Studies on Adsorbents for Uranium from Sea Water

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Nineteen adsorbents were tested to concentrate uranium from sea water. Mass distribution coefficients and percentage yields were determined for the adsorbents from low and high concentrations of uranium in the medium. Active carbon, hydrated aluminium oxide, copper ferrocyanide, potassium zinc ferrocyanide, calcium phosphate (acidic and basic) were found unsuitable either due to their solubility or chemical effect induced in them during their contact with sea water. Titanium phosphate though showed a large distribution coefficient of $\sim 7 \times 10^4$ in batch studies, reflected a slow pick-up rate during passage of large volumes of sea water through the column bed and yielded the poor recovery of $\sim 26\%$. In contrast, hydrated titanium oxide showed a fast pick-up rate (T $\sim$ 2 min) in the batch studies and a good yield of $92 \pm 3\%$ was obtained by the passage of 75 l of sea water spiked with uranium to 4 times the concentration of open ocean water. Maximum amount of uranium that could be obtained on this bed was 1.4 mg U/g. This adsorbent could be utilised to concentrate uranium from sea water if the practical problems of compaction and algal growth are eliminated.

Ocean is a potential reservoir of many marine chemicals and pharmaceuticals and efforts are made to tap this source for the chemicals of interest. Uranium is present at a relatively low and uniform concentration throughout the depths of the oceans and even with a conservative figure of $10^{-3}$ ppm total amount of uranium in ocean water works out to be about $10^{10}$ tons. This enormous figure has attracted the attention of many workers to utilize ocean water as an alternate source to the depleting mineral deposits on land. Attempts are being made to concentrate uranium from sea water on certain inorganic precipitates and inorganic and organic ion exchangers in order to use it as a reserve for the increasing power needs of the nations. Davies et al. have attempted extraction of this element by cycling sea water through beds of inorganic exchangers - hydrous titanium oxide and basic zinc carbonate. Keen has attempted to establish the optimum conditions needed for the maximum adsorption efficiency for once through passage of sea water through definite amounts of hydrous titanium oxide resins. The adsorption efficiency is found to be around 45%. In such studies, solubility will be one of the limiting factors in determining the efficiency of the exchangers.

In the present work, a number of adsorbents are studied with respect to the scavenging capacity for uranium from sea water. The effect of different modes of resin preparations on adsorption efficiency is ascertained. Systematic studies are made of the concentration of uranium under batch and column conditions on hydrous titanium oxide and titanium phosphates, as their chemical analogues are available as minerals in abundant quantities in India.

**Materials and Methods**

Nineteen inorganic exchangers were tried as adsorbents for uranium from seawater. Some of them were obtained as AnalaR chemicals from BDH and others were prepared in laboratory under specified conditions. The list of exchangers used and the character of the resins is given in Table 1. The method of preparation of the exchangers made in our laboratory is given below.

**Preparation of exchangers — Copper ferrocyanide:**

To 500 ml of 0.05M CuSO$_4$ solution was added 0.05M potassium ferrocyanide till no further precipitation was obtained with a small quantity of supernatant.

**Potassium zinc ferrocyanide:** To 500 ml of 0.05M zinc acetate was added 0.05M potassium ferrocyanide till no further precipitation was obtained with a small quantity of supernatant.

**Calcium phosphate (basic):** Solution (500 ml) of 0.02M CaCl$_2$ was mixed with 0.05M disodium hydrogen phosphate and pH adjusted to 7.

**Calcium phosphate (acidic):** Solution (500 ml) of 0.02M CaCl$_2$ was mixed with 0.05M monosodium dihydrogen phosphate and the pH adjusted to 6.

**Zirconium phosphate:** With 500 ml of 0.02M ZrOCl$_2$ in 4N HCl, 0.05M monosodium dihydrogen phosphate was mixed and gently boiled for 30 min.

**Titanium phosphate:** Solution (500 ml) of 15% TiCl$_4$ was taken and 0.05M monosodium dihydrogen phosphate was added with constant stirring.

**Hydrated titanium oxide:** Solution (500 ml) of 15% TiCl$_4$ was neutralized with 10% NaOH and 10% excess to the stoichiometric amount was added.

**Titanium oxide sol-gel:** Solution (500 ml) of 15% TiCl$_4$ was made to 3M in NaCl and 10% NaOH was added carefully and with constant stirring till a
faint permanent milky appearance was obtained. The sol thus obtained was gelled by boiling gently for about 30 min.

The precipitates obtained in all the above cases were filtered and collected over a Whatman No. 1 filter paper under suction. They were washed thoroughly free of electrolytes (particularly Cl- by AgNO₃ test). The precipitates were then transferred into a plastic tray and air dried for weeks at room temperature. For certain experiments, the air-dried materials were powdered and sieved through meshes of specified size range and kept in oven at 100°C for constant weights.

Adsorption studies — The per cent adsorption values on various adsorbents were determined as follows:

A known amount of adsorbent is added to a suitable volume of sea water containing a known amount of uranium at a pH and kept overnight to reach equilibrium. Uranium is determined in both the adsorbent phase and in solution.

\[ K_d = \frac{C_{soln}}{C_{ads}} \]

where \( K_d \) is the distribution coefficient (ratio of the concentration of uranium in the adsorbent to the concentration in solution at equilibrium) was determined for some exchangers at pH 5. The general technique adopted in determining these is the same as that described above. The absorbent amount used is 0.2 g.

Variation of adsorption efficiency with time for titanium phosphate column was determined by passing sea water labelled with uranium to a concentration level of \( \sim 37 \mu g/litre \) through a 3 g bed of titanium phosphate.

Rate of pick-up of uranium on hydrated titanium oxide for different concentrations of uranium was studied to determine the concentration dependence of the 50% pick-up time.

**Table 1 — Nature of the Exchangers Used**

| Exchanger                  | Nature      | Mesh size
|---------------------------|-------------|-----------
| Hydrated aluminium oxide  | Basic       | 60-120    |
| Silica gel                |             |           |
| Manganese dioxide powder  |             |           |
| Iron sulphide             |             |           |
| Hydrated aluminium phosphate |         | 16-25     |
| Active carbon             |             | 16-25     |
| Wood charcoal             |             | 16-25     |
| Fullers earth             |             | 16-25     |
| Copper ferrocyanide       |             | 16-25     |
| Potassium zinc ferrocyanide |         | 16-25     |
| Prepared in Lab.          |             |           |
| Calcium phosphate         | Acidic      |           |
| do                        | Basic       |           |
| Zirconium phosphate       | Acidic, room temp. |     |
| do                        | Acidic, 100°C dried | |
| Titanium phosphate        | Acidic, room temp. |     |
| do                        | Acidic, 100°C dried |     |
| Hydrated titanium oxide   | Basic       | 16-25     |
| do                        | Room temp. dried | 100°C dried |

**HTO column adsorption studies** — HTO column adsorption experiments were done by placing \( \sim 12 \) g of HTO exchanger in a glass burette (1.2 cm diam. and 50 cm long) and then percolating filtered sea water through the column bed at known flow rates. In these studies sea water labelled to \( \sim 38 \mu g/litre \) was passed through the bed. Experiments were also done with seawater \( \sim 13 \mu g/litre \) on 5 g beds for large volumes of the order of 75 litres.

Uranium retention studies on HTO columns — Experiments were carried out by passing filtered sea water \( \sim 3 \mu g/litre \) at 0.1 ml/min through a 5 g HTO column (16-80 mesh) initially loaded with uranium to a concentration of 1.6 mg/g.

**Uranium estimation procedures** — For the analytical determination of uranium in sea water the method described by Sarma and Krishnamoorthy was adopted with small modifications. Uranium in sea water was coprecipitated on 50 mg Fe(III) precipitated as hydroxide \( \times 4 \) times). The coprecipitation recovery for uranium in these 4 ferric hydroxide precipitations together is 0.95 ± 0.02, when ferric hydroxide adsorbed on the walls of the container is washed with strong acid. Uranium-containing ferric chloride solution was extracted with methyl isobutyl ketone in 6N HCl medium instead of extraction into ethyl acetate in presence of aluminium nitrate salting out agent in 0.5N HNO₃ medium.

The determination of uranium in the adsorbent phase generally involved the following steps: dissolution of the exchanger, passing through Dowex-1 column, solvent extraction with MIBK and electroplating of uranium. The steps employed were the same in general for all types of exchangers except that the Dowex-1 column conditions varied for different matrices. For determination of uranium in copper ferrocyanide and potassium zinc ferrocyanide, the exchangers were dissolved in HNO₃, oxidized with bromate, taken up in 1N HF and passed through a Dowex-1 column (200 mesh) to eliminate copper and zinc. Calcium phosphate was dissolved in 1 N HNO₃ and passed through Dowex-50 to remove phosphate as \( \text{H}_3\text{PO}_4 \) and uranium was eluted with 6N HCl. The effluent was evaporated to dryness, taken up in concentrated HCl, passed through Dowex-1, uranium eluted and estimated as above. Titanium phosphate columns were dissolved by repeated evaporation with HF containing 10% \( \text{H}_2\text{SO}_4 \) converted to chloride form taken up in 8N HCl-1N HF, passed through Dowex-1 and uranium eluted with 0.3N HCl. Titanium oxide columns were treated with 1M (NH₄)₂C₂O₄ solution in which uranium extraction efficiency was found to be \( \sim 87\% \). The (NH₄)₂C₂O₄ extract was evaporated to dryness, taken up in 8N HCl-1N HF and proceeded as described under titanium phosphate.

**Results and Discussion**

A broad spectrum of substances has been examined for the uranium adsorption efficiency. Nineteen matrices have been selected for these studies with due consideration for their utility and availability. Table 2 presents per cent adsorption of uranium on these matrices under various concentrations of
uranium in the aqueous phase. It can be seen that wood charcoal and hydrated aluminium oxide are not useful for concentrating uranium from large volumes of sea water because of the low concentration of uranium in sea water. Even though iron sulphide and calcium phosphate (acidic and basic) show good pick-up yields of more than 95%, they are not of much utility because of their appreciable solubilities and the rusting of iron sulphide with time. It is of interest to note that Davies et al. 4 have found that basic zinc carbonate and an arsenic-containing organic resin to be of no practical utility because of their large solubilities in sea water even though their Kd values for U are high.

Data (Table 2) show zirconium and titanium phosphates and titanium oxide solgel as promising matrices and further detailed studies of uranium adsorption are carried out on these matrices. Kd values are determined at low concentrations of uranium and are presented in Table 3. The values vary from 1 × 10^3 to 7.4 × 10^4.

Phosphates show higher Kd values than the hydrated titanium oxide and its solgel. Hence column adsorption studies are carried out with titanium phosphate having the largest Kd value of 7.4 × 10^4 to establish the optimum column conditions such as flow rates, etc., and the results are given in Table 4. Even at as high a flow rate of 127.5 ml/min, in the first 1 litre the adsorption efficiency is not too small a figure (62%). However, differential adsorption efficiency given in column 6 show a decreasing trend (except for a few variations). The integral adsorption efficiency given in column 5 is a sum of these effects and the adsorption yield falls to a value as low as 33% at the end of 6 hr. After a break of 20 min, the experiment is continued at different flow rates and the overall trends in the differential and integral adsorption yields remained the same but somewhat accentuated for the former, even reaching negative values in some case indicating that the uranium adsorbed on the column in the initial stages is getting leached out in the later steps, leading to higher concentrations in the eluent than in the feed material. Also it can be seen that the overall pick-up appears very low (~26%). Hence the material appears to be not of much practical utility because of its slow pick-up rates and possible elution.

Experiments are carried out by batch technique to see the adsorption kinetics of uranium on hydrous titanium oxide and its concentration dependence. Results at 3 uranium concentration levels are given in Table 5. The concentration dependence of the half times is given by the equation

\[ \frac{(T_{1/2})_1}{(T_{1/2})_2} = \left( \frac{C_1}{C_2} \right)^{0.65} \]

The results indicate that the lower the uranium concentration in solution, lesser the time taken for its uptake on the matrix.
The above batch experiments are followed by column experiments similar to those carried out for titanium phosphate. The results (Table 6) indicate that even at higher flow rates of about 50 ml/min corresponding to 0.25 min contact time, high percentage adsorption is observed. The foregoing discussion thus indicates that hydrous titanium oxide is the only matrix of promise for adsorbing uranium at high flow rates. Davies et al. have pointed out its useful property—low solubility in sea water. An experiment carried out to see the maximum amount of uranium that could be extracted on hydrous titanium oxide yields high per cent adsorption yield of 92 ± 3% on a 5 g column for 75 litres of sea water spiked to ~13 μg/litre; but further passage of sea water could not be continued due to the problems of compaction and algal growth. At the later stages of the experiment the flow rate tends to be very low (0.3 ml/min). The uranium content on the column corresponds to 0.02% U₃O₈ on the resin.

As it is not practicable to establish the maximum amount of uranium that can be obtained on hydrous titanium oxide column, the same is determined by the reverse method. A 5 g hydrous titanium oxide bed is initially loaded with 8 mg uranium. Large volume of sea water (~10 litres) is passed and the elution of uranium from the bed is studied by determining the uranium concentrations in the effluent. The results (Fig. 1) shows a sharp elution peak at around 1000 column volumes and the elution tapered off to a stable level of ~35 μg/litre. The net amount of uranium retained on the resin is 1.4 mg/g. This suggests that if one can solve the mechanical compaction problem and algal growth, it may be possible to concentrate uranium from sea water on the resin to the extent of 0.17% U₃O₈ in the resin.

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