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THE ADSORPTION OF URANIUM FROM SOLUTIONS
BY ACTIVATED CARBON

by

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James C. Goodrich

DEDICATION

James C. Goodrich died July 13, 1949, at 31 years of age. He was born in Kansas City, Missouri. He was educated at Oberlin College where he received his baccalaureate degree in chemistry in 1938. He worked on Chemical Kinetics under Professor Eastman at the University of California where he received his Doctor of Philosophy degree in 1941.

Dr. Goodrich was possessed of a keen and sensitive mind and was devoted to the cause of science. At the time of his death he was, among other things, working on the problem of the adsorption of uranium on activated carbon. This paper, which reports some of the results of this work, is offered in his name.

INTRODUCTION

The relative rarity of uranium in nature and its diffuse modes of occurrence frequently mean that, in the processes of its recovery, it is often present in very dilute solutions. Chemical technology recognizes a general problem in the recovery of materials from dilute solutions, and various ways have been devised for accomplishing this result. Among these methods is that of selectively adsorbing the desired element or compound on a solid material introduced into the solution, removing the adsorbent by filtration or decantation, and then recovering the adsorbed material by a suitable extractive process.

Because of its wide utilization as an adsorbent in various decolorizing operations and because of its successful use for selectively adsorbing gold and silver in cyaniding processes, it was natural to attempt to recover uranium from its various solutions by the use of activated carbon.

EXPERIMENTAL WORK

Nature of the Charcoal

Source

The material selected for the adsorption experiments was a commercial steam-activated gas-mask-type charcoal manufactured from coconut shells. The original minus 6-mesh plus 10-mesh sample was sufficient for all of the tests to be described. Finer particle sizes were obtained by crushing and screening portions of the original sample.

Ash Content

A pure water leach of the charcoal gave a solution with a pH of 10 to 10.2, presumably because of the presence of 2.8 to 3.1 per cent of an alkaline ash. The ash is of interest because of the possibility of uranium being adsorbed by exchange with a constituent of the ash. Leaching with pure acids at final pH's in the range of 1 to 3 removed 90 per cent or more of the ash, as shown in Table 1.

TABLE 1. ASH CONTENT OF CHARCOAL (PER CENT)
AFTER ACID LEACHING. INITIAL ASH =
2.8 PER CENT

Final pH	HClO ₄	HCl	HNO ₃	H ₂ SO ₄
1.0	0.13	-	-	-
2.0	0.21	0.21	0.21	0.13
3.0	0.28	-	-	-

The milliequivalents of acid required to obtain an equilibrium pH of 1.0, 2.0, and 3.0 in 100 cc. of 100 mg./l. uranyl solutions containing 1 g. of carbon were 11.74, 2.03, and 0.87, respectively, for nitric acid and 11.66, 2.07, and 0.87 for perchloric acid. These results suggest that ash does not play a role in adsorption and the experiments to be described were conducted without de-ashing the charcoal.

Specific Surface

The specific surface area of the charcoal was determined by measuring the adsorption of acetic acid by material of different particle sizes according to the method of Lemieux and Morrison(1) and Kipling(2).

The data of Table 2 show that the specific surface area of this charcoal is independent of particle size and that the internal surface area, available for adsorption, is overwhelmingly larger than the external surface area.

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- (1) Lemieux and Morrison, Can. Jour. Research, 25 B, 440 (1947).
(2) J. J. Kipling, J. Chem. Soc. 1948, 1483.

TABLE 2. SPECIFIC SURFACE AREA DETERMINATIONS

Mesh Size	Max. Adsorption* HAc, Meq./g.	HAc** Specific Surface, m. ² /g.
-6 +10	4.8 ±0.1	706
-50	4.7	691
-100	4.7	691
-140	4.7	691
-200	4.6	676

* Uncorrected for acid consumed in leading ash, estimated as 0.8 meq. or less.

** Using a value of $24.3 \text{ \AA}^2$ for surface occupied by each acetic acid molecule.

Adsorption Measurements

Procedure

After crushing to pass a screen of desired mesh size, the charcoal was reduced to approximately 1-gram samples by coning and quartering, dried to constant weight at 150-160°C., and stored in a desiccator. One gram of charcoal, weighed to the nearest milligram, was added to 100 cc. of the solution being studied in a 250-cc. glass-stoppered Erlenmeyer flask. The solutions used were unbuffered simple solutions of uranyl salts plus an amount of the corresponding free acid to give the desired equilibrium pH.

The flask was mechanically shaken for predetermined times at a temperature of 25° ±2°C. The solution was then filtered and the filtrate analyzed for uranium by the colorimetric alkaline-peroxide method which gives an accuracy of

±5 per cent, except at the lowest concentrations where the accuracy may be only ±10 per cent. Any removal of uranium by the filter paper was not detectable. The pH, determined with a Beckman Model G pH meter, is believed to be accurate to 0.02 pH unit.

Particle Size

The data of Table 3 show the relationships between particle size, the equilibrium amount of uranium adsorbed from a uranyl nitrate solution at pH 2 by 10 grams per liter of the charcoal, and the rate of attainment of equilibrium.

TABLE 3. EFFECT OF CARBON PARTICLE SIZE ON THE RATE AND EQUILIBRIUM AMOUNTS OF URANIUM ADSORPTION FROM URANYL NITRATE SOLUTION AT pH 2.0

Initial uranium concentration - 202 mg./l.
Amount of charcoal - 10 g./l.

Mesh Size		Per Cent Uranium Adsorbed and Final pH					
		Time, Hours					
		1/12	1	4	24	48	114
-6 +10	%	6	11	16	21	28	36
	pH	1.95	1.98	1.98	1.97	1.98	1.95
-50	%	31	31	31	35	33	41
	pH	2.00	1.98	2.00	2.01	1.98	1.95
-100	%	41	41	41	45	-	-
	pH	1.98	1.95	1.98	1.99	-	-
-140	%	41	41	41	45	-	-
	pH	2.00	1.98	1.99	2.00	-	-
-200	%	41	41	45	45	-	-
	pH	1.98	1.96	1.98	1.99	-	-

Equilibrium was attained more rapidly with the finer particle sizes. Whereas the minus 6-, plus 10-mesh material had not quite reached an equilibrium condition at 114 hours, the minus 100-mesh and finer required only 24 hours or less. The amount of uranium adsorbed at equilibrium apparently is not affected by particle size.

The pH

A very striking decrease in adsorption occurs as the pH is decreased, particularly between pH 3 and 2. This effect is shown in Figure 1 for solutions of uranyl nitrate, chloride, sulphate, and perchlorate at initial uranium concentrations of 100 mg./l. The abrupt change in the per cent of uranium adsorbed as the pH of the solution is changed is not affected appreciably by the nature of the anion. The behavior suggests that the uranium is being adsorbed in hydrolyzed form, although other interpretations are possible.

Uranium Concentration

The amount of uranium adsorbed by unit weight of charcoal per liter is shown graphically in Figure 2 as a function of the equilibrium concentration of uranium in uranyl sulphate, perchlorate, chloride, and nitrate solutions at approximately pH 2. There is some scatter in the experimental values, particularly for the perchlorate solutions. The sulphate values, if corrected from pH 2.03 to pH 2.00, would be about 6 per cent lower than shown. At the lower equilibrium concentrations, the nitrate and sulphate data are well represented by equations of the Freundlich type which are followed less accurately by the perchlorate data. The solid line of Figure 2 appears to be a fair over-all representation of the data and is defined by the equation

$$\frac{x}{m} = 0.64 C^{\frac{1}{2.275}}$$

FIGURE 1. EFFECT OF pH ON THE ADSORPTION FROM URANYL SOLUTIONS .

FIGURE 2. EFFECT OF CONCENTRATION ON THE ADSORPTION OF URANIUM FROM URANYL SOLUTIONS

where X = mg. of uranium adsorbed, m = g. of charcoal per liter of solution, and C = the equilibrium concentration of uranium in solution in mg. per liter.

Temperature

Table 4 lists the per cent of uranium adsorbed by 10 grams per liter of the charcoal from a uranyl nitrate solution having a pH of 2.0 and an initial uranium concentration of 100 mg. per liter at 0°, 25°, and 100°C. Under these conditions, temperature has no effect on uranium adsorption within the limits of experimental error.

TABLE 4. EFFECT OF TEMPERATURE ON THE ADSORPTION OF URANIUM FROM A URANYL NITRATE SOLUTION AT pH 2.0

Initial uranium concentration - 100 mg./l.
10 g. charcoal per liter
48 hours' agitation

Temperature, °C.	Uranium Adsorbed, %
0	36
25	38
100	32

Reversibility

A single experiment was conducted to establish the reversibility of the adsorption process by approaching the equilibrium point from the opposite direction.

From a uranyl nitrate solution at pH 2.0, one gram of charcoal adsorbs 3.50 mg. of uranium from 100 cc. of solution originally containing 10 mg. of uranium. The same amount of charcoal adsorbs 4.75 mg. of uranium from 50 cc. of a solution of twice the above concentration. After loading a one-gram sample of charcoal with 4.75 mg. of uranium under the second set of conditions, the solution was diluted to 100 cc. (pH 2.0), thereby yielding the first set of conditions mentioned, and again equilibrated. The carbon was found to contain 3.50 mg. of uranium, indicating that the adsorption of uranium by charcoal from a uranyl nitrate solution at pH 2.0 is a reversible process.

The Amount of Charcoal

The per cent of uranium adsorbed from uranyl nitrate solution (pH 2.0) is plotted in Figure 3 as a function of the initial uranium concentration for various amounts of charcoal. The solid line represents the experimental data for nitrate solutions given in Figure 2. The broken lines, for amounts of carbon greater than 10 grams per liter, were calculated from the equation previously given. This equation accurately represents the data for nitrate solutions in the range of equilibrium concentrations of uranium of 0 to 200 mg. per liter. The calculations were spot checked and found to compare satisfactorily with experimental values, as shown in Table 5.

FIGURE 3. PER CENT URANIUM ADSORBED AS FUNCTION OF THE AMOUNT OF CARBON PRESENT AND INITIAL URANIUM CONCENTRATION.

TABLE 5. COMPARISON OF OBSERVED AND CALCULATED
VALUES FOR ADSORPTION FROM URANYL
NITRATE SOLUTIONS AT pH 2.0

Initial uranium concentration - 215
mg./l.
Agitation time - 96 hours
Minus 100-mesh charcoal

Charcoal, g./l.	pH	Uranium Adsorbed, Per Cent	
		Calculated	Observed*
50	1.97	81	81
30	1.98	61	67
20	1.98	49	52
10	1.98	29	28

* Average of 2 determinations.

DISCUSSION OF RESULTS

The adsorption of ions from solutions by various adsorbents has been discussed by Freundlich.³ As he has pointed out, it is not always easy to distinguish apolar adsorption from the polar type encountered in zeolitic and other base-exchange materials. In fact, it is apparent that we are usually dealing with a mixture of both types. Perhaps the concept of the ionic atmosphere may ultimately prove to be useful in interpreting adsorption phenomena.

Adsorption on charcoal is ordinarily considered, however, to be typically apolar and the carbon is thought of as adsorbing compounds rather than exchanging ions. Traube's rule, which states that of organic compounds of a given series, those of higher molecular weight are more actively adsorbed, is often generalized to state that complicated and heavy molecules are adsorbed more readily than

3. Freundlich, H., "Colloid and Capillary Chemistry", E. P. Dutton and Company, New York, p. 201 et seq.

lighter and simpler ones. These generalizations are, however, oversimplifications of an essentially complex phenomenon.

As applied to uranium solutions, our lack of knowledge of the nature of carbon adsorption must be added to our lack of knowledge of the uranium solutions themselves. The ionic species present in a simple solution of uranyl nitrate and nitric acid at various pH values can still be only surmised. Of particular significance, however, may be the rapid change in adsorption which occurs in these solutions at pH 2. It has been suggested that this is attributable to hydration of the UO_2 ion. Kraus and Nelson⁴ have reported indications of the existence of a compound $U(OH)_4$ in the hydrolysis of UCl_5 at pH 2. The presence of such a compound in the present experiments would, of course, involve a reduction of U(VI) to U(IV). Such a reduction appears improbable, but one recalls discussions of the question of whether gold is adsorbed in the metallic state from complex cyanide solutions by carbon.

It is apparent from these initial experiments that any practical application of carbon adsorption for the recovery of uranium from solutions will have to be based on a thorough study of the fundamental factors involved. The experimental work so far has established that: low pH values reduce the adsorption of uranium; a marked change in the adsorption of U(VI) occurs at approximately pH 2; under a given set of conditions, the adsorption of uranium follows a typical Freundlich isotherm; the particle size of the charcoal affects the rate of adsorption but not the amount of uranium adsorbed at equilibrium; the temperature coefficient of adsorption is negligible; and the adsorption of uranium by activated charcoal from uranyl solutions is a reversible process.

4. Kraus and Nelson, AECD, 2394, p. 8.