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REMOVAL OF HEAVY METALS FROM WASTEWATERS BY CELLULOSE XANTHATE CHELATING EXCHANGERS

The synthesis of the cellulose xanthate for metal removal has been carried out under conditions different from those currently adopted in the rayon industry. Cheap, stable and water insoluble materials suitable for removing heavy metals from industrial wastewaters have been obtained.

The products in sodium and magnesium forms were tested with synthetic and industrial wastewaters containing Cu, Hg, Ag and Cd either in batch or in column operations.

Results showed that the cellulose xanthate, in magnesium form, is stable at room temperature for at least 1 year; it has a removal capacity of about 0.8 mmol of metal/g and a sparingly water solubility (10%). It can also be used in column operation as "polishing" according to its swelling and mechanical properties. The exhausted materials after metal uptake can be successfully post-treated either thermally or by chemical oxidation with sodium hydrochlorite for metals recovery and reuse.

1. INTRODUCTION

The removal of toxic metals from wastewaters is generally achieved by processes such as chemical precipitation (hydroxides, sulphides, oxides), ion exchange, adsorption, etc. [1]–[4]. Recently research on synthetic or semi-synthetic polyelectrolytes for metal removal in order to lower the process costs has been carried out [5]–[7]. In this context selectivity of metal ions was the fundamental parameter to overcome problems associated with the production and disposal of toxic sludges on concentrated streams.

In 1973, SWANSON studied a precipitation process utilizing starch (a cheap and natural product), in which xanthate groups were synthesized [8], [9]. Later WING and co-workers [10] synthesized and insoluble starch xanthate by preliminary crosslinking the natural starch with epichlorohydrin. This leads to higher preparation costs. In the meantime HANWAY [11], [12] studied the possibility of utilizing cellulose xanthate (an intermediate product in viscose

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manufacture) as a precipitating reagent for metal immobilization. He obtained a water insoluble product which was stable at room temperature for at least three months. Recently [13], [14] the use of starch xanthate products has been further investigated.

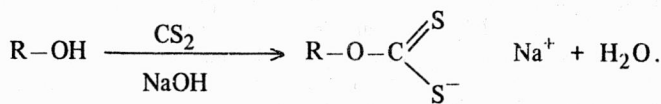
It was found that processing of the water soluble starch xanthate allowed us to lower metal concentration in the effluent to ppb levels for many heavy metals like Hg, Cd, Cu, Ag, Ni, Cr(III) in a large pH interval (between 3 and 11) and at high ionic strengths [13], [15], [16]. However, a cationic polyelectrolyte must be used to improve metal removal.

The starch xanthate process has been developed to a pilot scale level and it has been applied to chloralkali wastewaters for mercury removal and recovery [17]. At the same time, research has been carried out [18], in order to develop new ways of synthesizing xanthate products of high stability, high water insolubility, high metal uptake, and low cost.

In this paper, the synthesis and properties of cellulose xanthate as cheap, stable and effective material for metal removal are described.

2. EXPERIMENTAL

Generally the xanthation reaction is carried out according to the reaction:



The synthesis was optimized by investigating the effect of the following parameters:

degree of polymerization of the starting cellulose;

NaOH/cellulose molar ratio during the synthesis;

content of CS₂ in the xanthation reaction;

different purification and dewatering operations of the products to increase their stability at room temperature.

In fig. 1 the solubility of the obtained xanthate products as a function of the degree of polymerization (DP) of the cellulosic substrate is shown.

Table 1 reports the characteristics of different cellulose xanthates (CX) for rayon production and for metal removal, respectively. The main differences are referred to the polymerization degree and to the water solubility.

The best conditions found for the synthesis of CX compounds are as follows. The cellulose sheets (PD ~ 2200) were contacted with 11% NaOH solution at 20°C for 1 h. The alkali cellulose so formed was then pressed up to a cellulose/alkali cellulose weight ratio equal to 0.5. Afterwards the material was mechanically disintegrated in small particles at 30°C for 20 min. The alkali-cellulose was then placed in a closed reactor at 32°C under nitrogen blanket, CS₂ added (35% in weight to the starting cellulose) and the mixture allowed to rest for 1.5 h.

After filtration the cellulose xanthate, sodium form (CX-Na) was dewatered under vacuum and dried.

The Mg form of the CX was obtained by treating an aliquot of the CX-Na, prepared in the way described above, with a MgSO₄ saturated solution at 0°C. The product (CX-Mg) was then filtered and dewatered as before.

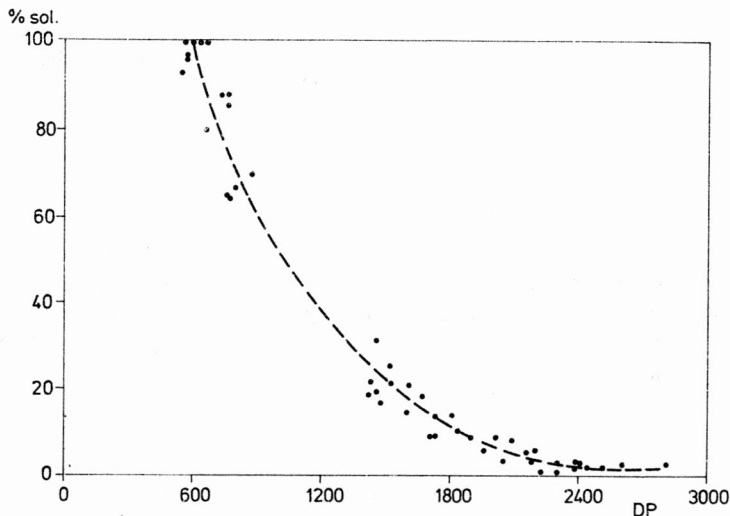


Fig. 1. Solubility (%) of the cellulose xanthate (Na form) versus the polymerization degree (DP) of the cellulose utilized in the synthesis

Table 1

Characteristics of cellulose xanthates used for rayon production and those required for heavy metal removal

| Parameter | Cellulose xanthate | |
|----------------------------|--------------------|---------------|
| | Rayon | Metal removal |
| Polymerization degree (DP) | 300 | ~ 2200 |
| NaOH/cellulose ratio | 0.47 | 0.23 |
| Degree of substitution | 60 | 56 |
| Solubility in water (%) | 100 | 2.7 |

After preparation the compounds were stored in closed vessels at room temperature.

The characterization of both the products has been carried out by standard analytical procedures. The total reactive sulphur was determined by iodometric titration [19], and the soluble xanthic sulphur by elimination of the soluble impurities on anionic exchanger Amberlite IRA 400, OH form [20], and iodometric titration of the filtered solution.

The "operative" water solubility was evaluated by preparing a slurry of CX in water, stirring it at room temperature for 30 min filtering (rapid paper) the mixture, and iodometric titrating the filtered solution and rinsing waters.

The H_2S (from sulphides and trithiocarbonates) and CS_2 (from xanthate and trithiocarbonate) contents were determined by standard methods [21].

The metal removal capacity of the materials was determined by measuring the metal uptake according to the following procedure. An aqueous CX slurry was added to the solution con-

taining ionic copper ($500 \mu\text{g}/\text{cm}^3$) at pH 5; the pH was maintained constant by a "pH-stat" system, and the Cu^{2+} activity in solution was followed by Cu^{2+} selective electrode (Metrohm EA 306-Cu) and double junction reference electrode (Metrohm EA 440 Ag/AgCl).

All metals concentration were determined by standard AAS.

3. RESULTS AND DISCUSSION

Table 2 presents the total sulphur, the xanthic sulphur, and the H_2S and CS_2 contents obtained from different amounts of cellulose during the synthesis carried out with a 11.5% NaOH. The analytical characterization of the cellulose xanthates in sodium (CX-Na) and magnesium (CX-Mg) forms is reported in tab. 3.

Table 2

Analytical results obtained for the alkali-cellulose and CX/Na after two different preparations. Concentration of NaOH, 11.5%

| Alkali-cellulose | | | Cellulose xanthate-Na form | | | |
|------------------|-----------------|----------|----------------------------|----------------------------|-----------------------------------|------------------|
| <i>A</i> (%) | <i>B</i> (%) | <i>R</i> | S (total) (%) | S (CS_2) (%) | S (H_2S) (%) | S (xanth) (%) |
| 38.3 | 9.2 | 0.24 | 8.02 | 7.70 | 0.32 | 7.06 |
| 42.5 | 9.6 | 0.23 | 8.53 | 8.09 | 0.44 | 7.21 |

A – cellulose content in the alkali-cellulose.

B – NaOH content in the alkali-cellulose.

R – NaOH/cellulose ratio.

Table 3

Analytical characterization of cellulose xanthates, sodium and magnesium forms

| Parameter | CX-Na | CX-Mg |
|-----------------------------------|-------------|-------------|
| Total reactive sulphur (meq S/g) | 2.65 | 0.81 |
| Total xanthic sulphur (meq S/g) | 1.0 | 0.77 |
| Soluble xanthic sulphur (meq S/g) | 0.18 | 0.04 |
| Removal capacity at pH (meq S/g) | 2.50 | 0.80 |
| Water content (%) | 8.0 | 6.0 |
| Water solubility (%) | 53.6 | 11.1 |
| Stability at room temperature | > 12 months | > 12 months |

The results show that the removal capacity of CX-Na is higher than that of CX-Mg (2.50 and 0.80 meq/g, respectively). It is worth noting that CX-Na is soluble in water in at least 50%: during the metal uptake colloidal yellow highly swelled suspensions are formed. CX-Mg solubility in water amounts only to 10%; it swells moderately and it is resistant to mechanical stresses.

The results of CX-Mg kinetic runs, carried out in continuous stirred tank reactors (CSTR) as reported in fig. 2, show that the kinetics of metal uptake decreases with increasing the atomic weight of the metal. It has been proved that the amount of Mg released in solution was considerably higher than the metal uptake. This seems to indicate that some Mg was still present in the CX-Mg and it was not completely washed off during purification of the compound. During the runs, the pH of the solutions increased from 5 to 9 due to synthesis of the precipitating reagent causing alkalinization; a contemporary precipitation of some metal hydroxides cannot be excluded.

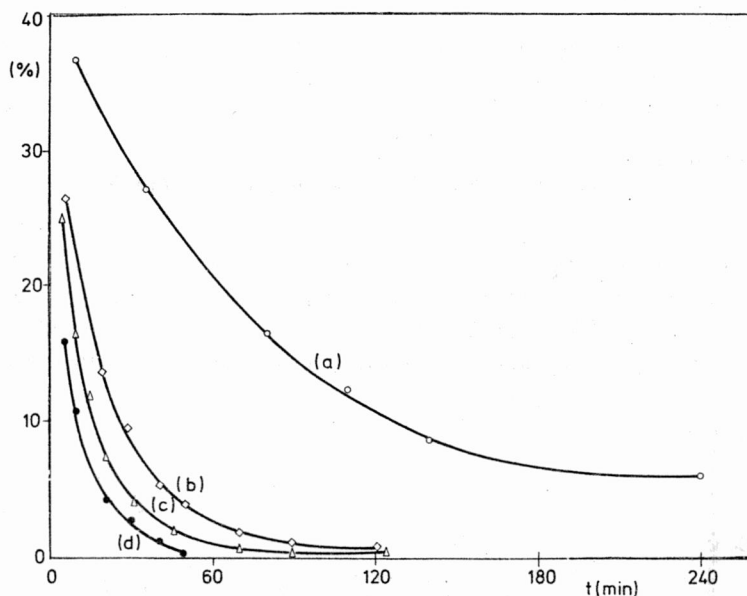


Fig. 2. Residual metal concentration in solution (%) as a function of time after treatment with CX-Mg
 · Molar ratio CX-Mg/metal = 1; initial metal concentration = $30 \mu\text{g}/\text{cm}^3$;
 initial (final) pH = 5 (9); (a) - Hg; (b) - Cd; (c) - Ag; (d) - Cu

Both CX-Na and CX-Mg were tested on laboratory scale with synthetic and industrial wastewaters containing Cu, Ag, Hg, and Cd. The results showed that both materials can be used for metal removal: CX-Na is effective in continuously stirred tank reactors (CSTR) in the same way as the water soluble starch xanthate material [17], while CX-Mg can also be used in column operations.

Table 4 reports the data obtained from column experiments in which aqueous solutions of Cu, Ag, Cd, and Hg ($30 \mu\text{g}/\text{cm}^3$) were fed separately. The flow rate was $10 \text{ cm}^3/\text{cm}^3 \cdot \text{h}$. The data show that Cu, Ag, Cd, and Hg concentrations below the current Italian limits to the effluents [22] are reached after treating 65, 168, 130, and $45 \text{ cm}^3/\text{cm}^3 \cdot \text{r}$, respectively. The corresponding operating capacities are 9.28, 19.9, 16.7, and 5.5 mg of metal/g CX-Mg, which are, of course, only a fraction of the total available capacity.

Table 4

Experimental results obtained by column operation utilizing cellulose xanthate, Mg form
Flow velocity, $10 \text{ cm}^3/\text{cm}^3 \cdot \text{r} \cdot \text{h}$; total capacity of CX-Mg, 1.2 mmol/g . Separate experiments
for each metal solution

| Parameter | Cu | Ag | Cd | Hg |
|--|------|------|------|-------|
| Initial concentration ($\mu\text{g}/\text{cm}^3$) | 30 | 30 | 30 | 30 |
| Initial pH value | 6.5 | 6.6 | 7.0 | 7.2 |
| Amount of CX-Mg used (g) | 8.4 | 7.6 | 7.0 | 7.3 |
| Bed volume (cm^3) | 40 | 30 | 30 | 30 |
| Effluent concentration limits in Italy ($\mu\text{g}/\text{cm}^3$) | 0.1 | 0.2* | 0.02 | 0.005 |
| Treated water ($\text{cm}^3/\text{cm}^3 \cdot \text{r}$)** | 65 | 168 | 130 | 45 |
| Operative exchange capacity** (mmol/g CX-Mg) | 0.15 | 0.18 | 0.15 | 0.028 |

* USA regulation.

** Runs in which a leakage was obtained corresponding to the effluents concentration limits imposed by Italian law.

Further analytical investigations for dissolved species in solution gave following results: sulphides, not detectable; CS_2 , traces; COD, $< 10 \mu\text{g}/\text{cm}^3$. This was a clear indication that the organic matrix of CX-Mg was stable during the runs. An interesting application of CX-Mg column operation is polishing unit for removing trace amounts of metals (which were not

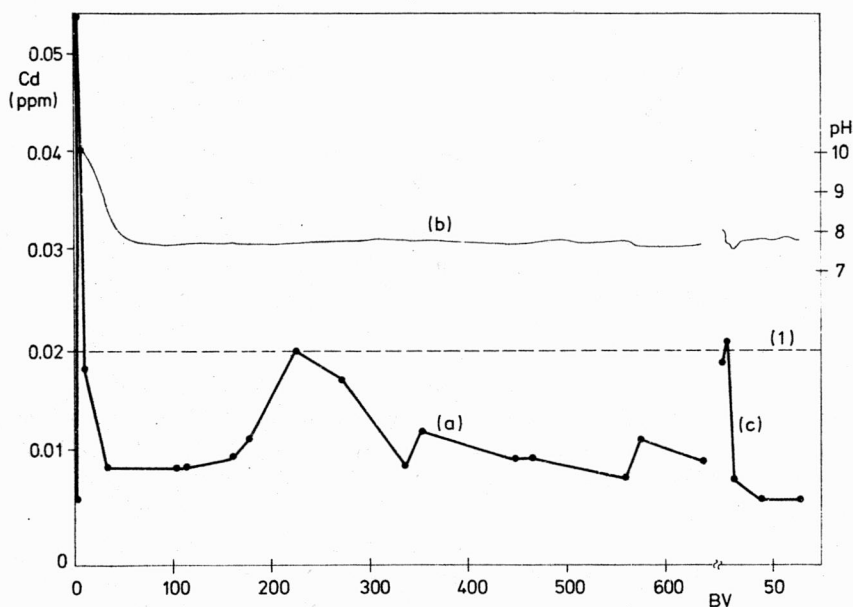


Fig. 3. Removal of trace amounts of cadmium (curve a) from a galvanic effluent treated with CX-Mg in column operation

Initial pH value - 9.6; initial Cd concentration - $0.054 \mu\text{g}/\text{cm}^3$; curve (b) - pH; curve (c) - run interrupted for 3 months; (1) - Italian limit for discharge of Cd into the effluents

sufficiently removed by traditional wastewater processes). As an example, fig. 3 shows the results obtained using a CX-Mg column fed with a plating rinsing wastewater after treatment by conventional ion-exchange and containing $0.054 \mu\text{g Cd/cm}^3$. It is worth noting that the content of Cd in the product water is lower than $0.02 \mu\text{g/cm}^3$ (fig. 3, (1)) which is the Italian limit for cadmium discharge into the effluents. The run was interrupted for at least 3 months (fig. 3, (c)). Afterwards the metal removal capability was the same as before, thus confirming the good stability CX-Mg.

The exhausted materials after metal uptake were post-treated either thermally or by chemical oxidation (except for Ag) with sodium hypochlorite in acidic media for metals recovery and reuse. The data (tab. 5) indicate a yield between 70 and 90%.

Table 5
Metal recovery from exhausted CX-Mg by chemical oxidation with 8% NaClO solution (150% of the stoichiometric amount) at pH = 3.5 with HCl and by incineration at 600°C

| Parameter | Cu | Ag | Cd |
|------------------------------------|-------|-------|-------|
| Metal content (g) | 0.121 | 0.246 | 0.152 |
| Total amount of treated sludge (g) | 8.4 | 7.6 | 7.0 |
| Yield of metal recovery (%) | | | |
| by incineration | 89 | 89 | 77 |
| by chemical oxidation | 72 | — | 89 |

4. CONCLUSIONS

Synthesis of cellulose xanthate materials capable of removing metals from wastewaters has been carried out. Two different products have been obtained: the sodium and magnesium xanthates.

Satisfactory performances were obtained using the CX-Mg compound. It is highly water insoluble, stable at least for 1 year, its total metal uptake, determined by potentiometric methods, is 0.8 meq/g and its physical characteristics are suitable for use in column operations.

Both CX-Na and CX-Mg could be used in batch (CSTR) operations, while good results were obtained when CX-Mg was used as "polishing" for removing relatively low metal concentrations still present in the wastewaters after conventional treatment processes.

The metals after uptake can be recovered by treating the materials either thermally or by chemical oxidation.

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USUWANIE METALI CIĘŻKICH ZE ŚCIEKÓW
PRZEZ CHELATUJĄCE WYMIENIACZE KSANTANOWE

Syntezę ksantatu używanego do usuwania metali prowadzono w różnych warunkach przystosowanych do produkcji sztucznego jedwabiu. W wyniku otrzymano tanie, trwałe i nierozpuszczalne w wodzie tworzywo odpowiednie do usuwania metali ciężkich ze ścieków przemysłowych. Zarówno forma sodowa jak i

magnezowa otrzymanego ksantatu była testowana w syntetycznych i przemysłowych ściekach zawierających miedź, rtęć, srebro i kadm albo w procesie okresowym, albo kolumnowym.

Otrzymane wyniki wskazują, że ksantat w formie magnezowej jest trwały w temperaturze pokojowej przez co najmniej rok. Jego zdolność do usuwania metali wynosi około 0,8 mmola metalu/g, a rozpuszczalność w wodzie jest niewielka (10%). Ksantat ten może być również użyty podczas pracy kolumny jako „wyładowacz” z powodu swoich właściwości spęczniających i mechanicznych. Zużyty ksantat po absorpcji metalu może być wtórnie oczyszczany albo termicznie, albo przez chemiczne utlenienie z chlorowodorkiem sodu w celu odzysku metali i ponownego użycia.

УДАЛЕНИЕ ТЯЖЕЛЫХ МЕТАЛЛОВ ИЗ СТОЧНЫХ ВОД ЧЕРЕЗ ХЕЛАТИРУЮЩИЕ КСАНТОГЕНАТНЫЕ ИОНООБМЕННИКИ

Синтез ксантогената, употребляемого для удаления металлов, проводили в разных условиях, приспособленных для производства искусственного шелка. В результате этого получили дешевый, устойчивый и нерастворимый в воде материал, подходящий для удаления тяжелых металлов из промышленных сточных вод. Как натриевая, так и магниевая формы полученного ксантогената были тестированы в синтетических и промышленных сточных водах, содержащих медь, ртуть, серебро и кадмий или в периодическом, или колонном процессах.

Полученные результаты показывают, что ксантогенат в магниевой форме является устойчивым в комнатной температуре минимально в течение года. Его способность к удалению металлов составляет около 0,8 ммоль металла/г, а растворимость в воде является небольшой (10%). Этот ксантогенат может также применяться во время работы колонны в качестве “валцующего материала” из-за своих вспучивающих и механических свойств. И использованный ксантогенат после абсорбции металла может быть повторно очищен термически или посредством химического окисления с хлоргидратом натрия с целью регенерации и повторного употребления.