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REMOVAL OF MERCURY BY PRECIPITATION WITH STARCH XANTHATE

1. INTRODUCTION

Toxic metals can be removed from wastewaters by different processes, such as the precipitation of oxides, hydroxides, sulphides or carbonates, ion exchange, adsorption and electrodeposition or membrane processes. Application of each of them is connected with different problems and operation difficulties [2], [3], [6]. The main problems of precipitation are connected with reagent cost and optimization of operating conditions, considering the complexity of the waters to be treated and the disposal of resultant toxic sludge. The use of precipitating reagents in the form of wide-spread renewable products with functional groups of a high reactivity with toxic metal ions offers a solution to these problems. Promising results have been obtained when metal ions were removed by precipitation with starch xanthate [8], [9]. A further advantage of this process is that it produces a sludge from which the metal may be recovered.

Table 1

Composition of wastewaters containing mercury

Skład ścieków zawierających rtęć

Composition	Chlorine–soda	Petrochemical industries (mercury for catalysis)
Mercury, total, mg/dm^3	1–10	1–50
Iron, mg/dm^3	–	2–6
Aluminum, mg/dm^3	–	1–6
Silica, mg/dm^3	–	10–50
Chloride, mg/dm^3	6000–60000	20000–50000
Active chlorine (Cl_2), mg/dm^3	0–100	–
Suspended solids, mg/dm^3	100–400	50–500
Organics, mg/dm^3	–	100–200
pH	10	0.2–0.8
Flow rate, m^3/h	15–60	10–20

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This paper reports preliminary results from the study on the mercury removal from aqueous solutions that simulate the effluents (tab. 1) from chlorine and soda plants [5] and from petrochemical processing plants [1] by precipitating it with starch xanthate. Mercury was chosen because of its high toxicity and its capacity of accumulation in the food chain as well as due to its possible reactions with other substances to be found in discharge wastewaters.

In this paper the applicability aspects and feasibility of the mercury removal method herein proposed are emphasized.

2. EXPERIMENTAL

2.1. REAGENTS

Starch xanthate was synthetized, as reported in [4]. To purify this viscous substancer containing sulphide impurities due to the xanthation process, a strong base anion exchanges (Amberlite IRA–400, standard grade, Carlo Erba) was used. The following procedure ha been applied: 4 g of commercial xanthate were dissolved in 50 cm^3 of distilled water and 12 g of the anion exachanger were added. The mixture, diluted to 100 cm^3, was stirred magnetically for 10 min. Thereupon, the solution was filtered through glass wool and diluted to 250 cm^3 Purified starch xanthate was standardized by iodimetric titration according to the following procedure: 10 cm^3 of 10 % acetic acid solution and 100 cm^3 of xanthate solution were poured into stoppered flask containing 25 cm^3 of 0.1 N iodine solution. The flask was stirred for 15 min and then excess of I_2 was back-titrated with standard 0.1 N thiosulphate standard solution until decolouring was observed. Thiosulphate standard solution was Merck standard.

Mercury solution was prepared from BDH A. A. purity mercury nitrate. All other reagents were of analytical grade.

2.2. APPARATUS

Vittadini Multistirrer with 8 cm blades and automatic speed and running time controls, model 430 Perkin–Elmer atomic absorption spectrophotometer, model 361 Amel pH-meter and model 1330 Perkin–Elmer IR spectrophotometer were used.

2.3. PROCEDURE

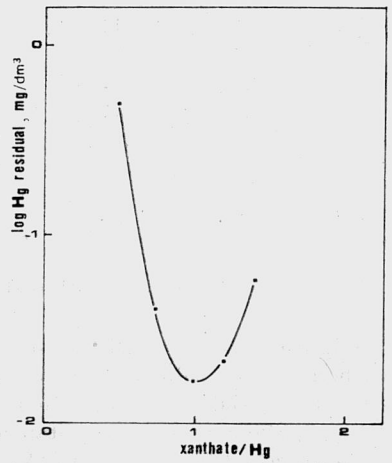
The experiments were carried out at constant temperature (293 K); 500 cm^3 of the mercury sample solution at concentrations ranging from 1 to 10 mg/dm^3 were placed in a 1000 cm^3 high-shape beaker. Prior to the test, pH of the solution was adjusted with HNO_3 or NaOH. Because of the characteristics of the industrial wastewaters (tab. 1) we have used $NaNO_3$ in order to bring ionic strength to 0.1 M. The so-obtained solution was stirred at 50 rpm by means of a multistirrer so that the reagent system inside the beaker be uniformly mixed. Then the prefixed amount of starch xanthate was gradually added. The suspension was stirred at the same speed for 2 h, the time compatible with that applied in industrial scale. Preliminary tests showed that a two hour stirring was sufficient to ensure completion of the precipitation, at least in the absence of chlorides. After two hour settling, the precipitate was separated from the liquid phase by 15 min centrifugation. The supernatant was then analyzed for mercury content by atomic absorption spectrometry.

3. RESULTS

Preliminary tests were performed in the 2–12 pH range at a xanthate to mercury stoichiometric molar ratio of 2:1. This stoichiometry was based on the generally assumed reaction between xanthate and bivalent metals [7], [10]:

$$2\ \text{starch–OCSS}^- + \text{Me}^{2+} \rightarrow (\text{starch–OCSS})_2\text{Me}.$$

Tests showed the presence of a colloidal precipitate which, however, could not be separated. Therefore, it was of no interest for mercury removal. Further tests performed



Residual mercury versus xanthate: mercury molar ratio in absence of chlorides at pH 2 and initial mercury concentration 10 mg/dm³
Each point represents the mean value of five measurements

Rtęć resztkowa w zależności od molarnego stosunku ksantogenianu do rtęci przy pH 2, nieobecności chlorków i początkowym stężeniu rtęci równym 10 mg/dm³

at lower molar ratios showed that the precipitate could easily be separated from the liquid phase. That is why the xanthate to mercury ratio was taken as a parameter, its optimum value was determined as 1:1, i.e. half of the initially assumed stoichiometer value. One of the experimental curves is shown in the figure. Similar patterns were also obtained at the high values of pH.

3.1. TESTS IN ABSENCE OF CHLORIDES

Results of tests carried out in the pH ranging from 2 to 12 may be summarized as follows:

good reproducibility of mercury removal results ($\pm 0.02\,\%$),

very low residual mercury concentration ($< 20\ \mu g/dm^3$),

initial mercury concentration is inversely proportional to the time required for first appearance of visible precipitate.

The data obtained for tests conducted at pH 2 are given as an example in tab. 2.

Table 2

Residual mercury concentration at pH = 2 in absence of chlorides, xanthate: mercury ratio = 1:1

Resztkowe stężenie rtęci przy pH = 2 i w braku chlorków, stosunek ksantogenianu do rtęci = 1:1

Initial mercury concentration mg/dm³	* min	Residual mercury concentration μg/dm³ ± SD **	Mercury removal %
10	5	17 ± 6	99.83
5	13	7 ± 1	99.83
3	20	9 ± 1	99.70
2	30	7 ± 1	99.65
1	70	12 ± 1	98.80

* Time required for precipitates to appear.
** Mean of at least five measurements.

3.2. TESTS IN PRESENCE OF CHLORIDES

Tests performed at pH ⩽ 9, in presence of 0.05 M Cl^-, showed, in general, that mercury removal efficiency during two hour reaction did not exceed 70–80%, its residual concentration being some mg/dm³ when the initial value was 10 mg/dm³. These tests also showed that levels of mercury removal comparable with those obtained in the absence of chlorides could be obtained when the reaction lasted for a few days. At pH 9 this may be due to the formation of chloro-complexes which seem to exert a precipitation-inhibiting kinetic effect. The tests conducted at pH 10 and 11, at which chloro-complexes are not formed even if the concentration of chlorides is high, have shown that the efficiences of mercury removal are comparable with those obtained in the absence of chlorides (tab. 3).

3.3. ANALYSIS OF PRECIPITATES

Infrared and X-ray analyses of the precipitates have shown that their behaviour is similar to that of mercury sulphide, probably because an Hg–S bond is formed and crystal arrangement is cubic.

4. CONCLUSIONS

The results obtained show that, in absence of chlorides and within the considered pH range (2–12), mercury can be removed quantitatively to a final residual level of < 20 μg by precipitation with starch xanthate if this reagent is added in 1:1 xanthate: mercury molar ratio.

The presence of mercury chloro-complexes, such as those in solution containing 0.1 M NaCl at pH ⩽ 9, affects considerably the kinetics of mercury precipitation by xanthate. In such conditions mercury removal comparable with that obtained at the absence of chlo-

rides requires the reaction time as long as some days. Very good removal can also be obtained in presence of 1 M NaCl in a suitable time at pH $\geqslant$ 10.

Before the waste treatment phase is considered, research should be, however, performed in order to reveal the reaction mechanisms. The definition of the compound formed after xanthate is added to mercuric solution is a matter of primary importance as far as the explanation of stoichiometry and kinetics is concerned.

Table 3

Residual mercury concentrations vs precipitation times at different pH values and Cl^- concentrations (initial mercury concentration = 10 mg/dm^3; xanthate: mercury ratio = 1:1)

Resztkowe stężenia rtęci w zależności od czasu strącania w różnych wartościach pH i stężeniach Cl^- (początkowe stężenia rtęci — 10 mg/dm^3; stosunek ksantogenianu do rtęci 1:1)

Cl^- concentration M	pH	Residual mercury concentration mg/dm^3
0.1	2	2.80
0.1	9	2.31
0.1	11	0.036
1.0	11	0.040

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