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CARBON BED TREATMENT
OF AQUEOUS PLANT WASTE
FOR REMOVAL OF ORGANIC MATERIALS

August 1969

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FOR REMOVAL OF ORGANIC MATERIALS

By

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R. E. Lerch

ABSTRACT

A bed of activated carbon was shown to quantitatively remove CCl_4 , TBP, DBBP, HDEHP, and TOPO from high salt aqueous waste concentrate solutions. The TBP-carbon bed or the DBBP-carbon bed would in turn "extract" plutonium from the aqueous waste solution. Recovery of the extracted plutonium and/or regeneration of the carbon bed are probably not economically feasible.

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CARBON BED TREATMENT OF AQUEOUS PLANT WASTES FOR REMOVAL OF ORGANIC MATERIALS

INTRODUCTION

Organic materials, in the form of dissolved organic, entrained organic (emulsions) or "slugs" of free organic, are currently being sent to aqueous waste cribs following chemical processing of reactor fuels. Since it is desirable to remove these organic materials, mainly CCl_4 , TBP, and DBBP, from the aqueous waste stream and activated carbon has been known to adsorb certain organic species, the possibility of using carbon to remove these small amounts of organic material was suggested.⁽¹⁾ The main objective of this program, therefore, was to define the degree of removal of these organic materials from the aqueous stream by passing the stream through a bed of activated carbon. In addition, it was desirable to know whether the adsorbed organic material would then extract dilute concentrations of radionuclides from the aqueous stream.

SUMMARY

Use of activated carbon to remove CCl_4 , TBP, DBBP, HDEHP, and TOPO from high salt aqueous waste streams was shown to be highly feasible. Removal of these various forms of organic material was nearly quantitative over a wide range of aqueous flow rates (10^2 - 10^3 gal/ft²-hr) and feed conditions. Also, TBP and DBBP were found to be quite effective in "extracting" plutonium (but not americium) once the organic material had been adsorbed onto the carbon. Recovery of the extracted plutonium and/or regeneration of the carbon bed are probably not economically feasible.

Three types of activated carbon were particularly effective in removing these organic materials. They were Filtrasorb-400 (Calgon Corporation), Filtrasorb-300 (Calgon Corporation), and a Pittsburgh Coke and Chemical carbon.

EXPERIMENTAL

CHEMICALS

The following chemicals were used as received: dibutylbutylphosphonate (DBBP, Virginia Carolina Chemical Company); tributylphosphate (TBP, Commercial Solvents Company); trioctylphosphine oxide (TOPO, Commercial Grade, Eastman-Kodak Company); di(2-ethylhexyl)phosphoric acid (HDEHP, Victor Chemical Works); carbon tetrachloride (CCl_4 , CP Grade, Mallinckrodt Chemical Works).

CARBON

In all, nine different types of activated carbon were evaluated for organic adsorption. They were:

Filtrisorb-400	Calgon Corporation
Filtrisorb-300	Calgon Corporation
Pittsburgh	Pittsburgh Coke and Chemical
Nuchar Granular	West Virginia Pulp & Paper Company
Witco 517	Witco Chemical
Witco 718	Witco Chemical
Super Westchar	Western Filter Company
Cocoanut	Fisher Scientific Company
Barnebey	Barnebey-Cheney Chemical

All except Witco-718 were ground to -18+50 mesh* prior to use. Witco-718 was -18+40 mesh.

EQUIPMENT

The column used in these experiments is shown in Figure 1. It was designed to handle variable feed-solution flow rates and was equipped with an air vent for easy backwashing.

A Research Specialties 600 series gas chromatograph was used for all gas chromatographic determinations, and standard alpha and gamma counting equipment was used for all radiological determinations.

* U.S. Standard Sieve Series (1940)

Figure 1. Carbon-Organic Loading Column

RESULTS AND DISCUSSION

PRELIMINARY LOADING EXPERIMENTS

A sample of Pittsburgh Coke and Chemical activated carbon was initially tested for organic adsorption. It was found that CCl_4 , TBP, and DBBP adsorbed onto the activated carbon (-18+50 mesh) from a high salt waste concentrate aqueous stream (0.25M HNO_3 , 5.5 to 6.5M in total nitrate salts)* to the extent of 280, 430, and 610 ml of organic per liter of carbon, respectively. The organic content in the aqueous effluent (as analyzed by gas chromatography) was negligible (i.e. <10 ppb) until the carbon bed was completely saturated with organic.

OPERATING CONDITIONS

All experiments conducted in this study were done at room temperature. A single loading run at 50°C using CAX solution showed a very slight decrease in the amount of organic loaded, probably due to the slight increase in the solubility of the organic in water, at the higher temperature.

The flow rate of a typical carbon bed (Pittsburgh Coke and Chemical Carbon, -18+50 mesh) was measured for both water and the high salt waste concentrate solution as a function of the pressure applied to the feed solution. Pressure was adjusted by varying the height of the liquid above the top of the bed. Results (Figure 2) indicated that a typical carbon bed could be operated at feed rates between 10^2 and 10^3 gal/ft²-hr without appreciable pressure drop across the bed.

EVALUATION OF VARIOUS ACTIVATED CARBONS

The loading capacities of nine different grades of activated carbon were evaluated in this study, and the following five organic solutions were used in the evaluation:

* See Appendix for actual solution make-up.

Figure 2. Liquid Flow Rate Through Carbon Bed

- Synthetic CAX solution (30% TBP, 70% CCl_4)
- Synthetic CWX solution (30% DBBP, 70% CCl_4)
- HDEHP solution (0.3M HDEHP, 0.2M TBP in NPH* diluent)
- TOPO solution (0.15M TOPO in CCl_4)
- TOPO-DBBP solution (0.10M TOPO, 30% DBBP, 70% CCl_4)

The relative organic capacities of the various carbons are listed in Table 1. A comparison of the loading capacities of the nine types of carbon is shown in Figure 3. Bed capacities were measured by loading the organic solution onto an aqueous-soaked column of the activated carbon, then washing the excess organic from the carbon with 12 to 15 column volumes** of 2M nitric acid. The carbon columns were prewashed with water prior to organic loading to simulate loading from an aqueous medium since, in this particular study, we were interested in the removal of organic materials from an aqueous waste stream. The actual loading capacities of the various carbons would probably have been larger if the organic material had been loaded directly onto the dry carbon. In addition, some grades of carbon were pretreated with 2M nitric acid to decrease the amount of gassing (usually due to NO_2 from HNO_3 decomposition) prior to actual evaluation.

The adsorption of the organic material onto the carbon did not appear to be selective; instead, the carbon adsorbed any organic it contacted. Gas chromatographic analysis of the first traces of excess organic coming off the carbon showed essentially the same organic composition as the original feed material. This suggests that more aqueous waste could be treated (per unit of carbon bed) for removal of TBP, DBBP, TOPO, etc. if the organic diluent (e.g., CCl_4 , NPH) were removed prior to carbon bed treatment of the aqueous waste solution.

* NPH is the Hanford designation for a mixture of normal paraffin hydrocarbons, primarily C_{10} through C_{14} .

** One column volume is the total volume occupied by the carbon in the column, including the void space.

Table 1. Loading Capacities of Various Activated Carbons

Carbon Type (a)	Density, (b) g C/ml bed	CAX, ml Org/liter C	CWX, ml Org/liter C	HDEHP, ml Org/liter C	TOPO, ml Org/liter C	TOPO-DBBP, ml Org/liter C
Nuchar Granular	0.22	282	266			
Pittsburgh	0.33	343	409	368	342	345
Filtrisorb-400	0.34	332	443	390	350	316
Filtrisorb-300	0.35	291	284	418	297	300
Witco-Grade 517	0.34	270	261	248	281	258
Witco-Grade 718	0.44	220		219	246	186
Cocoanut - Lot 7760	0.39	250	241	264	241	217
Super Westchar 64242	0.46	268	238	260	257	250
Barnebey-Cheney PC 8592	0.45	206	240			

(a) All of the carbons except Witco-718 were ground to -18+50 mesh (U.S. Standard Sieve size);
Witco-718 was ground to -18+40 mesh.

(b) Bulk packing density of a freshly degassed column of carbon.

Figure 3. Organic Loading Capacities of Various Carbons

On the basis of over-all loading capacity for the five organic solutions used in this evaluation as well as loading characteristics (e.g., gassing, floating, etc.), the Pittsburgh carbon and the Filtrasorb-300 and Filtrasorb-400 carbons were judged to be the most desirable carbons for use in removal of organic materials from aqueous waste streams.

BED RECOVERY AND REGENERATION

A bed of Pittsburgh activated carbon (-18+50 mesh) was loaded with synthetic CAX solution (30% TBP-70% CCl_4). The loaded bed was washed with 6-bed volumes of acetone followed by 18-bed volumes of 2M nitric acid. The bed was then reloaded with more synthetic CAX solution and the operation was repeated. The results (Table 2) indicate that acetone is only partially effective in regenerating the carbon bed.

Table 2. Effect of Acetone Wash on Carbon Reloading Capacity

<u>Loading</u>	<u>CAX, ml Org/liter C</u>	<u>Percent Loaded</u>
1st	341	100
2nd	300	88
3rd	244	71

A second carbon bed (Filtrasorb-400, -18+50 mesh) was loaded with synthetic CAX solution, washed with 2M nitric acid, and then steam-distilled (100 °C). Following steam distillation, the bed was reloaded with more synthetic CAX solution, and the operation was repeated. The results (Table 3) indicate that low temperature steam distillation is only partially effective in regenerating the carbon bed.

Table 3. *Effect of Steam Distillation on Carbon Bed Reloading Capacity*

<u>Loading</u>	<u>Steam Used, (a)</u> <u>bed volumes</u>	<u>CAX,</u> <u>ml Org/liter C</u>	<u>Percent</u> <u>Loaded</u>
1st		330	100
2nd	8 1/2	176	53
3rd	7	170	52
4th	17	170	52

(a) *Measured as liquid*

RADIONUCLIDE SORPTION

Many organic materials adsorb onto carbon without loss of their "reactivity" if the adsorption process does not tie up their functional groups. Therefore, it was of interest to know whether or not certain radionuclides would be extracted by certain adsorbed organics. The behavior of plutonium and americium were of particular interest.

Plutonium

Several columns of activated carbon (Pittsburgh Coke and Chemical, -18+50 mesh) were loaded with either synthetic CAX solution (30% TBP, 70% CCl_4) or synthetic CWX solution (30% DBBP, 70% CCl_4). A measured amount of the high salt waste concentrate solution (see Appendix) containing ^{238}Pu tracer (4.75×10^5 d/m/ml) was fed to these carbon-organic columns, and the column effluent was analyzed for plutonium. The loaded carbon beds containing either the TBP or DBBP were found to produce nearly quantitative extraction of the plutonium from the waste steam. A typical loading profile showing plutonium leakage for loading ^{238}Pu onto a TBP-carbon bed is shown in Figure 4. The actual loading capacities of TBP or DBBP carbon beds for extraction of plutonium were not determined.

Figure 4. *Plutonium Leakage During Loading of ^{238}Pu on a TBP-Carbon Bed*

Attempts at eluting the extracted plutonium from the loaded organic-carbon beds were only partially successful. The plutonium-organic complex was essentially unaffected by washing with either dilute nitric acid (0.25M) or dilute hydrofluoric acid (0.25M). A typical leakage curve for loading ^{238}Pu onto a DBBP-carbon bed and then washing the loaded bed is shown in Figure 5. Actual plutonium leakage during the loading, 8M HNO_3 wash, and 0.5M HNO_3 wash cycles were 0.6, 0.3, and 0.8%, respectively.

A solution of ferrous sulfamate (0.05M) in dilute nitric acid (0.25M) was somewhat effective in removing the extracted plutonium from a TBP-carbon bed. However, column gassing was so extreme that total disruption of the carbon bed occurred.

Americium

Americium was not extracted by either TBP-carbon or DBBP-carbon beds under normal loading conditions (0.25M HNO_3 , 5 to 7M total nitrates). A typical loading profile showing americium leakage during loading of ^{241}Am onto a TBP-carbon bed is shown in Figure 6. Similar curves were found for DBBP-carbon beds. However, americium did extract when the feed solution pH was greater than one and when the feed solution flow rate through the carbon bed was very slow (<3 bed volumes/hr). The slow flow rate and relatively high pH probably rule out use of organic-carbon beds for removal of americium from plant waste streams.

REMOVAL OF PLANT "SOLIDS"

During treatment of aqueous plant waste one is often confronted with "solids" (mainly organic emulsions containing fines or undissolved ash). When a synthetic feed solution containing 20% by volume of these solids was fed to a carbon bed containing a 48-mesh filter, the solids accumulated on the top

Figure 5. Plutonium Leakage During Loading and Washing ^{238}Pu on a DBBP-Carbon Bed

Figure 6. Americium Leakage During Loading of ^{241}Am on a TBP-Carbon Bed

of the bed and then gradually filtered through the carbon bed. As the solids passed through the bed, the organic material adsorbed onto the carbon (until the bed was completely saturated) while the fines passed through the bed. No appreciable drop in solution flow rate occurred during this loading sequence, which indicated that no plugging of the carbon bed occurred.

CONCLUSIONS AND RECOMMENDATIONS

Removal of CCl_4 , TBP, DBBP, HDEHP, and TOPO from high salt aqueous waste streams by adsorption onto activated carbon appears to be quite feasible. However preliminary studies, using acetone or low temperature steam, indicate that regeneration of the carbon bed is not economically feasible.

Further studies should include the following:

- Scale-up to larger capacity carbon beds
- Determination of optimum bed height to diameter ratio
- Examination of other possible solvents for regeneration of the carbon bed.

ACKNOWLEDGEMENTS

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APPENDIXHigh Salt Waste Concentrate Solution Make-Up⁽²⁾

<u>Substance</u>	<u>Concentration</u>
HNO ₃	0.25 <u>M</u>
AlF(NO ₃) ₂	0.4 - 0.9 <u>M</u>
Al(NO ₃) ₃	0.15 <u>M</u>
Mg(NO ₃) ₂	0.45 <u>M</u>
Ca(NO ₃) ₂	0.25 <u>M</u>
Fe(NO ₃) ₃	0.08 <u>M</u>
Na ₂ SO ₄	0.04 <u>M</u>
NaNO ₃	1.36 <u>M</u>
KNO ₃	0.96 <u>M</u>
Pu ^(a)	1.0 mg/liter
Am ^(a)	0.1 mg/liter
Total nitrate is 5.46 - 6.46 <u>M</u>	

(a) *Optional*

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2. L. E. Bruns (ARHCO). *Unpublished Data. (Private Communication to R. E. Lerch), September 1968.*

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