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Alkylated Carbon for Perchlorate Remediation

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Background

Perchlorate contamination of ground and surface water is an ongoing problem at a number of sites, principally in the Western U.S. The contamination is a result of historical activities such as previously acceptable disposal procedures and testing of solid rocket motors(1). Perchlorate is highly soluble and environmentally mobile; one result of this behavior is the presence of up to 8 ppb of perchlorate in Lake Mead at the inlet to Las Vegas' municipal water system due to migration of perchlorate from the Kerr-McGee site near Henderson, NV(1). The health effects of exposure to low levels of perchlorate are not well known, but state action levels for perchlorate in drinking water are as low as 1 ppb (2). The responsibility for perchlorate remediation in many of these sites falls to DoD, and development of innovative approaches to remediate this problem has been an active area of research sponsored by SERDP.

A number of methods are available for the remediation of perchlorate contaminated environments(1,3-5). The most widely applied techniques are bioremediation and ion exchange. Most promising for in situ remediation of contaminated sites is bioremediation, in which perchlorate is reduced to chloride(2,6). However, bioremediation is not currently acceptable for the treatment of potable water. Consequently, ion exchange is used for the removal of perchlorate from drinking water.

Ion exchange is currently used at several sites for perchlorate remediation. However, perchlorate removal is a challenging application for most ion exchange resins, which have limited capacity for perchlorate adsorption due to competition by other anions present in drinking water, most notably sulfate and nitrate(7). To address this problem, ion exchange resins with high selectivity for poorly solvated anions, such as perchlorate, have been developed by Gu and coworkers and have much higher usable capacities for perchlorate adsorption(5,7,8). These resins cannot be effectively regenerated using brine, and alternative regeneration technologies have been developed.

Currently, modified activated carbons are under consideration for use in perchlorate remediation of drinking water. Conceptually, activated carbons function similarly to ion exchange resins in that in both cases, perchlorate is adsorbed to cationic surface sites. This has been clearly demonstrated for activated carbons by Cannon and coworkers who have treated activated carbon with ammonia to increase the net positive charge of the activated carbon and thereby, its perchlorate adsorption capacity(9,10).

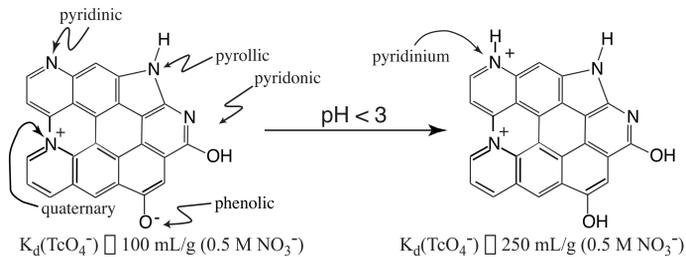
Activated carbons are much less expensive (~\$25 per cu. ft.) than ion exchange resins, which cost ~\$200 per cu. ft. for nitrate selective resins and ~\$750 per cu. ft. for perchlorate selective resins. However, due to the large usable capacities of the ion exchange resins, perchlorate removal by ion exchange resins is currently more economical than by activated carbon.

Objective

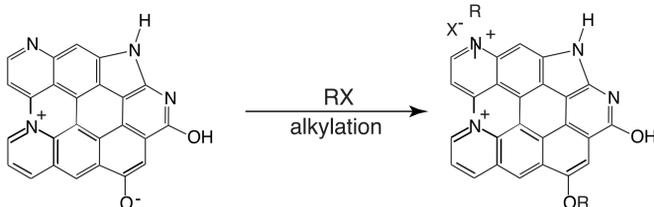
The goal of this project is to determine whether the perchlorate capacity of activated carbon can be further increased by alkylation to convert anionic and neutral sites on the surface of activated carbon into neutral and cationic sites respectively. Furthermore, the alkylated sites should have a greater selectivity for poorly solvated anions such as perchlorate. The long-term goal is to develop less expensive materials for perchlorate sorption.

Structure of activated carbon (why would alkylation be desirable?)

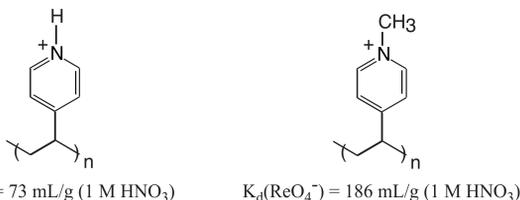
Activated carbon is generally illustrated as a small graphitic sheet decorated on the edge with various functional groups as illustrated below(11-13). The oxygenated phenolic sites are anionic at environmentally relevant pHs, and the pyridinic sites are generally believed to have pKas slightly less than 7. At pH < 3, the affinity of activated carbon for pertechnetate is a factor of 2.5 greater than at pH 7 due to a combination of neutralizing the phenolic sites and protonating the pyridinic sites. In addition, Cannon and coworkers, have shown that nitrogen incorporation into the activated carbon increases the number of cationic sites(9,10).



Alkylation of activated carbon should increase its perchlorate sorption capacity in two ways. First, alkylation increases the net cationic charge of the activated carbon by transforming anionic phenolic groups into neutral ethers and neutral pyridinic groups into cationic pyridinium sites. This effect is roughly analogous to increasing the affinity of activated carbon for perchlorate by lowering the pH.



Second, alkylated pyridinium groups should have a stronger affinity for perchlorate than protonated pyridinium groups.



The effect of converting a pyridinic group into a pyridinium group is even more pronounced. The selectivity of Poly-(4-vinylpyridine), Reillex™-HP for perchlenate (which behaves like perchlorate) in 1 M HNO₃ is increased by a factor of 2.5 upon alkylation(16,17). The main reason for the difference is that the protonated weak-base pyridinium site is a much better hydrogen bond donor than the alkylated strong-base pyridinium site; hydrogen bonding to the anion increases the strength of the interaction between the anion and the cationic site.

Results

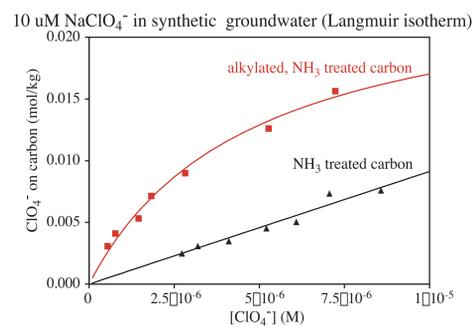
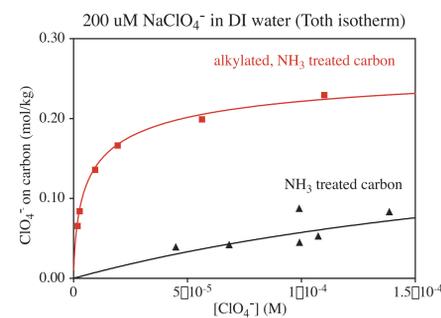
Experimental

The activated carbon used was hydrochloric acid washed General Carbon GC12□40, derived from bituminous coal. All other chemicals were obtained commercially and were treated prior to use. Synthetic groundwater is 0.2 mM NaCl, 0.4 mM Na₂SO₄, 0.1 mM NaNO₃, 2.5 mM NaHCO₃, 0.01 mM NaClO₄(9).

Ammonia treated carbon: Acid washed carbon was heated to 400 °C in a tube furnace under a slow flow of air for 4 hrs then under a 9:1 mixture of NH₃/N₂ for 4 hrs while the temperature was increased to 700 °C and held at that temperature for 4 hours. The carbon was allowed to cool under a nitrogen purge. The carbon was then heated to 100 °C under vacuum until the pressure was less than 30 mTorr.

Alkylated carbon: ammonia treated carbon (1 g) was added to a 23 mL Teflon lined autoclave, and 2 mL dimethyl sulfate was added. The autoclave was heated in an oven at 110 °C for 14 hours. The contents of the autoclave were placed in 100 mL water with ~10 g of NaHCO₃ and heated to reflux overnight to hydrolyze any remaining dimethylsulfate. The carbon was washed with 1 L of water and dried under vacuum at 110 °C until the pressure was less than 30 mTorr.

Adsorption Isotherms



Comparison of nitrogen content with perchlorate capacity

	N (meq/g)	ClO ₄ ⁻ capacity (10 ⁻⁴ M in DI)	ClO ₄ ⁻ capacity (10 ⁻⁶ M in groundwater)
GG 12□40	0.23	0.09 meq/g	
NH ₃ treated	1.06	0.06 meq/g	9□10 ⁻⁴ meq/g
alkylated	0.85	0.22 meq/g	4.4□10 ⁻³ meq/g

Conclusions

Alkylation increases the exchange capacity of activated carbon

- Alkylated carbons have ~4 times the capacity of the parent material
- Effect of alkylation is approximately as anticipated based on effects of low pH on activated carbon and the effects of alkylation on poly-(4-vinylpyridine)

Alkylation of activated carbon is not straightforward

- Conditions for alkylating poly-(4-vinylpyridine) do not work for activated carbon
- Alkyl halides do not alkylate activated carbon
- Removal of the counterion (methylsulfate, triflate) is difficult

Exchange capacity of the activated carbons is low

- Only a fraction of the nitrogen sites are available
- May be related to insufficient removal of the counterion (methylsulfate)
- Greater nitrogen content for the activated carbon would be desirable

Role of alkylation is not yet known

- Are the nitrogen and/or oxygen sites alkylated?

Acknowledgement

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