Bangladesh J. Sci. Ind. Res. **41**(3-4), 159-166, 2006

Studies on Preparation of Cobalt Carboxymethyl Cellulose from Agricultural Wastes

Ismet Ara Jahan,[a] and A. H. M. M. Rahman[b]

[a]Fibre and Polymer Division, BCSIR Laboratories Dhaka and
[b]Department of Applied Chemistry and Chemical Technology
University of Dhaka, Dhaka-1200, Bangladesh

Abstract

CMC was prepared from agricultural wastes-rice straw and wheat straw. This was then converted via its acidic form of CMC to CoCMC by reaction with Co (II) chloride. A maximum of about 7 % cobalt content in the product, CoCMC, obtained from both the sources was recorded, when 1.0 g of the acid form of CMC was treated with 5.0 g of Co (II) chloride in an overall mixture of 250 ml of water at 90^{O} C for 8 hours.

Introduction

The use of functionalized polymers in numerous applications has recently received considerable attention.[1-4] These polymers play a significant role in selective separation of metals. They have inherent advantages over single ion exchange resins.[5] In an earlier report some functionalized polymer complexes were described.[6,7]

Extensive works were done on carboxymethylation of cellulose using indigenous sources.[8-12] Some work was also done on preparation of NiCMC.[13] Preparation of CoCMC complex from water soluble sodium carboxymethyl cellulose has been reported.[14] We report now the preparation of CoCMC from the water insoluble acid form of CMC (HCMC) by reacting with Co (II) chloride. Considering the versatile property of CoCMC and considering rice straw and wheat straw as agriculturer wastes, we decided to prepare CoCMC fruitfully to utilize these waste materials.

Materials and Methods

Materials used

Rice straw (*Oriyza sativa*) and wheat straw (*Triticum aestivum*) were collected from the country site. Sodium hydroxide, monochloro acetic acid, copper sulphate, hydrochloric acid and cobalt (II) chloride used were of analar grade, (E Mark, Germany) absolute alcohol used was prepared by double distillation of rectified sprit over calcium oxide.

Preparation of HCMC

Cellulose was prepared from rice straw and wheat straw. It was then purified and analyzed by the usual method discussed in Method of Cellulose chemistry[15] and the isolated cellulose from these materials was found to contain 30.12 % and 30.5 % alpha cellulose respectively. Sodium carboxymethyl cellulose was prepared and purified by following the modified method.[17] Degree of substitution in each case was determined as 1.12 and 1.02 respectively by the modified copper precipitation method.[16] Water insoluble carboxymethyl cellulose i.e. the acid form of CMC was prepared from about 100 g of CMC from each of rice straw and wheat straw by the "acid wash" method.[16] It was then dried in vacuum and stored.

Preparation of CoCMC

1.0 g of HCMC was placed in a reaction vessel; 200 ml of de-ionized water was poured into it and allowed to stand for 12 h at a particular temperature (60^{O} C) in a thermostatic water bath. 50 ml of 10 % solution of cobalt (II) chloride was added dropwise into it with vigorous stirring. The reaction vessel was placed into a water bath with a condenser in reflux position whenever necessary for a predetermined period of time (2 hours). After the desired time period, the flask was removed from the bath and cooled to room temperature. The colour of the reaction mass was found to change from white to pink. The supernatant liquid was decanted off and then the residue was filtered under suction. The mass on the filter paper was washed several times with distilled water to free from the cobalt chloride. The purified product was then dried in vacuum and analyzed for its cobalt content.[18]

The above reaction was studied under varying conditions of temperatures and time. The range of temperatures was varied from 30^{O} C

Table I. Cobalt content in CoCMC samples prepared from rice straw at different time and temperature

Temp^{O} C (constant)	Time (variables)									
	30 min	1 h	2 h	3 h	4 h	5h	6h	7h	8h	10 h
30^{O} C	2.61	3.62	4.38	4.92	5.21	5.45	5.63	5.78	5.85	5.85
40^{O} C	3.18	4.12	4.91	5.41	5.72	5.93	6.08	6.15	6.22	6.22
50^{O} C	3.63	4.56	5.53	5.92	6.12	6.25	6.43	6.51	6.61	6.61
60^{O} C	3.81	4.84	5.92	6.25	6.45	6.61	6.75	6.81	6.86	6.86
70^{O} C	4.21	5.12	6.11	6.48	6.64	6.82	6.92	6.97	7.02	7.02
80^{O} C	4.45	5.26	6.19	6.51	6.73	6.91	6.98	7.05	7.08	7.08
90^{O} C	4.58	5.35	6.25	6.61	6.82	6.95	7.01	7.08	7.12	7.12
100^{O} C	4.58	5.36	6.26	6.61	6.82	6.95	7.01	7.08	7.12	7.12

to 100^{O} C and the time of reaction was varied from 30 mins to 10 hrs for each of the reaction under varied temperatures. The cobalt content in the products are shown in Tables I and II and graphically presented in Figs. 1, 2, 3 and 4.

Table II. Cobalt content in CoCMC samples when prepared from wheat straw at different time and temperature

Temp^{O} C (constant)	Time (variables)									
	30 min	1 h	2 h	3 h	4 h	5h	6h	7h	8h	10h
30^{O} C	2.41	3.61	4.26	4.65	4.93	5.23	5.46	5.61	5.74	5.75
40^{O} C	2.75	3.86	4.78	5.18	5.45	5.72	5.92	6.06	6.17	6.17
50^{O} C	3.02	4.11	5.19	5.58	5.88	6.11	6.32	6.44	6.56	6.56
60^{O} C	3.41	4.34	5.48	5.82	6.12	6.41	6.61	6.73	6.85	6.86
70^{O} C	3.65	4.56	5.74	6.03	6.31	6.58	6.74	6.87	6.95	6.95
80^{O} C	3.82	4.78	5.88	6.17	6.42	6.65	6.81	6.92	6.98	6.99
90^{O} C	3.95	4.91	5.92	6.22	6.48	6.71	6.85	6.95	7.03	7.04
100^{O} C	3.96	4.92	5.92	6.22	6.48	6.71	6.86	6.95	7.03	7.04

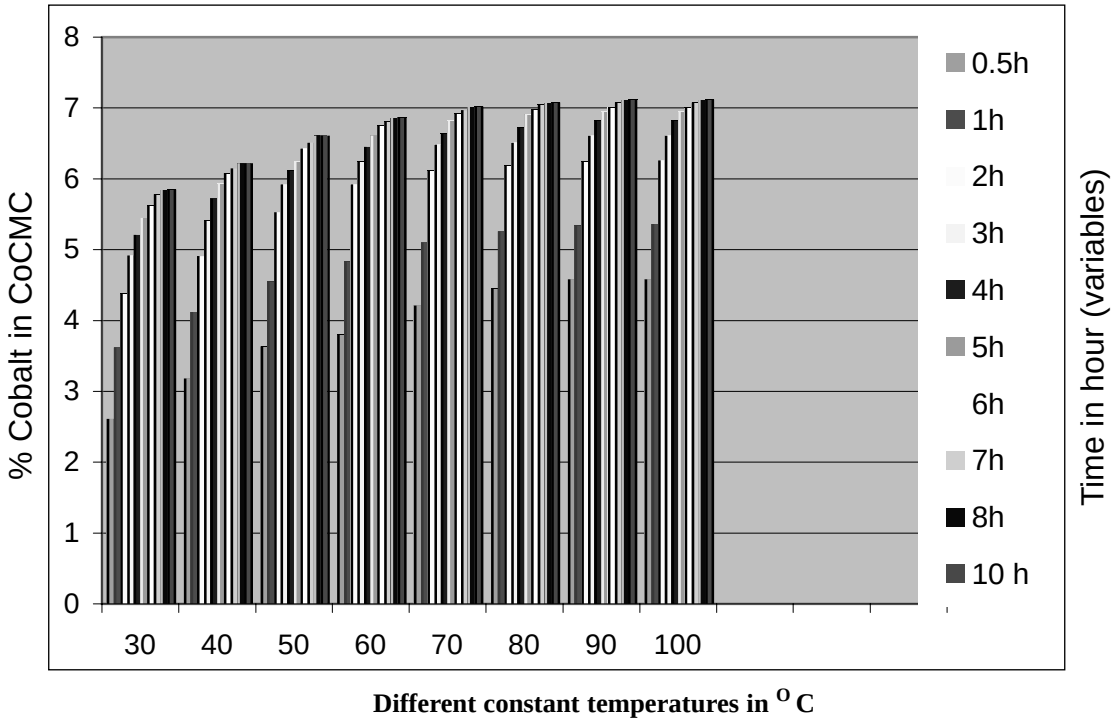

Fig. 1. Cobalt content in CoCMC samples when prepared from cellulose of rice straw at different constant temperature with the variation of time

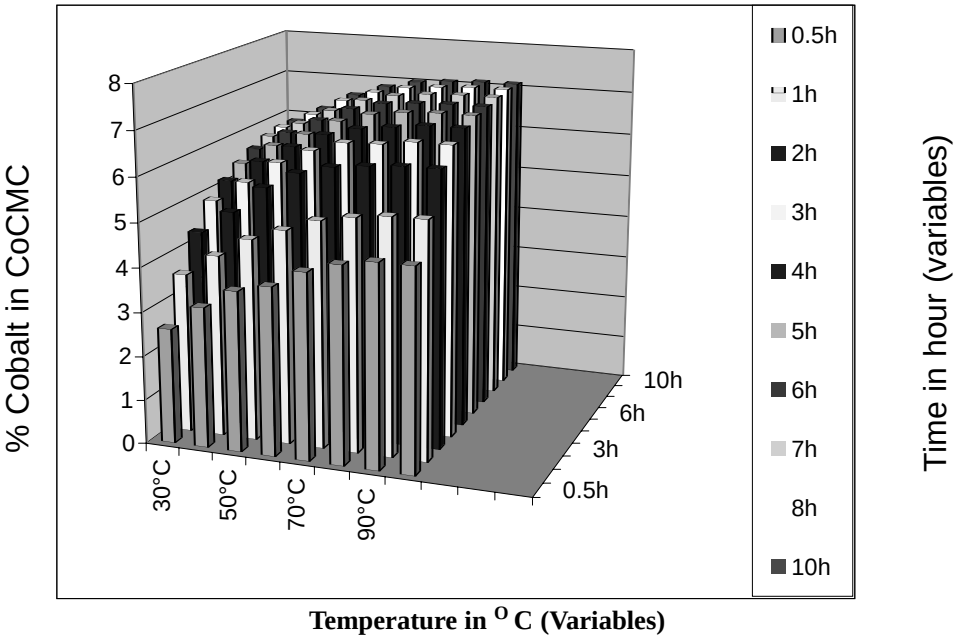

Fig. 2. Cobalt content in CoCMC when prepared from cellulose of rice straw at different constant time with the variation of temperature.

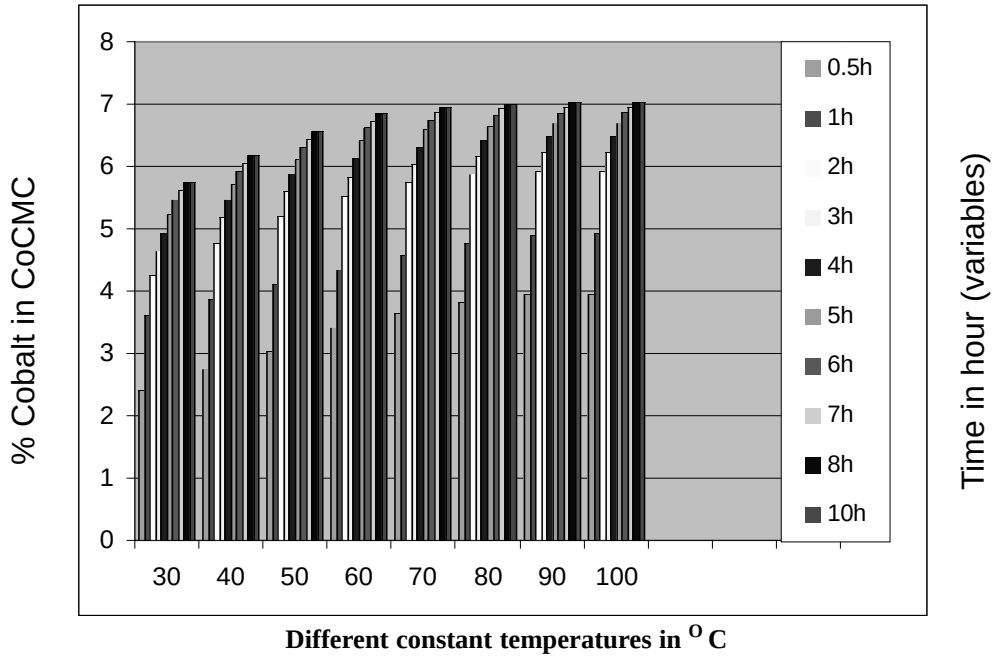

Fig. 3. Cobalt content in CoCMC samples when prepared from cellulose of wheat straw at different constant temperature with the variation of time

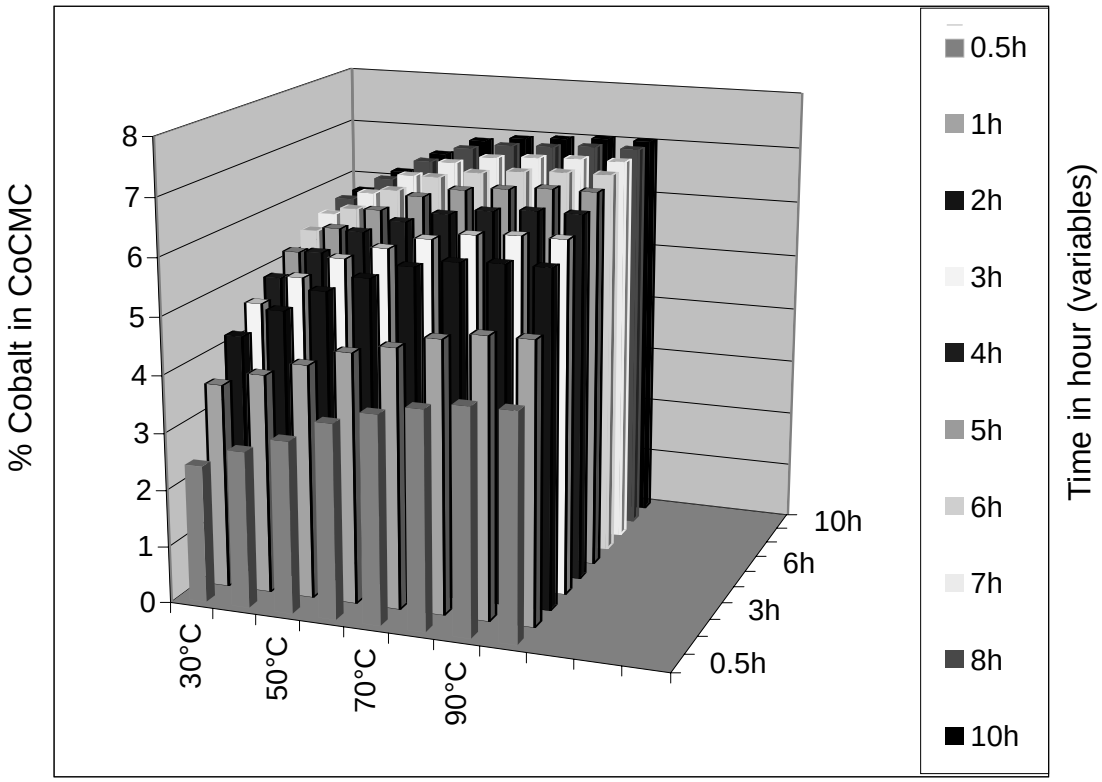

Fig. 4. Cobalt content in CoCMC when prepared from cellulose of wheat straw at different constant Time with the variation of Temperature.

Determination of cobalt content in CoCMC

(a) Extraction of cobalt: 1.0 g of CoCMC was extracted with 25 ml of 4 N H_2SO_4 for 6 hours and then filtered. The residue was extracted twice in the same way. The extracted solution was filtered through the filter paper (No. 1) and neutralized with ammonia solution and then made upto 100 ml. The cobalt content in the extracted sample (100 ml) was determined through the preparation of $Co[Hg(SCN)_4]$. This method is based on the fact that cobalt (II) in neutral solution forms a blue complex $Co[Hg(SCN)_4]$ when 1 mole of mercuric chloride is

mixed with 4 moles of ammonium thiocyanate in water.[18]

(b) Preparation of Co [Hg (SCN)$_4$]

To 25 ml of the extracted neutral solution, 5.2 ml of 6 % ammonium thiocyanate solution was added and mixed with 4.8 ml of 5.4 % mercuric chloride solution and stirred vigorously for a few minutes. The reaction mixture was left for about 2 hours. A dark blue precipitate of Co[Hg(SCN)$_4$] was formed. The precipitate was collected in a weighed sintered glass crucible (Porosity No. 4) and filtered under suction. The precipitate was washed with 2-3 ml of dilute solution of theprecipitating reagent which was prepared by adding 1.0 ml of each of the solutions of mercuric chloride (5.4 %) and ammonium thiocyanate (6 %) to 100 ml of water and finally washed with 5 ml of ice cold water. The purified sample was then dried in vacuum and then in an electric oven at 105^{O} C up to the constant weight.

The cobalt content in CoCMC samples was determined by calculating out the cobalt content in Co[Hg (SCN)$_4$] from the relation:

1.0 g of Co[Hg (SCN)$_4$] = 0.1198 g of Co^{+2}.

Each of the samples was prepared and analyzed for cobalt content at least twice and the average of the results was taken.

Results and Discussion

Water-soluble salt of carboxymethyl cellulose was prepared from alpha cellulose of rice straw and wheat straw and then converted into their corresponding water insoluble acid form of carboxymethyl cellulose (HCMC). This was then converted to CoCMC by reacting with Co (II) chloride.

Now if we look at each of the vertical column in both the Tablets I and II i.e. when the reaction time is maintained constant within the range of study, it appears that the cobalt content in CoCMC, irrespective of the source of preparation, increases gradually with the rise of temperature upto about 70^{O} C and then it slows down and ultimately no further increase in cobalt content is observed after about 90^{O} C.

Again if we go along any of the horizontal lines i.e. when the temperature remains constant and the reaction time varies within the range of study, we find that the cobalt content in the product, CoCMC, increases steadily with the increase of time and this trend of increase persists in all cases upto the reaction time of 7 or 8 hours and then no further increase in cobalt content in CoCMC takes place even if the reaction is prolonged beyond 8 hours. The graphs 1 to 4 also bear similar impressions as described.

From the results obtained (Table I and II) it is observed that CoCMC prepared from acid form of CMC can not be prepared beyond the maximum Co-content of 7.12 % from rice straw and 7.03 % from wheat straw under the reaction conditions employed during this research. So the study revealed that CoCMC with a maximum cobalt content of 7.12 % and 7.03 % respectively could be prepared when one g each of the acid form of CMCs from rice straw and wheat straw was impregnated with five times by weight of Cobalt (II) chloride in a mixture containing 250 ml of water and heated at 90^{O} C for 8 hours. This study may also be used for the selection of reaction parameters to obtain a CoCMC sample containing a predetermined amount of Co-content.

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