# General and Inorganic Chemistry

## Separation of copper and bichromate ions by complex methods

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Separation of $Cu^{2+}$ and $Cr_2O_7^{2-}$ has been studied by electrodialysis combined with preliminary adsorption on bentonite. The influence of concentration, pH, and electric current on the degree of desalination has been studied. The optimum conditions for almost complete separation of the ions studied have been found. Real galvanic sewage has been examined by this method.

**Key words:** separation; dialysis; bichromate; copper.

The electrodialysis of solutions containing chromium(VI) compounds has not been much studied and its application is confined mainly to dilute solutions,[1] which is associated with rapid membrane corrosion and passivation of anodes. At the same time, the problem of ion separation in sewage of the galvanic industry remains of prime importance.

### Experimental

A three-chamber cell, MA-40 and MK-40 membranes, and VT-1-0 titanium anodes, which manifest good properties in the electrolysis of bichromate solutions,[2] were used in the present work. The stability of the membranes to corrosion was monitored electrochemically by chronopotentiograms. It was established that the form of the curves remains constant after 200-h operation, which attests to the relative stability of the chosen membranes under these conditions. Both model solutions containing copper(II) and bichromate ions and real sewage from the galvanic industry were used in this study.

The conditions of the electrodialysis were optimized using model bichromate solutions over a wide range of bichromate ion concentrations from 0.1 to 80 g $L^{-1}$. Preliminary experiments showed that the degree of desalination in the middle chamber was independent of the pH of the solution studied (in the range 1—4). The optimum density of the polarizing current was 15 mA $cm^{-2}$, which corresponds to industrial loading.[2] Higher current densities at the MA-40 membrane result in the appearance of the limiting state, and it is known[3] that electrodialysis is the most efficient in the ranges before the limiting state. This circumstance determined the choice of the current densities in this work where the composition of the electrolyte in the anodic chamber also varied, because partial electrode passivation was observed in very concentrated solutions and at high pH. In some experiments, the anodic chamber was filled with the solution under study, and in some cases 1 *M* $H_2SO_4$ was used. The optimum time of the electrodialysis (1—2 h) was established in preliminary experiments.

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The bichromate and copper ions were analyzed by procedures described previously.[4,5]

Electrodialysis is most frequently used in combination with adsorption methods of purification. This approach has been also used for the separation of ions in sewage from the galvanic industry. To this end, the components of the solutions under study were adsorbed on montmorillonite clays. It is known that bentonite clays adsorb ions of heavy metals well, however, the composition of the exchange complex and the hydrophilic character of the clay particles led us to believe that it would not adsorb bichromate ions. The adsorption on clays was performed as described previously.[6] The investigation of certain parameters of an aqueous clay suspension allowed us to establish that the clay particles were negatively charged, and the pH of this suspension was equal to 9 due to the presence of the metaaluminate ion. As expected, bichromate ions were not adsorbed in this case. The pH values obtained for the suspension differ from those given in the literature,[6] which is related to some differences in the experimental conditions.

## Results and Discussion

Some results of ion separation by electrodialysis in a model system are presented in Table 1.

It can be seen from these data that the preliminary adsorption of the solution on bentonite clay does not decrease the bichromate ion concentration in a dilute solution and favors subsequent electrodialysis: under identical conditions, desalination in the middle chamber and concentration in the anodic chamber occur to a large degree.

**Table 1.** Results of the electrodialysis of model solutions

| Composition of the initial solution, $C$/g L$^{-1}$ | | Electrolyte in the chambers | Concentration in the chambers after dialysis, $C$/g L$^{-1}$ | |
|---|---|---|---|---|
| | | | $Cr_2O_7^{2-}$ | $Cu^{2+}$ |
| $Cr_2O_7^{2-}$ | $Cu^{2+}$ | Anodic<br>Average | Anodic<br>Average | Cathodic<br>Average |
| 50 | 10 | Acid | 8 | 11 |
| | | Solution | 41 | 9 |
| 20 | 0.753 | Acid | 3 | 0.090 |
| | | Solution | 17 | 0.524 |
| 20 | 0.753 | Solution | 24 | 0.911 |
| | | Solution | 16 | 0.530 |
| 1.11 | 0.081 | Acid | 0.11 | 0.033 |
| | | Solution | 0.86 | 0.019 |
| 1.11 | 0.081 | Solution | 1.32 | 0.101 |
| | | Solution | 0.88 | 0.039 |
| 20* | 0.502* | Acid | 3 | 0.098 |
| | | Solution | 17 | 0.323 |
| 20* | 0.502* | Solution | 23 | 0.596 |
| | | Solution | 16 | 0.323 |
| 1.11* | 0.011* | Acid | 0.44 | 0.007 |
| | | Solution | 0.54 | 0.003 |
| 1.11* | 0.011* | Solution | 1.58 | 0.018 |
| | | Solution | 0.49 | 0.003 |

*Note.* The cathodic chamber contained the solution in all experiments.

* After the preliminary adsorption on the clay.

This seems to occur for the following reasons. As is indicated above, an aqueous suspension of clay has pH $\sim$9, and contact between the dilute solution and the clay results in an increase in the pH of the starting solution. This results in the shift of the bichromate $\rightleftharpoons$ chromate equilibrium to the formation of the latter, which occurs at pH $\approx$ 7. The chromate ion is more mobile due to its smaller size, and thus the parameters of electrodialysis are enhanced after contact with the clay. This process is not observed in concentrated acidified solutions.

The exchange capacity of bentonite clay is small (about 100 mg-eqv $(100\ \mathrm{g})^{-1}$). The fairly large decrease in the concentration of copper ions during adsorption is associated not only with ion exchange but also with other processes, such as ion sorption and copper precipitation as hydroxide by a weakly alkaline aqueous suspension. Copper sorbed by the clay may be isolated by electrochemical methods if a paste electrode is prepared. In this process, metal is extracted in a high yield.[6]

The results of the electrodialysis of real sewage are presented in Table 2.

The data of Tables 1 and 2 show that preliminary adsorption of model sewage on the clay favors better separation of ions in dilute solutions. Complete ion separation and purification of the electrolyte as regards the components under investigation were achieved in the middle chamber for the sewage that corresponded in their composition to the washings of the galvanic industry. It follows from the results presented that the electrodialysis of bichromate ions in real sewage is worse than in model solutions, which is likely related to the strongly acidic character of the sewage. It is possible that isopolyions are formed in these solutions. They are significantly larger in

**Table 2.** Some results of the electrodialysis of real sewage

| Composition of the initial solution, $C$/g L$^{-1}$ | | Electrolyte in the chambers | Concentration in the chambers after dialysis, $C$/g L$^{-1}$ | |
|---|---|---|---|---|
| | | | $Cr_2O_7^{2-}$ | $Cu^{2+}$ |
| $Cr_2O_7^{2-}$ | $Cu^{2+}$ | Anodic<br>Average | Anodic<br>Average | Cathodic<br>Average |
| 50 | 6 | Acid | 5 | 1.3 |
| | | Solution | 43 | 4.2 |
| 50 | 6 | Solution | 54 | 7.2 |
| | | Solution | 43 | 4.2 |
| 0.05 | 0.006 | Acid | 0.022 | 0.003 |
| | | Solution | 0.025 | 0.002 |
| 50* | 5.3* | Acid | 5 | 1.2 |
| | | Solution | 42 | 4.0 |
| 0.05* | 0.002* | Acid | 0.44 | — |
| | | Solution | 0.001 | 0.001 |
| 0.05* | 0.002* | Solution | 0.093 | 0.001 |
| | | Solution | 0.001 | — |

*Note.* The cathodic chamber contained the solution in all experiments.

* After the preliminary adsorption on the clay.

size and are more strongly hydrated than bichromate, and therefore have less mobility. In addition, it is known that ions of the composition $CrO_2SO_4$ (see Ref. 7) are formed in the solutions of sulfuric acid. They may change the parameters of the process, and sulfate ions are able to compete with bichromate ions.

Thus, the combined methods may be successfully used for purification and ion separation in solutions formed after the washing of printing plates.

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