THE DESIGN OF SELECTIVE RESINS FOR THE REMOVAL OF PERTECHNETATE AND PERCHLORATE FROM GROUNDWATER

Gilbert M. Brown,[1] Peter V. Bonnesen,[1] Bruce A. Moyer,[1] Baohua Gu,[2] Spiro D. Alexandratos,[3] Vijay Patel,[3] and Robert Ober[3]
1 - Chem. and Anal. Sci. Div., Oak Ridge National Laboratory, Oak Ridge, TN 37831
2 - Envir. Sci. Div., Oak Ridge National Laboratory, Oak Ridge, TN 37831
3 - Department of Chemistry, University of Tennessee, Knoxville, TN 37996

INTRODUCTION

on the resins was determined by bringing 0.1g resin (dry weight equivalent) in contact with a solution containing initially 10 mg/L of ClO_4^- in 100 mL volume using methods described by Gu, et al. [1] The test solution was a simulant of a typical contaminated groundwater and consisted of 3 mM $NaHCO_3$, 1 mM $CaCl_2$, 0.5 mM $MgCl_2$, 0.5 mM Na_2SO_4, and 0.5 mM KNO_3. The solution following equilibration with the resin was analyzed for ClO_4^- concentration by means of an ion chromatograph, and the distribution coefficient, K'_d (mL/g), was calculated as the ratio of ClO_4^- sorbed (mg/g resin) to the concentration of ClO_4^- remaining in solution (mg/mL).

RESULTS AND DISCUSSION

Distribution Coefficients for Pertechnetate Sorption. Measurement of the distribution coefficient for TcO_4^- sorption to a series of resins has led to a scientific basis for pertechnetate selectivity based on systematic variations of the microenvironment of the exchange sites. These measurements support an electrostatic model which indicates that selectivity for TcO_4^- can be achieved by increasing the size of the cation and maintaining an environment of low polarity at the exchange site. The electrostatic model indicates that transfer of a large cation and a large anion from an aqueous to a non-aqueous phase are favored over the transfer of smaller cations and anions. In a resin, an environment favorable to TcO_4^- was created within a divinylbenzene-crosslinked poly(vinylbenzylchloride)-based resin by reacting trialkylamines having long hydrocarbon chains with the chloro group to create the quaternary ammonium ion exchange sites. The level of crosslinking and the size(s) of the alkyl substituents of the amine were varied for the macroreticular resin so that the distribution coefficient for pertechnetate ion sorption over the other anions commonly found in groundwater was greatly enhanced. The selectivity for large anions like pertechnetate over smaller anions generally increases with increasing size of the cationic site. We have found that selectivity for pertechnetate increases as the R group increases in the series methyl, ethyl, n-propyl, n-butyl, and n-hexyl. In fact, the equilibrium K'_d increases monotonically with increasing radius of the alkyl group. Concomitant with this increased selectivity, however, is a decrease in the rate of anion exchange (exchange kinetics), to the extent that it requires a few weeks for equilibrium to be reached for the resins where R is n-hexyl. A consideration of the rate of approach to equilibrium in time-dependent distribution coefficient measurements led us to prepare bifunctional resins that have exchange sites comprised of quaternary ammonium groups with large alkyl groups for high selectivity and small alkyl groups for improved kinetics. [2,3]

Our findings showed that resins with superior pertechnetate selectivity and breakthrough performance in column flow-through experiments could be obtained by incorporating two different types of strong-base anion exchange sites into the resin. The first type is derived from trialkyl amines in which the three identical alkyl groups each contain 5-8 carbon atoms; the second type is the same except the alkyl groups each contain 2-4 carbon atoms. The large alkyl groups enhance pertechnetate selectivity, whereas the smaller alkyl groups enhance the kinetics of the sorption process. In batch equilibrium measurements, the resin with the highest 24 hr K'_d contained exchange sites derived from tri-n-hexyl and tri-n-propyl amines. For column flow-through operations, the tri-n-hexyl/triethyl resins (for a given resin mesh size) processed more bed volumes for a given % breakthrough than the tri-n-hexyl/tri-n-propyl resins. These novel bifunctional resins are designed to incorporate together in one resin exchange sites that are highly selective for pertechnetate (but kinetically slow), with sites that are less selective (but kinetically fast). The resulting bifunctional resins have superior selectivity and the same or better exchange capacity compared to resins prepared from single tri-alkyl amines (such as tripropyl or tributyl amine alone), but that possess equivalent or faster exchange kinetics.

Field Tests of Pertechnetate Sorption. As a benchmark for our work, the synthetic resins including the novel bifunctional resins have been compared to the commercially available Purolite® A-520E resin (triethylamine sites) in current use for Tc removal at the Northwest Plume Treatment Facility at DOE's PGDP. A small-scale field demonstration of the synthetic resins RO-02-119 (trihexylamine/triethylamine, +40/-60 mesh) was conducted at the Northwest Plume Pump-and-Treat Facility at the PGDP site [4]. This synthetic resin was run in parallel with the Purolite resin, using 50 cm^3 bed volumes at a flow rate of 300 ml/min, so that the relative effectiveness of the two resins in removing TcO_4^- from the contaminated groundwater could be directly compared. Concentrations of TcO_4^- in the influent and the effluent were monitored periodically. Results indicated that the column containing the synthetic resin (RO-02-119) performed extremely well with respect to both Tc-99 removal and hydraulic flow characteristics. The breakthrough of Tc-99 appeared to increase relatively rapidly after ~600,000 BV groundwater had passed through the synthetic resin column. In contrast, we had difficulty in maintaining a good hydraulic flow through the Purolite® A-520E column, and after about 5 weeks of operation the column became clogged and flow was stopped. At 1% breakthrough of Tc-99, approximately 580,000 bed volumes of groundwater were treated by the synthetic resin whereas only about 105,000 bed volumes of groundwater were treated by the Purolite resin. Both our laboratory studies and field trials indicated that the performance of the bifunctional synthetic resin is superior to the commercial Purolite resin in terms of both TcO_4^- selectivity and hydraulic characteristics.

Distribution Coefficients for Perchlorate Sorption. Table 1 lists the K'_d values of a group of synthetic monofunctional and bifunctional resins at an initial ClO_4^- concentration of ~10 mg/L. Included are data for several commercial resins including the Purolite® A-520E resin which is among the best nitrate selective resins available. As observed for pertechnetate sorption, the bifunctional trihexylamine/triethylamine resin (RO-02-119) designed for high pertechnetate selectivity has superior selectivity for ClO_4^- sorption compared to the commercial Purolite® A-520E resin, removing ClO_4^- to below its detection limit from an initial concentration of 10 mg/L. A systematic study of the K'_d values for ClO_4^- sorption was conducted as a function of the length of the hydrocarbon chain (size of the alkyl groups). Results (Table 1) indicated that the K'_d values (24-h measurement) increased in the series of methyl<ethyl<propyl in the order expected from measurements on the sorption of pertechnetate. However the value for the resin with tributylamine functional groups shows a decrease. We did not observe this decrease in K'_d with pertechnetate sorption until the size of the alkyl group reached six carbons (trihexylamine). For perchlorate sorption to the bifunctional resins, the K'_d values indicate that the triethylamine-trihexylamine resin is the most selective. This was not the case for pertechnetate sorption. The bifunctional resins based on the combinations of tripropylamine-trihexylamine and tributylamine-trihexylamine were more selective for 24-h measurements of K'_d.

CONCLUSIONS

Systematic variation of the chemical and physical properties of the exchange site of anion exchange resins has lead to experimental support of an electrostatic model which suggested that selectivity for large poorly hydrated anions can be achieved by increasing the size of the organic resin bound cation and by maintaining an environment of low polarity at the exchange site. Consideration of anion exchange kinetics led to the development of bifunctional anion exchange resins. These resins were developed for TcO_4^- sorption, and they have excellent selectivity for ClO_4^- sorption as well.

ACKNOWLEDGEMENTS
Development of a Tc selective resin was sponsored by the Efficient Separations and Processing Crosscutting Program, Office of Science and Technology, Office of Environmental Management, U.S. Department of Energy, under contract DE-AC05-96OR22464 with Oak Ridge National Laboratory, which is managed by Lockheed Martin Energy Research Corporation. Funding for perchlorate sorption research was provided by Lockheed Martin Corporation, project number ERD-98-1644.

Table 1. Comparison of K'_d values for ClO_4^- and TcO_4^- sorption to selected resins[1].

Resin	**Amine**	**%DVB**	**TAEC** [2] (meq/g)	**ClO_4^- 24 h *K'd*** (mL/g)	**Tc-24 h *K'd*** [4] (mL/g)
VP-01-165	$(Methyl)_3N$	10	3.77	86,800	6,400
VP-01-168	$(Ethyl)_3N$	10	2.84	166,000	16,200
VP-02-152	$(Propyl)_3N$	10	2.33	588,000	22,300
VP-02-083	$(Butyl)_3N$	10	1.66	319,000	31,800
Amberlite® IRA-900	$(Methyl)_3N$	5	3.56	40,100	2,500
Purolite® A-520E	$(Ethyl)_3N$	5	2.80	203,000	12,800
Sybron Ionac® SR-6	$(Butyl)_3N$	5	1.80	250,000	20,700
RO-02-119	Et_3N/Hex_3N	5	2.53	>3,300,000 [3]	38,000
RO-02-61	Pr_3N/Hex_3N	5	2.15	523,000	38,200

1. All K'_d values have a ±5% uncertainty. All resins are crosslinked with divinylbenzene (DVB). Initial ClO_4^- concentration was 10 mg/L.
2. TAEC = Total anion exchange capacity.
3. K'_d values were estimated as the equilibrium concentration approached zero (with a detection limit of ~3 μg/L).
4. K'_d values for TcO_4^- sorption determined with high electrolyte Groundwater Test Solution accounting for lower absolute value relative to ClO_4^- coefficients.

REFERENCES

[1] Gu, B., Brown, G. M., Alexandratos, S. D., Ober, R., Dale, J. A., and Plant, S, To be presented at the Am Chem Soc Meeting, New Orleans, 1999.
[2] Brown, G. M.; Bonnesen, P. V.; Presley, D. J.; Bates, L. M.; Moyer, B. A.; Alexandratos, S. D.; Patel, V.; Ober, R.; Gu, B.; Liang, L. *American Chemical Society National Meeting.* San Francisco, April 13-17, **1997**.
[3]. Brown, G. M.; Alexandratos, S. D.; Bates, L. M.; Bonnesen, P. V.; Hussain, L. A.; Moyer, B. A.; Patel, V. *Program and Abstracts, Ninth Symposium on Separation Science and Technoogy for Energy Applications. October 22-26,* **1995***.* p 50.
[4] Gu, B.; Liang, L.; Brown, G. M.; Bonnesen, P. V.; Moyer, B. A.; Alexandratos, S. D.; Ober, R.

1998, *ORNL/TM-13593*, Oak Ridge National Laboratory, Oak Ridge, TN.