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Bromide removal from chloride solutions by combined electrolysis and anion exchange processes

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ABSTRACT

Selective bromide removal from chloride solution was carried out by combined electrolysis and anion exchange processes. First the bromide was oxidized to bromine in an electrolysis cell. Then Br_2 was combined with Br^- and or Cl^- to form complex anions ($Br_xCl_y^-$) mainly as Br_3^-, Br_2Cl^- or $BrCl_2^-$ that have high selectivity to anion exchange resins. The results showed that the separation factor of Br increased from 2.5 when Br^- was not oxidized to about 30–50 when oxidation was applied. Moreover, the total Br capacity increased from about 3 to more than 9 meq. Br/g. The Br capacity of the resin depends on chloride and bromide concentrations in solution, probably because they influence the transition of Br_3^- to Br_2Cl^- and to $BrCl_2^-$. Regeneration occurred after reducing the bromine with $NaHSO_3$ to bromide. The concentration of bromide in the column regeneration solution was about hundred times higher than in the feed solution.

Keywords: Trihalomethane; Br removal; Anion-exchange; Disinfection

1. Introduction

Trihalomethanes (THMs) are disinfection byproducts (DBPs) produced by chlorination of drinking water containing organics. Although bromide is not toxic, recently there has been increased interest in the presence of bromides in drinking water because chlorination leads to the formation of carcinogenic brominated disinfection byproducts (DBPs) that are more toxic than their chlorinated analogues. Moreover, if disinfection is carried out by ozonation, bromide can be oxidized at a pH above 6.0 to bromate (BrO_3^-), which is extremely toxic. Bromide is commonly discharged to surface waters through burning coal in power plants and industrial wastewater treatment processes which increase bromide concentrations in surface waters used as potable drinking water. Generally, waste water containing bromide is mixed with a high concentration of chloride and there is no efficient industrial system to remove and recycle the brome. The goal of this study is to find an efficient way to selectively remove bromide from chloride solutions by using combined electrolysis and anion exchange process. Commercial anion exchange resins are more selective to bromide than chloride, but the separation factor is in the range 2–4 [1] and the capacity of the anion exchange resin to bromide in concentrated chloride solution is low. In Ref [2] it was shown that by oxidizing the Br^- to Br_2 by Cl_2 it was possible to reduce Br concentration in 4M KCl solution from 7.5 mM to less than 1.5 mM. In our study, we oxidized the Br- in an electrolysis cell. By passing the chloride-bromide solution through an electrolysis cell, the bromide is transformed to bromine and then to other complex anions such as Br_3^-, Br_2Cl^- and $BrCl_2^-$ [3,4] that have higher selectivity (30–55) to anion exchange resins. Consequently, the capacity to Br is significantly increased. In this research, prior to the anion exchange process, we passed different synthetic solutions containing chlorides and bromides through an electrolysis cell to study the various parameters that influence the process. It was found that the total capacity to Cl^- and Br depends on the solution composition. When chloride and bromide concentration was relatively low (about 25–55 mM Cl^- and 10 mM Br^-) the total capacity to Br+Cl increased after electrolysis from 2.7 meq./g up to 7.5–10 meq./g, the Br capacity of the resin increased up

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to 7.3 meq Br./g and the separation factor increased from 2.5 up to 30–55. However, when chloride concentration was increased, the Br capacity of the resin decreased to 3.0 meq. Br/g. As the result of the relative high Br resin capacity and improved separation factor in diluted solutions, separation of Br from Cl was obtained on column operation; see Fig. 7.

The following reactions may occur in solutions containing Br^- and Cl^- ions during electrolysis:

$$2Br^- \rightarrow Br_2 + 2e \qquad E = -1.1\ V$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e \qquad E = -1.23\ V$$

$$Br_2 + 2H_2O \leftrightarrow HOBr + H_3O^+ + Br^- \qquad K = 5.8 \times 10^{-9}$$

$$HOBr + H_2O \leftrightarrow H_3O^+ + OBr^- \qquad Ka = 2 \times 10^{-9}$$

$$3OBr^- \leftrightarrow BrO_3^- + 2\ Br^-$$

$$Br_2 + Br^- \leftrightarrow Br_3^-$$

$$Br_2 + Cl^- \leftrightarrow Br_2Cl^-$$

$$Br_2Cl^- + Cl^- \leftrightarrow BrCl_2^- + Br^-$$

$$SO_3^- + Br_2 + H_2O \rightarrow SO_4^- + 2Br^- + 2H^+$$

At low pH in chloride solutions the bromine combines with Cl^- to form complex anions such as Br_2Cl^- and $BrCl_2^-$ that have high affinity to anion exchangers. When Cl^- concentration in resin is decreased, Br concentration increases (Fig. 1). As to every ion-exchange site of the anion exchanger, complex anions consisting of several atoms are attached. As a result, the apparent Br capacity is significantly increased. To regenerate the anion exchange resin, it is necessary to reduce the bromine to bromide, e.g. by $NaHSO_3$, and then to replace all the halides in the resin by large anions such as SO_4^- or NO_3^-. According to the ratio between Br and Cl in the regeneration solution of the resin, the structure of the complexed ions (BrxCly) may be deduced.

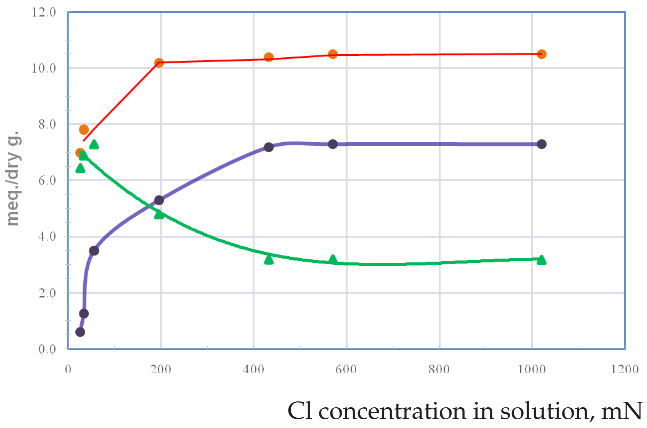

Fig. 1. Concentration of Br and Cl in resin and total capacity vs. Cl concentration in solution. Br concentration in solution was 10 mN. ● - Total Capacity ● - Cl in resin ▲ - Br in resin.

2. Experimental

2.1. Electrolysis

Two liters of 10 mM Br solution containing various chloride concentrations were passed through an electrolysis cell at a flow rate of 1 l h^{-1} and at current of 1 A . The surface area was 12 cm^2 and the distance between electrodes was 11 mm. The cathode was stainless steel and the anode was platinized titanium. Titration with $NaHSO_3$ showed that, under these conditions, all the bromides were oxidized to bromine.

2.2. Br capacity in batch experiments

To prevent possible reduction of bromine by reducing groups that may exist in the anion exchange polymer, it was immersed for 2 h in 1% NaClO. Then, two liters of the electrolyzed solution containing 10 mM Br-and various chloride concentrations were mixed at pH < 3.5 with one gram of this dry anion exchange resin in Cl form. In the next step, after two hours of mixing, the resin was separated from the solution and washed with deionized water. Then, the resin was regenerated with 50 ml 5% $NaHSO_3$ and 25 ml 1 N KNO_3. Resin capacity for Br and Cl was calculated from the quantities of Br^- and Cl^- in the regeneration solutions. As the total capacity increased by a factor of 3, probably complex anions composed of three atoms were attached to the resin.

The anion exchanger which was used (Relite -3AS, Manufactured by Mitsbubishi Co.) is highly porous copolymer of Styrene –DVB and has quaternary ammonium groups. The ion-exchange capacity is 1.2 eq./l and swelling of 54–59%.

Br- and Cl- was measured by ion exchange chromatographer. We used Dionex ion Chromatographer-LC 20 equipped with AS9-Sc column.

2.3. Column operation

Column operation was carried out with 165 ml and 180 ml of strong base anion exchange resin ‘Relite 3AS’; the diameter of the column was 16 mm, length was 82 cm, and solution flow rate was 0.5–1 l h^{-1}. Regeneration was carried out with 0.3 l of 2.5 M $NaHSO_3$ and 0.3 l of 1 M Na_2SO_4. In all the experiments, a synthetic solution was used which contained 10 mN of Br^- and 32 or 65 mN of Cl^-.

3. Results and discussion

3.1. Batch experiments

3.1.1. Influence of chloride concentration on Br capacity

As the result of formation of the complex anions (such as Br_3^-, Br_2Cl^- and $BrCl_2$) the total capacity increased by a factor of 3 and the capacity to Br increased to 7.3 meq.Br/g. (Fig. 1). The increased capacity probably resulted from the formation of complex anions having three atoms (or more). When chloride concentration in solution increased m the capacity decreased for Br and increased for chloride (see Fig. 1). The total capacity did not change significantly with an increase of Cl concentration in solution and was about 8–10 meq/g. This proved that at high Cl concentration, only complex anions consisting of at least 3 atoms were attached to the anion exchanger.

3.1.2. Influence of the ratio Cl/Br concentration in solution on the separation factor (K) and the Br molar fraction in resin

The separation factor (K) was calculated from total Cl and Br concentrations in the solution and in the resin attained after applying a reduction process, according to the following equation:

$$K = Br_{r.}\, Cl_s / Br_{s.}\, Cl_r$$

where the subscripts r and s respectively denote resin and solution, concentration units in resin are given in meq./g, and in solution in mM.

The results (Fig. 2) show that by electrolysis which resulted in formation of complex Br-Cl anions, the separation factor k increased from 2.5 to up to 30–55. The separation factor depended on the different anions concentrations in solution which changed with Cl concentration. When Cl concentration in solution was lower than 50 mM, probably most of the Br was in the form of Br_2Cl^- and Br_3^- and the Br molar fraction in resin was high (0.66–0.92). However, when Cl concentration increased,probably most of the Br was in the form of $BrCl_2^-$ and therefore the Br molar fraction in the resin (X_{Br}) decreased to 0.31, as can be seen in Fig. 3. When Cl concentration in solution was very low (25 mM), the Br molar fraction in resin increased to 0.92, indicating the presence of Br_3^- in the resin.

3.2. Column operation

The first run was carried out with 180 ml resin (58 g), with feed solution of 65 mM Cl^- and 10 mM Br^- without electrolysis. Fig. 4 shows that after passing a small volume of solution through the column, the concentration of Br at the exit was significantly increased. The column was regenerated with 0.40 l of 1M Na_2SO_4. From the column, 61.7 meq. Br and 128 meq. Cl were removed. The total anion exchange capacity was 1.05 eq./l resin which is about 3.2 meq./dry g. The second run was carried out with the same solution composition as the first run, but was first passed through an electrolysis unit and then through the anion exchanger. Fig. 4 shows that [Br] at exit of the column decreased to about 1.5–2.0 mM, and even after passing 31 l (which is 170 BV) [Br] in the solution leaving the column did not change. The regeneration was carried out with 0.24 l of 2.5M $NaHS0_3$ and 0.20 l of 1M Na_2SO_4. From the column 284 meq of Br and 199 meq of Cl were removed. The total capacity was 483 meq which is 8.3 meq/g. or 2.7 meq./l. Capacity for Br was 4.9 meq/g. which fits the batch experiments (Fig 1, 3). Fig. 5 shows that during regeneration, certain separation between Br and Cl is obtained. The concentration of Br in regeneration solution reaches 800–1200 mN and can be recovered by methods such as evaporation.

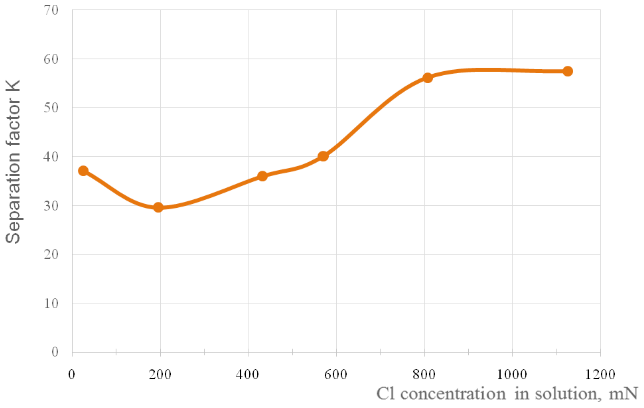

Fig. 2. Separation factor K vs. Cl^- concentration in solution.

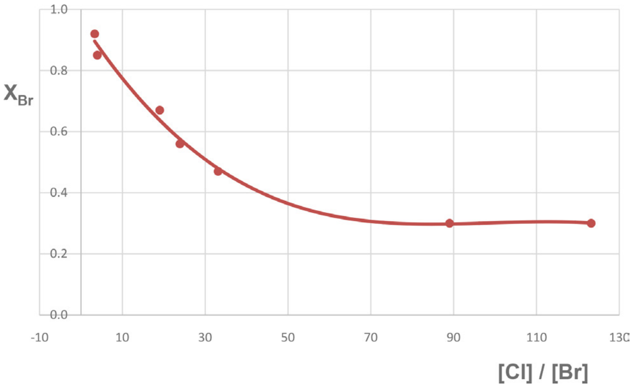

Fig. 3. Br molar fraction in resin vs. [Cl] / [Br] in solution.

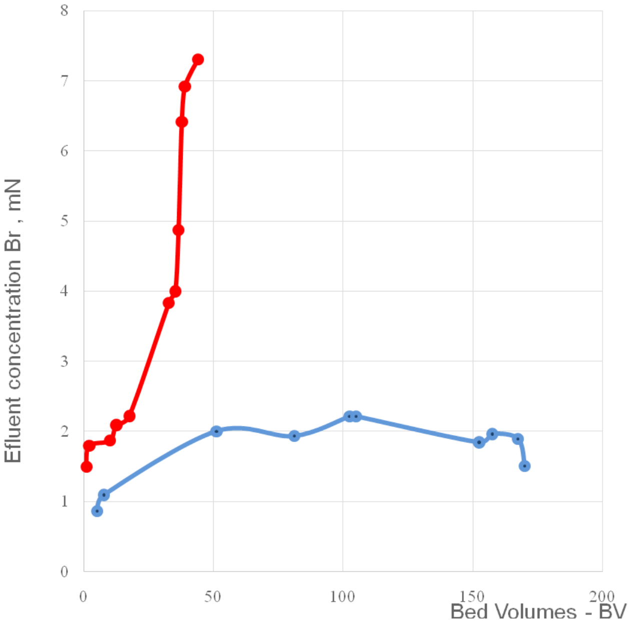

Fig. 4. Effluent Br concentration vs. BV with 180 ml Relite 3AS ● with and without ● electrolysis. Solution flow rate was 0.5 l/h and current 0.5 A. Inlet concentrations: Br - 10 mN and Cl - 65 mN. BV = (volume of solution)/((volume of resin).

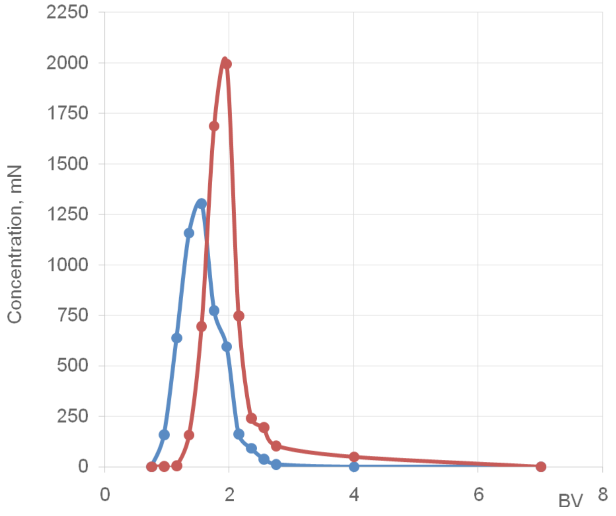

Fig. 5. Concentrations of Br$^-$ and Cl$^-$ in outlet of regeneration solution vs. BV. Cl$^-$ ——— Br$^-$ ———.

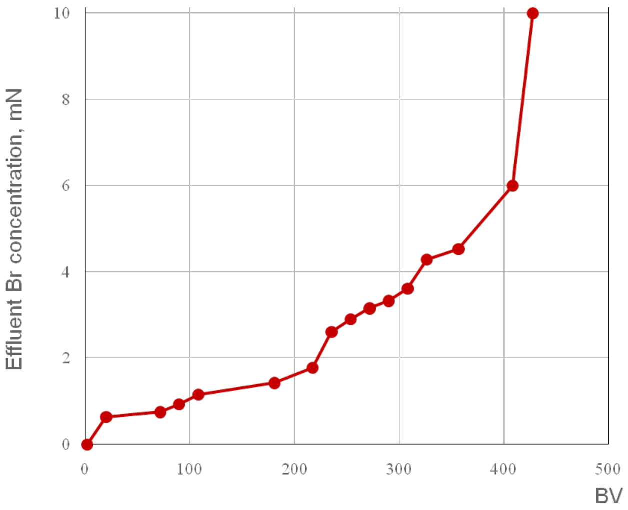

Fig. 6. Effluent Br concentration vs. BV with oxidation of Br. Current 1.0 A. Inlet concentrations: Br - 10 mN and Cl - 32 mN.

In the next cycle, with the same resin Cl$^-$ concentration was reduced to 32 mN and Br$^-$ concentration was the same at 10 mN. Resin volume was 165 ml and its weight was 53 g. The current was 1 A and solution flow rate was 1 l/h. Fig. 6 shows that it was necessary to transfer 70 l of solution (424 BV) until breakthrough. The total capacity of the column was 469 meq (8.9 meq./g or 2.8 meq/l), resin capacity for Br was 8.3 meq./g and for Cl$^-$ 0.6 meq./g. Br molar fraction in the column was 0.94 and corresponds to previous results (see Fig. 3). As the reaction between Bromine and $NaHSO_3$ is exothermic, and to prevent a sharp temperature increase in the column, the regeneration was carried out with gradual increase of $NaHSO_3$ concentration, from 1.25 to 2.5 M. On regeneration of the resin (Fig. 7) separation between Br and Cl was obtained, mainly as the result of lower [Cl]/[Br] ratio in the feed solution (3.2) which probably caused the creation of Br_3^- and consequently, the high concentration of Br in the anion exchange resin (see Fig. 3).

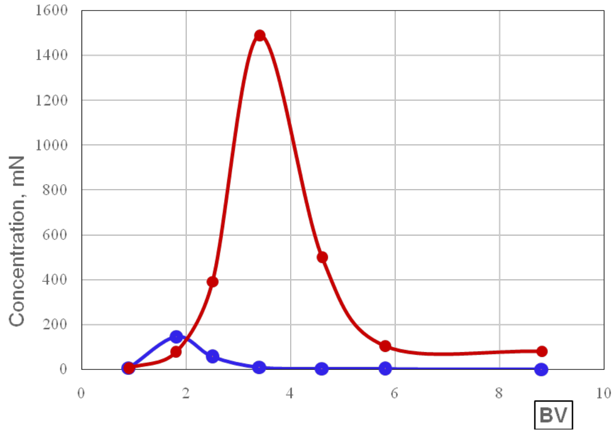

Fig. 7. Regeneration of 165 ml ion-exchange resin Relite 3 AS with Sodium hydrogen sulfite. Its concentration increased gradually from 1.25 to 2.5 M. Finally, the resin was washed with 200 ml of 1M Na_2SO_4. —●— Cl —●— Br

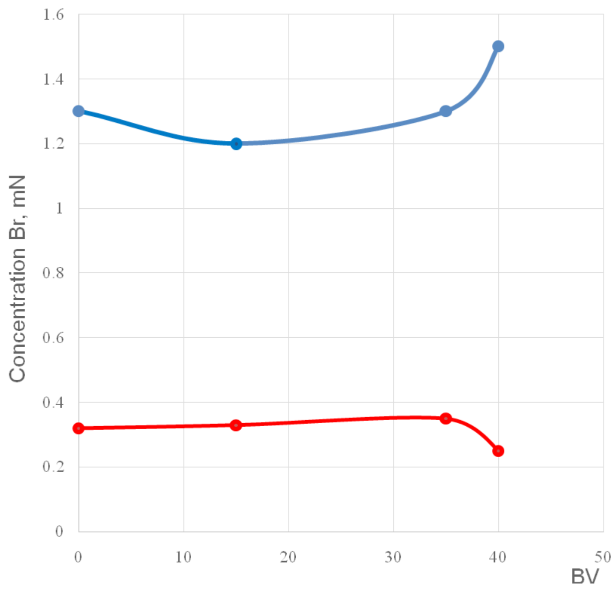

Fig. 8. Outlet Br concentration vs. BV. Resin volume was 180 ml (Relite 3AS). First step: ——— Inlet Br concentration was 9.3 mN, and in outlet it dropped to about 1.3 mN. After second step Br concentration decreased to 0.36 mN ———.

By transferring the feed solution through the anion exchange column, about 80–85% of the bromide was removed. Further decrease of the bromide in feed solution was obtained by again passing the solution through the electrolysis unit and anion exchange column (see Fig. 8). The two-step operation decreased the residual Br$^-$ concentration to 0.3–0.4 mN.

4. Conclusions

1) The selectivity of strong base anion exchange resin to Br$^-$ in Cl$^-$ solution can be increased significantly by oxidation of the Br$^-$ to Br_2 in an electrolysis cell. The total capacity increased about three-fold,

probably because complex anions such as Br_3^-, Br_2Cl^- and $BrCl_2^-$ were formed. When Cl^- concentration in solution was increased,probably more $BrCl_2^-$ were created and the capacity to Br decreased from 7.3 meq./g to 3.0 meq./g (Fig.1).

2) By passing the solution through an electrolysis cell and then through a strong base anion exchange resin, Br concentration in a relatively diluted chloride solution (65 mN) was reduced from about 10 mN to 1.5–2.2 mN. By applying a two-step operation, the Br concentration was reduced to 0.3–0.4 mN (Fig. 8).
3) Separation between Br and Cl was achieved with strong base anion exchanger when Cl^- concentration was reduced to 32 mN (Fig. 7).
4) Bromide concentration in the regenerated solution was about 100 times higher (900–950 mN) than in the feed solution and can be recycled by evaporation or other methods.

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