 6.38, 7.09, 8 and 9.47 using HCl or NaOH solution. For this jar test experiment, the coagulant (aluminium sulphate) and flocculant (QR2) doses were fixed, respectively, at 500 mg/L and 100 mg/L.

1.2.3 Effect of flocculant dose

The effect of the flocculant dose was studied for QR2. In order to determine the optimal flocculant dose, 60, 80, 100, 120 and 140 mg of QR2 were added to a series of four water samples (100 mL for each) after a rapid mixing coagulation at 200 r/min, using aluminium sulphate as a coagulant. The tests of coagulation-flocculation were carried at optimum pH determined previously (Section 1.2.2) and the speed mixing flocculation was kept at 50 r/min.

1.2.4 Effect of flocculation mixing speed

The flocculation mixing speed was a significant parameter for the flocculation. A series of mixing speeds (30, 40, 50, 60 and 70 r/min) were tested during the flocculation at the optimal experimental conditions, i.e., pH = 8; coagulant and flocculant doses of 500 mg/L and 100 mg/L, respectively; and a mixing coagulation speed of 200 r/min.

1.2.5 Effects of DS and DP on flocculation performance

In the first step, the effects of DS and DP for the different qualities of CMCNa were studied. The performances of the prepared materials (abatement turbidity of the treated water) were evaluated according to the suitable coagulation-flocculation conditions for the developed flocculants.

In the second step, a comparative study of the flocculation performances achieved by the three prepared materials and that reached when using a commercial counterpart (A_{100}PWG) was performed. The coagulation-flocculation of the commercial A_{100}PWG flocculant was carried out under their optimum conditions, usually used in wastewater treatment industries. In such conditions, the comparison of the flocculants performances could be considered viable.

2 Results and discussion

2.1 Effects of pH on coagulation-flocculation process

As shown in Fig. 2, the maximum of turbidity abatement, approximately 90%, is obtained at about pH 7–8. Such pH values fall within the range of the optimal pH usually used in this kind of treatment (Edeline, 1992).

2.2 Effect of flocculant dose

Figure 3 shows the effect of the flocculant dose on the turbidity abatement. The most effective dose of the flocculating agent was found to be 100 mg/L of water to be treated. This dose is in the range of the normal anionic polyelectrolyte concentration used in this kind of treatment (Water Treatment Handbook, 1989). It corresponds to the maximum turbidity removal (close to 93%).

The increasing and decreasing trend in the turbidity abatement can be explained by the fact that for up to 100 mg/L, the increase of flocculant dose enhances the aggregation and consequently the particle settling. However, over the optimal dose, the excess of the flocculating agent would disturb sedimentation and cause the redispersion of the aggregated particles (Abdel-Shafy et al., 1987).

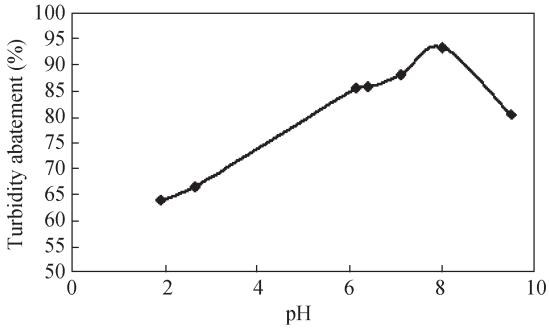

Fig. 2 Effect of pH on coagulation-flocculation performance.

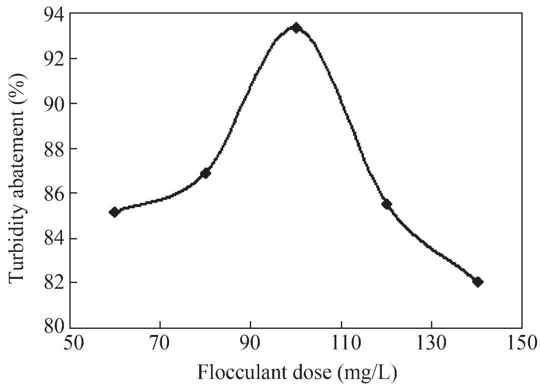

Fig. 3 Effect of the flocculant concentration on coagulation-flocculation performance.

2.3 Effect of flocculation mixing speed

The effect of the flocculation mixing speed was determined. Figure 4 shows a transition value around 50 r/min. For lower mixing speed, the turbidity abatement is relatively high and varies from 93% to 95%. However, up to 50 r/min, the turbidity abatement undergoes a notable decrease to reach 86%. The higher mixing speed leads to the break of the formed aggregated particles.

2.4 Effects of DS and DP on flocculation

Figure 5 shows the coupled effect of DS and DP on the flocculation performance. It can be observed that, when DS increases (DP decreases simultaneously), flocculation performance decreases from 95% for QR2 to 93% for QE2. These results are in agreement with literature (Edeline,

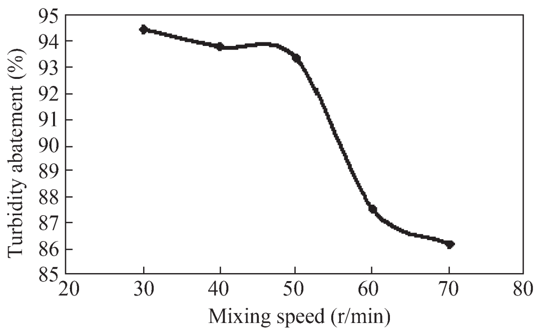

Fig. 4 Effect of the mixing speed on coagulation-flocculation performance.

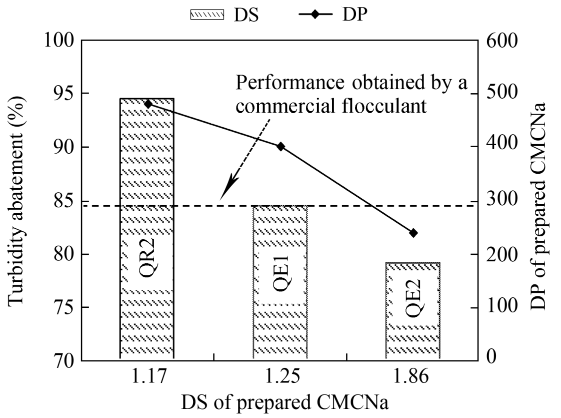

Fig. 5 Effect of DS and DP on the treatment performance.

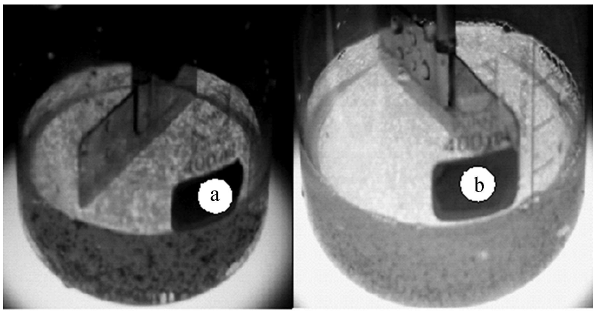

Fig. 6 Comparison of the shape of flocs obtained by the prepared and commercial flocculant. (a) flocs obtained by a QR2 flocculant; (b) flocs obtained by the commercial flocculant (A_{100}PWG).

1992), and indicates that coagulation-flocculation takes place following bridging mechanism, for which the performance of polyelectrolyte increases when DP increases and DS decreases

The comparative study of the three prepared CMCNa materials (QR2, QE1 and QE2) and the commercial flocculant (A_{100}PWG) is also studied. As shown in Figs. 5 and 6, the performance of the prepared flocculant (QR2) is 10% higher than that achieved by the commercial derivative. It can be deduced that the obtained flocs using QR2 as flocculant are bigger and heavier than those arising from the system based on the commercial polyacrylamide-based agent. The flocculation performances of the studied systems can be classified (from the lowest to the highest) as follows: QE2 < A_{100}PWG ≈ QE1 < QR2.

3 Conclusions

Three sodium carboxymethylcellulose (CMCNa) samples were prepared from an agricultural waste (date palms rachis) and used as flocculant for water turbidity removal. They were found to be eco-friendly and chemically efficient for water treatment. The best flocculation performance was observed at 100 mg/L of QR2 (DS = 1.17, DP = 480), pH 8 and a flocculation mixing speed 30 r/min. The comparative study with a commercial flocculant (A_{100}PWG) showed that QR2 has a better performance. The difference of the turbidity abatement between QR2 and A_{100}PWG reached 10%.

Acknowledgments

This work was supported by the Institute of Cooperation Francaise of the Embassy of France in Tunisia (IFC Tunisia) and by the Region Rhône Alpes (MIRA program). The author would like to thank Prof. BELGACEM Naceur for his valuable advice and assistance.

References

Abdel-Shafy H I, Abdel-Basir S E, 1991. Chemical treatment of industrial wastewater. *Evironmental Management Health*, 2(3): 19–23.

Abdel-Shafy H I, Abo-El-Wafa O, Azzam M A, 1987. Chemical treatment of industrial effluent. International Conference on Heavy metals in the Environment, New Orleans, 452.

Aguir C, M'henni M F, 2006. Experimental study on carboxymethylation of cellulose extracted from Posidonia oceanica. *Journal of Applied Polymer Science*, 98: 1808–1816.

Anuradha M, Malvika B, 2006. The flocculation performance of Tamarindus mucilage in relation to removal of vat and direct dyes. *Bioresource Technology*, 97: 1055–1059.

Baar A, Kulicke W, Szablikowski K, Kiesewetter R, 1994. Nuclear magnetic resonance spectroscopic characterization of carboxymethylcellulose. *Chemistry and Physics*, 195: 1483–1492.

Barai B K, Singhal R S, Kulkarni P R, 1997. Optimization of a process for preparing carboxymethylcellulose from water hyacinth (*Eichornia crassipes*). *Carbohydrate Polymers*, 32: 229–231.

Barba C, Rinaudo M, Farriol X, 2002. Synthesis and characterization of carboxymethyl celluloses (CMC) from non-wood fibers. I. Accessibility of cellulose fibers and CMC synthesis. *Cellulose*, 9: 327–335.

Barber E, 1961. CMC as a paper machine additive. *Journal Tappi*, 44: 179–185.

Botdrof J, Soap B, 1962. CMC in liquid detergents. *Chemical Specialties*, 38: 55–58.

Bromley D, Gamal El-Din M, Smith D W, 2002. A low cost treatment process to reduce phosphorus and suspended solids in liquid wastes from animal farm operations. In: Proceedings of the Fourth International Livestock Waste Management Symposioum and Technology Expo Malaysia Society of Animal Production, Penang, Malaysia, 215.

Edeline F, 1992. The Purge Physico-chemical of the Waters: Theory and Technology (2nd ed.). ISBN 2-87080-022-3. 212.

Grau P, 1991. Textile industry wastewaters treatment. *Water Science and Technology*, 24(1): 97–103.

Heinze T, Heinze U, Klemm D, 1994. Viscosity behaviour of multivalent metal ion-containing carboxymethyl cellulose solutions. *Die Angewandte Makromolekulare Chemie*, 220(3848): 123–132.

Heinze T, Pfeiffer K, 1999. Studies on the synthesis and characterization of carboxymethylcellulose. *Die Angewandte Makromolekulare Chemie*, 266(4638): 37–45.

Hidayati S, Rahayu K, Haryadi D, 2000. Bleaching of sugar cane bagasse as raw material for producing CMC. *Agrosains*, 13(1): 134–148.

Ismail M A, 1978. Chemical coagulation. *Proccedings of Florida State Hortorticultural Society*, 91: 142–150.

Kauper P, Kulicke W M, Horner S, Saake B, Puls J, Kunze

J, 1998. Development and evaluation of methods for determining the pattern of functionalization in sodium carboxymethylcelluloses. *Die Angewandte Makromolekulare Chemie*, 260(4571): 53–63.

Khiari R, Mhenni M F, Belgacem M N, Mauret E, 2010. Chemical composition and pulping of date palm rachis and Posidonia oceanica – A comparison with other wood and non-wood fibre sources. *Bioresource Technology*, 101: 775–780.

Lin X Q, Qu T Z, Qi S Q, 1990. Kinetics of the carboxymethylation of cellulose in the isopropyl alcohol system. *Acta Polymerica*, 41(4): 220–222.

Mann G, Kunze J, Loth F, Fink H P, 1998. Cellulose ethers with a block-like distribution of the substituents by structure-selective derivatization of cellulose. *Polymer*, 39(14): 3155–3165.

Olaru N, Olaru L, Stoleriu A, Timpu D, 1998. Carboxymethylcellulose synthesis in organic media containing ethanol and/or acetone. *Journal of Applied Polymer Science*, 67: 481–486.

Tapio S, Daniel V, Erkki P, 1994. Kinetic study of the carboxymethylation of cellulose. *Industrial & Engineering Chemistry Research*, 33: 1454–1459.

Tatsi A A, Zouboulis A I, Matis K A, Samara P, 2003. Coagulation-flocculation pre-treatment of sanitary landfill leachates. *Chemosphere*, 53: 737–744.

Togrul H, Arslan N, 2003. Production of carboxymethyl cellulose from sugar beet pulp cellulose and rheological behaviour of carboxymethyl cellulose. *Carbohydrate Polymers*, 54: 73–82.

Water Treatment Handbook, 1989. 9th edition, volume 1. ISBN 2.9503984.0.5.

Wise L E, Murphy M, d'Addieco A A, 1946. Chlorite holocellulose: its fractionation and bearing on summative wood analysis and on studies on the hemicellulose. *Paper Trade Journal*, 122(2): 35–43.

Yokota H, 1985. The mechanism of cellulose alkalization in the isopropyl alcohol-water-sodium hydroxide-cellulose system. *Journal of Applied Polymer Science*, 30: 263–277.