UNIVERSITY of DELAWARE

The removal of fluoride from water using functionalized carbon materials

Ching-Lung Chen[1], Sang-Won Park[2], Jenn Feng Su[1], Yu-Han Yu[1], C. P. Huang[1]
1: Department of Civil and Environmental Engineering, University of Delaware, Newark, DE, USA 19716
2. College of Environment, Keimyung University, Daegu, Korea

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Outline

1. Introduction
2. Objectives
3. Materials and Methods
4. Results and Discussion
5. Conclusions

Applications

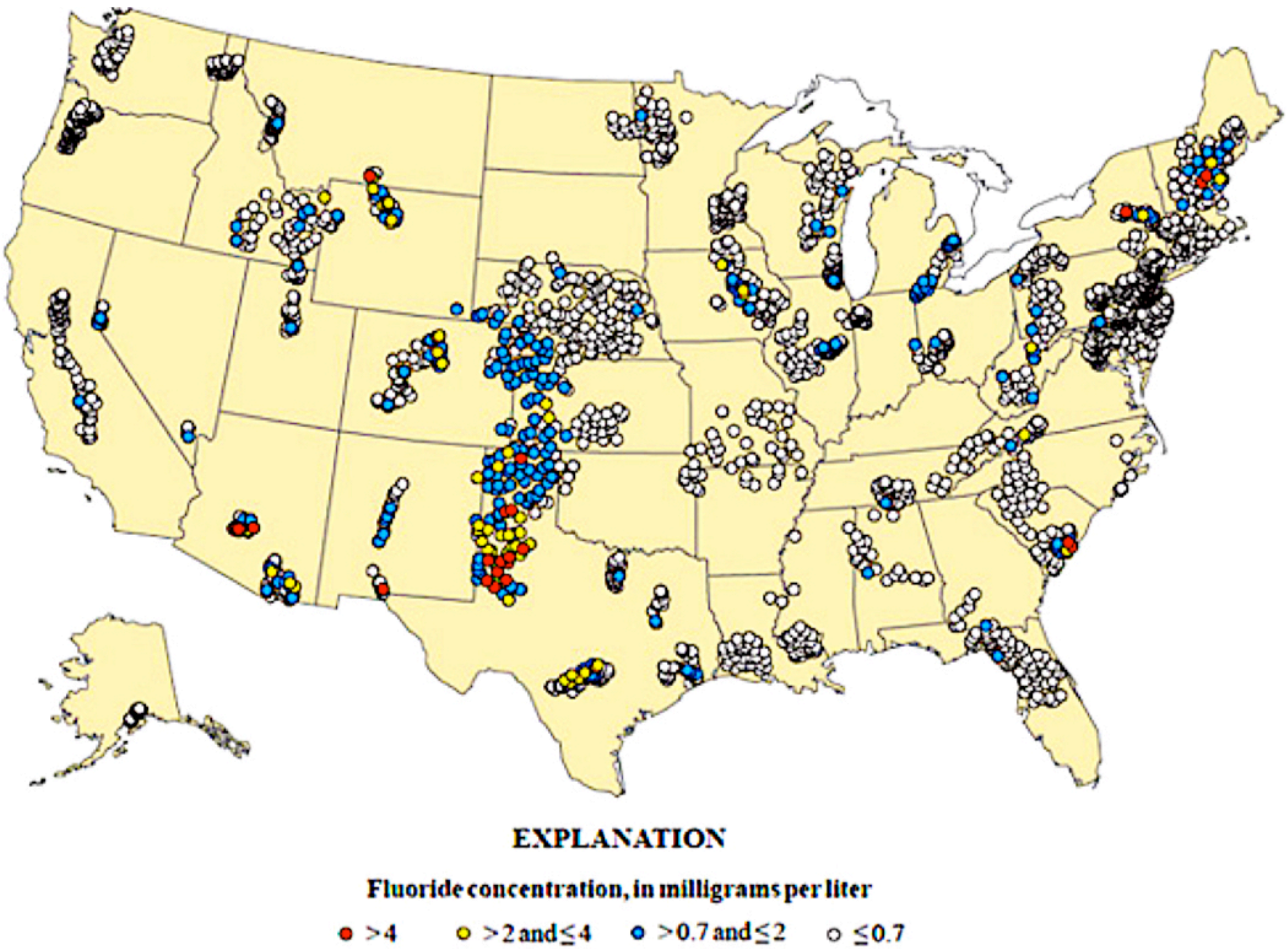
- ❖ **Industrial uses**

1. **Mining (Na_3AlF_6, aluminium smelting)**
2. **Semi-conductor (HF)**

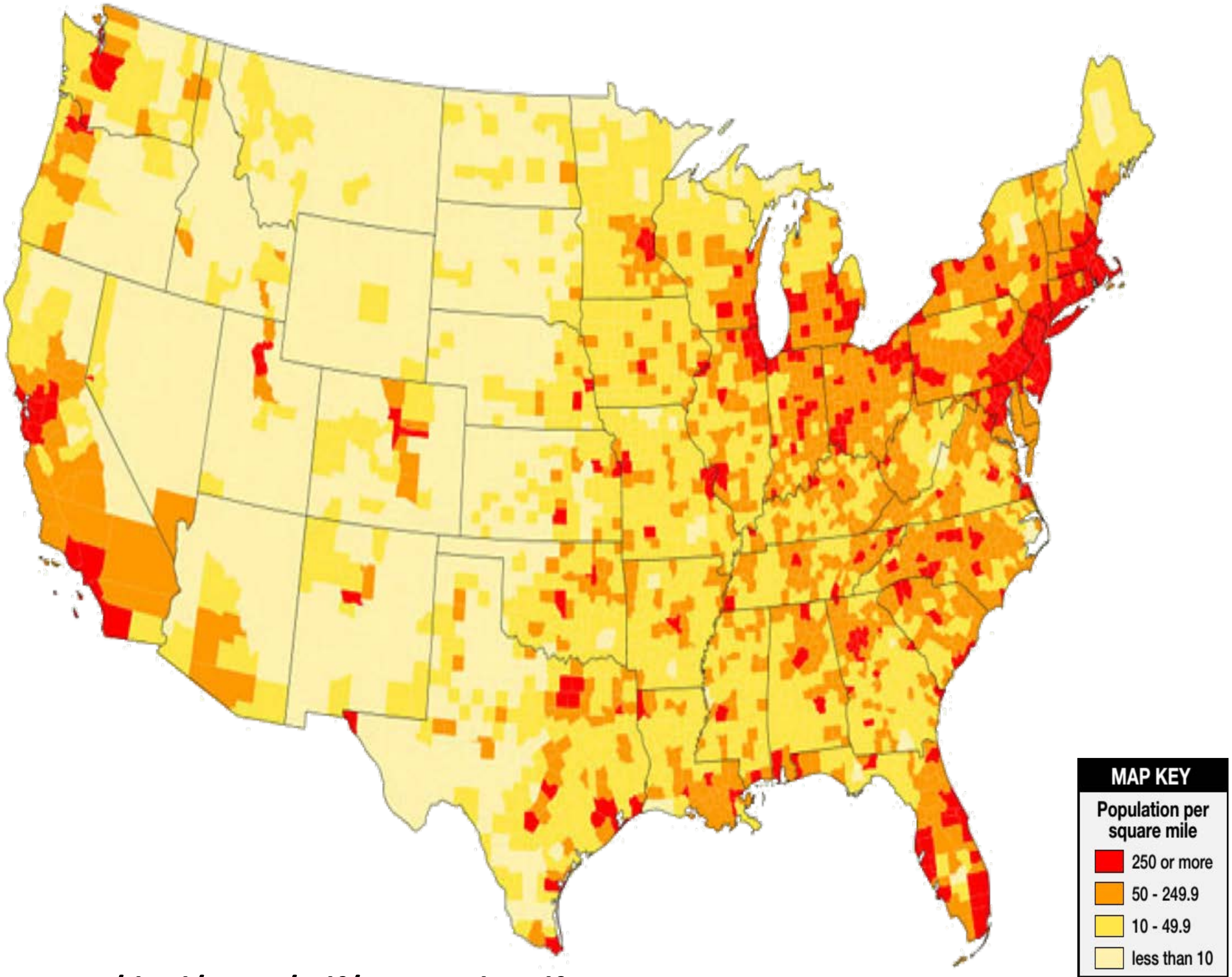
- ❖ **Cavity prevention**

http://mainland.cctt.org/istf2011/pages/Background/UsingRadiation.asp
http://www.pediatricdentistryorthodontics.com/toothpaste-what-to-look-for/

Fluoride Distribution in US



Population Density of the U.S.

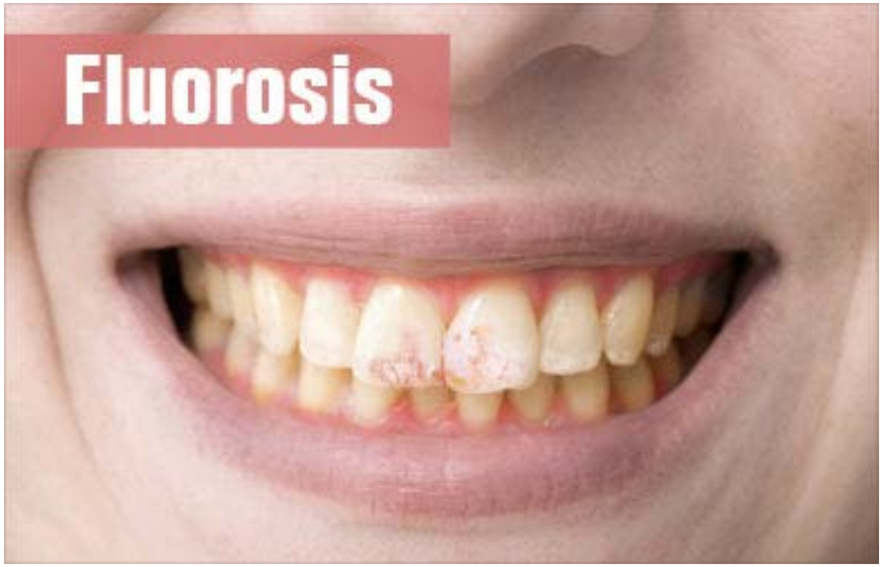


http://www.census.gov/dmd/www/pdf/512popdn.pdf

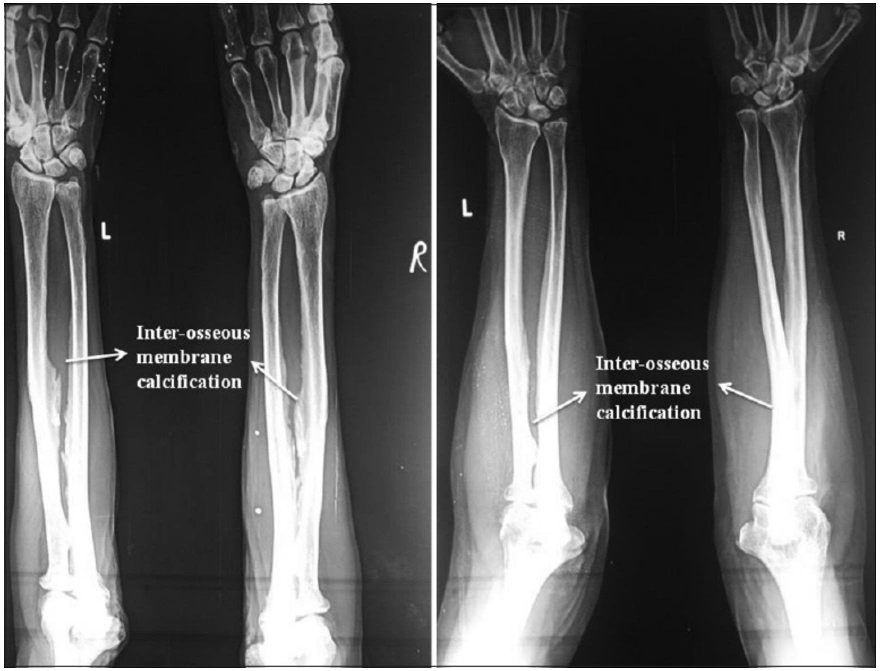
Global Fluoride Distribution

http://www.bgs.ac.uk/research/groundwater/health/fluoride.html

Human Health



1.5 ~ 4 mg/L
Dental fluorosis



> 4 mg/L
Bone calcification

http://www.abc.net.au/health/library/stories/2005/06/16/1831822.htm

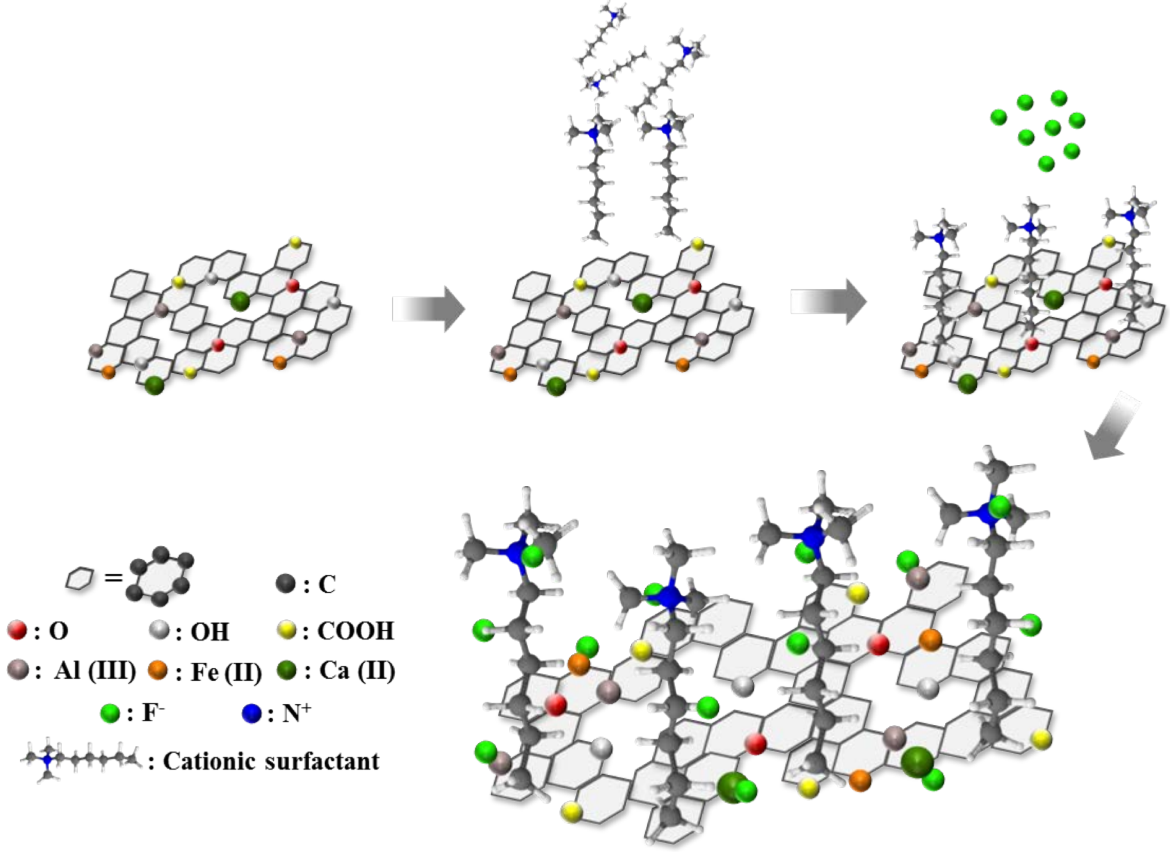
Mn Shruthi et al, 2016

Current Regulatory Status

- USEPA is in the process of reviewing fluoride regulation
  - Enforceable regulation
    - Maximum Contaminant Level (MCL) : 4 mg/L
  - Non- enforceable regulation
    - Secondary standard : 2 mg/L

Fluoride adsorption

- **Hypothesis**
  – Fluoride could be adsorbed by functionalized activated carbon via electrostatic reaction



Objectives

1. To fabricate and characterize activated carbon for fluoride removal

2. To understand the mechanism of functionalized activated carbon to fluoride adsorption

3. To assess the performance of regenerated functionalized activated carbons

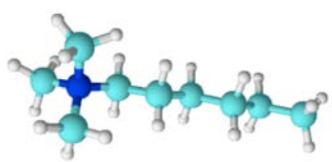
Carbon materials

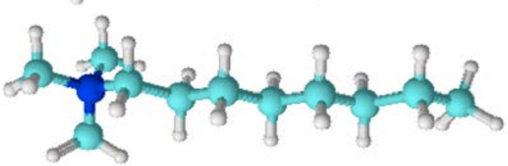
Activated carbon	Base material	Asp (m^2/g)	pH_{zpc}	Ash content (% total mass)
Nuchar SA (PAC)[a]	Wood	1351	3.5	6.3
Filtrasorb 400 (GAC)[a]	Bituminous coal	1236	8.2	5.4
KAC (GAC)[b]	Bituminous coal	1000	6.8	11.6

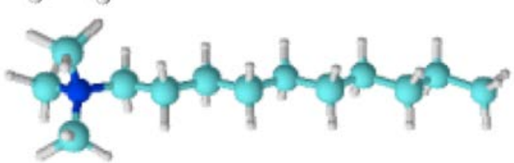
[a] From Corapciohlu and Huang (1987)
[b] This study

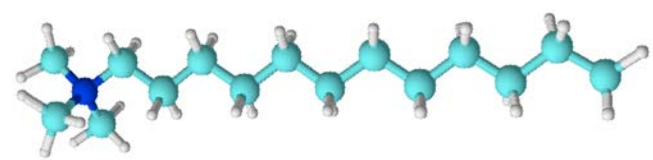
Cationic surfactants (Quats)

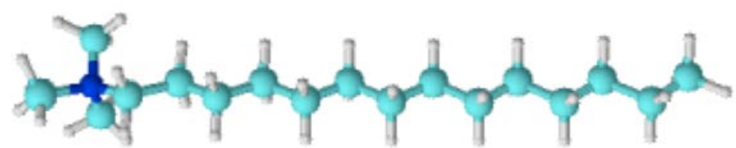
	Moiety	Chain Length (Å)	CMC (mM)
Hexyltrimethylammonium (HTMA)	$CH_3\text{-}(CH_2)_5N^+(CH_3)_3$	9.13	495.0
Octyltrimethylammonium (OTMA)	$CH_3\text{-}(CH_2)_7N^+(CH_3)_3$	11.66	140.0
Decyltrimethylammonium (DCTMA)	$CH_3\text{-}(CH_2)_9N^+(CH_3)_3$	14.19	51.3
Dodecyltrimethylammonium (DDTMA)	$CH_3\text{-}(CH_2)_{11}N^+(CH_3)_3$	16.72	15.0
Tetradecyltrimethylammonium (TDTMA)	$CH_3\text{-}(CH_2)_{13}N^+(CH_3)_3$	19.25	1.6
Hexadecyltrimethylammonium (HDTMA)	$CH_3\text{-}(CH_2)_{15}N^+(CH_3)_3$	21.78	0.97


HTMA


OTMA


DCTMA

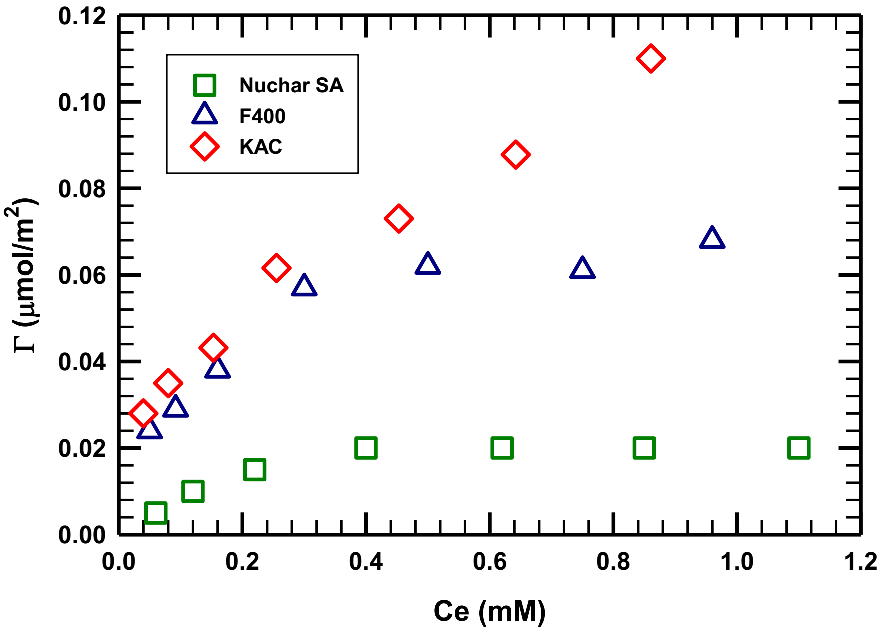

DDTMA

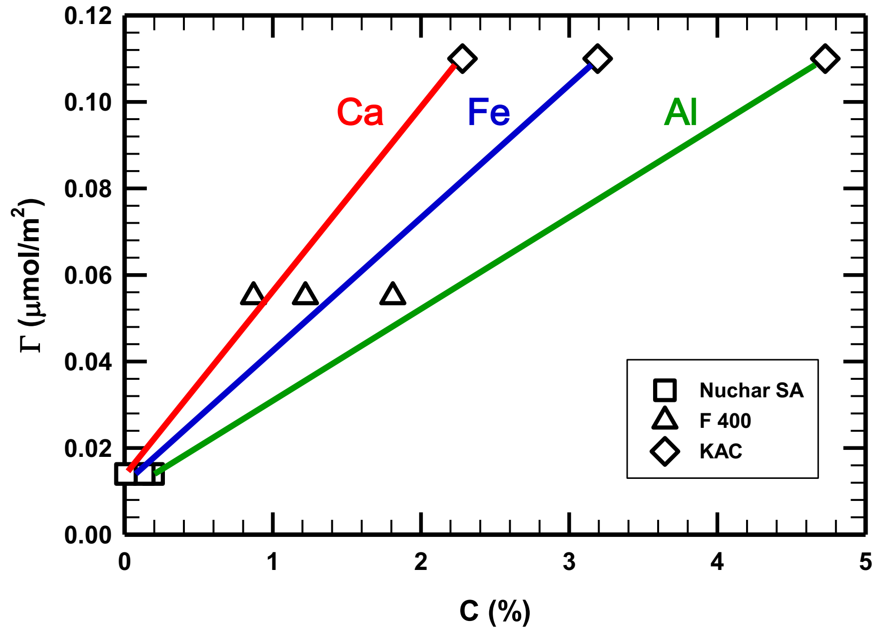

TDTMA


HDTMA

Results and Discussion

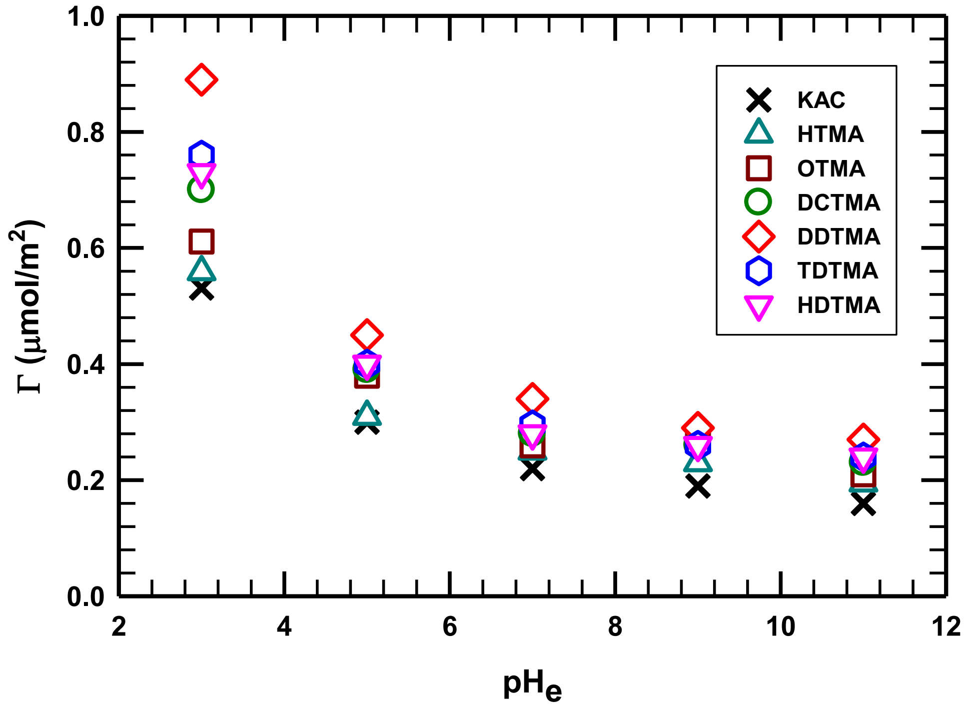
Effect of carbon ash





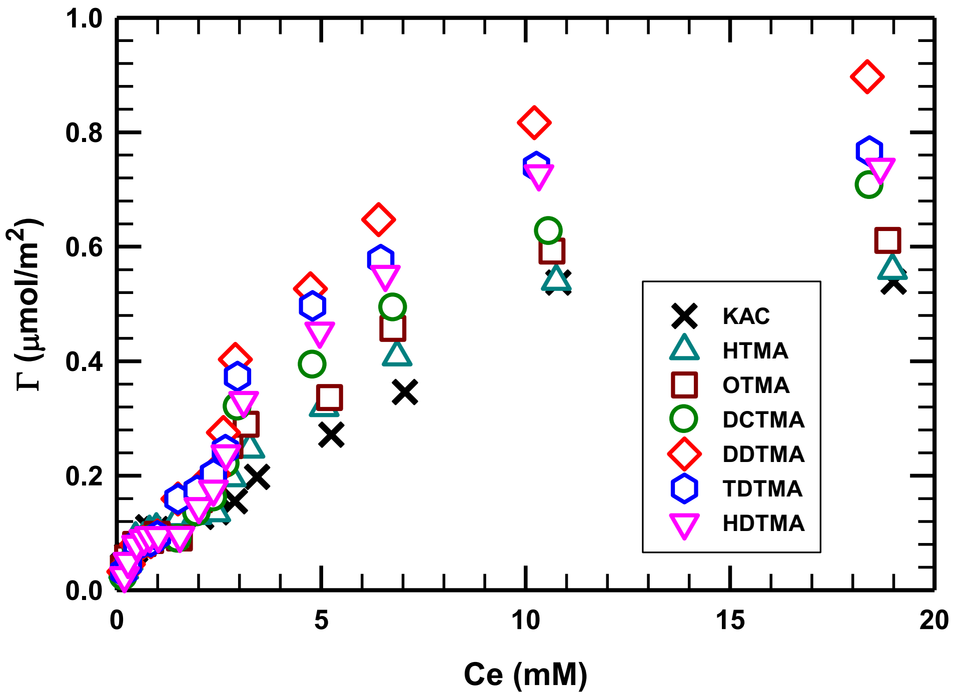
Effect of ash composition for fluoride removal by plain activated carbon.
Experimental conditions: [AC] = 2 g/L, I = 10^{-2} M NaCl, pH = 7.

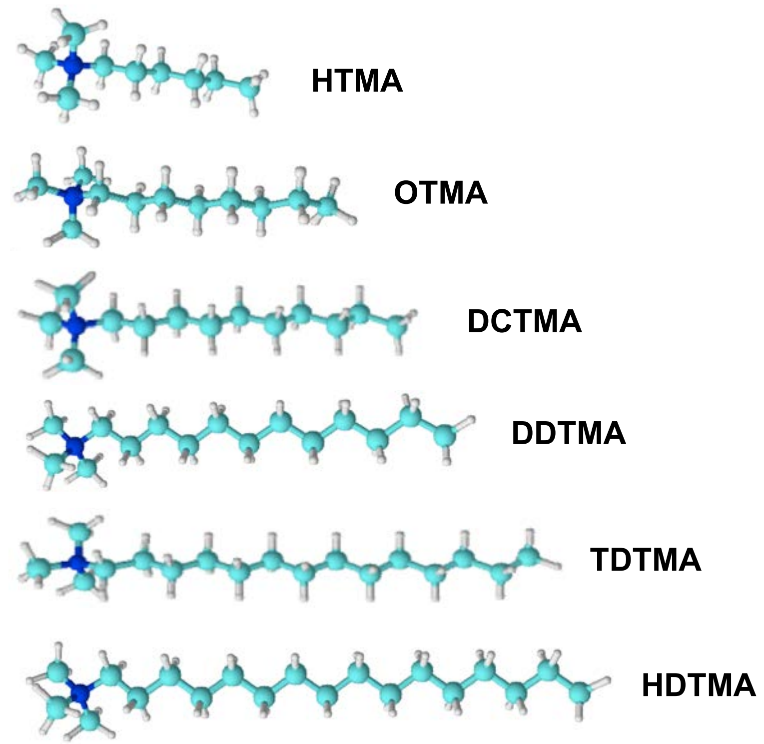
Effect of pH



Effect of pH on fluoride removal by functionalized KAC functionalized with HTMA, OTMA, DCTMA, DDTMA, TDTMA, and HDTMA.
Experimental conditions: [FAC] = 2 g/L, I = 10^{-2} M NaCl. AC modified with 10 mM of Quats.

Adsorption isotherm

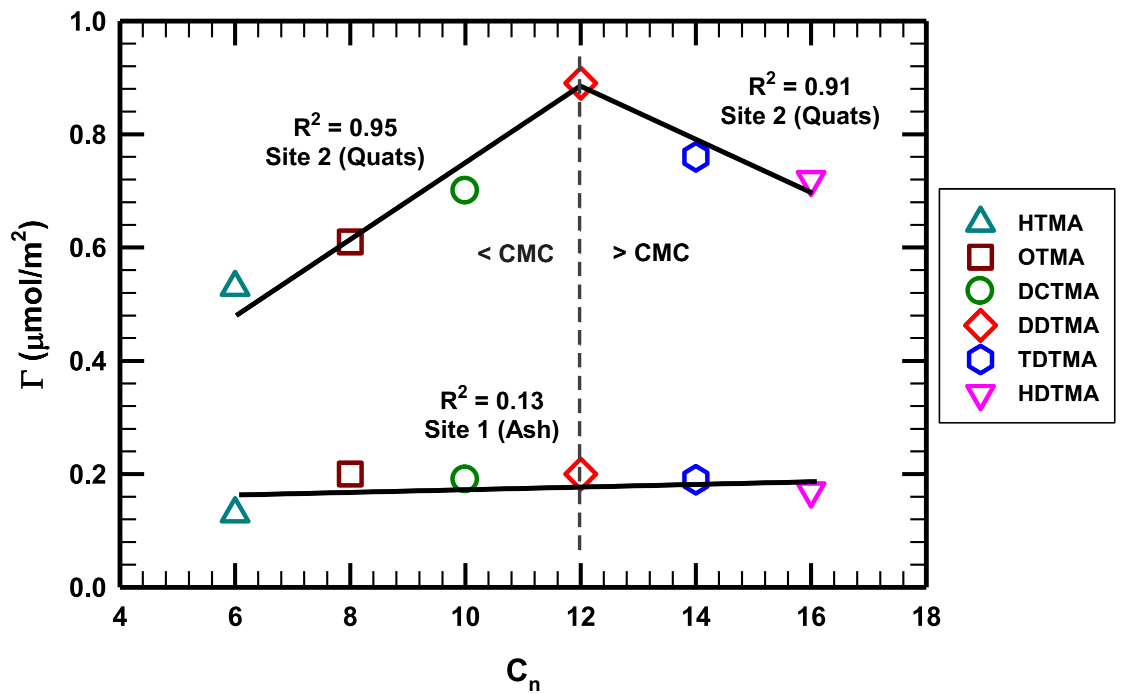




Adsorption of fluoride on KAC functionalized HTMA, OTMA, DCTMA, DDTMA, TDTMA, and HDTMA.

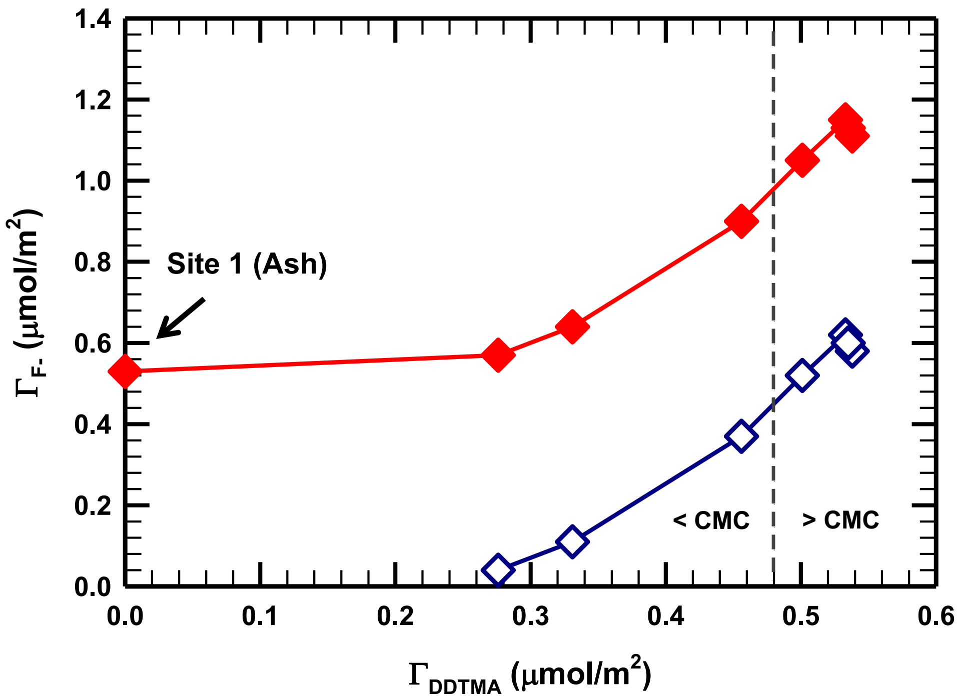
Experimental conditions: [FAC] = 2.0 g/L, I = 10^{-2} M NaCl, KAC modified with 10 mM of Quats, solution pH = 3.

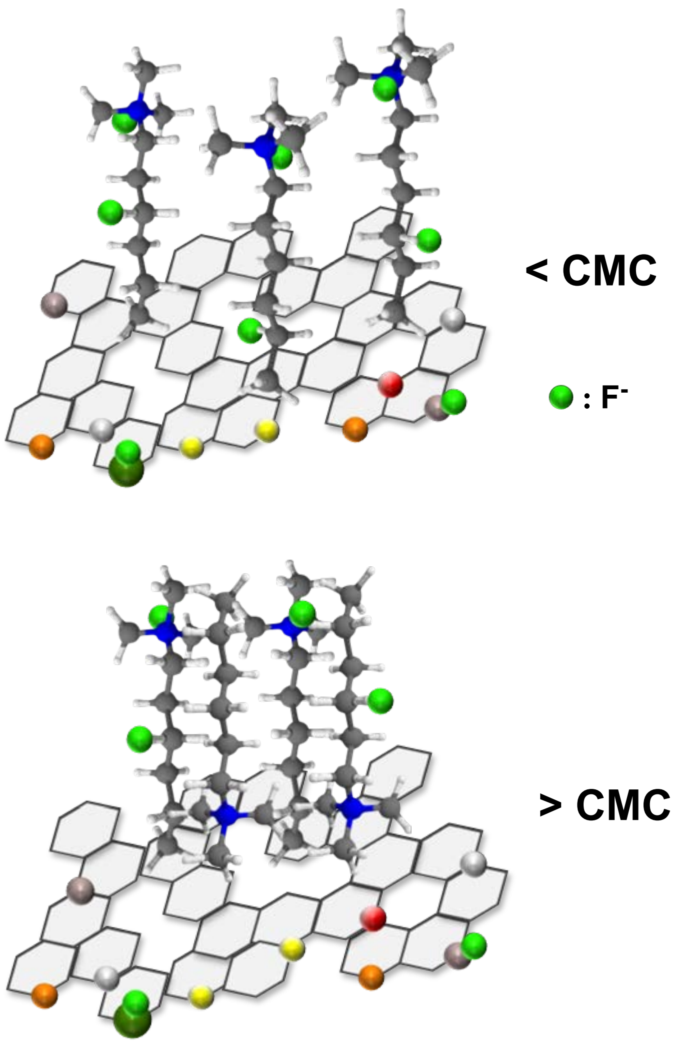
Effect of carbon numbers



Adsorption of fluoride on KAC functionalized with HTMA, OTMA, DCTMA, DDTMA, TDTMA, and HDTMA.
Experimental conditions: [FAC] = 2.0 g/L, I = 10^{-2} M NaCl, KAC modified with 10 mM of Quats, solution pH = 3.

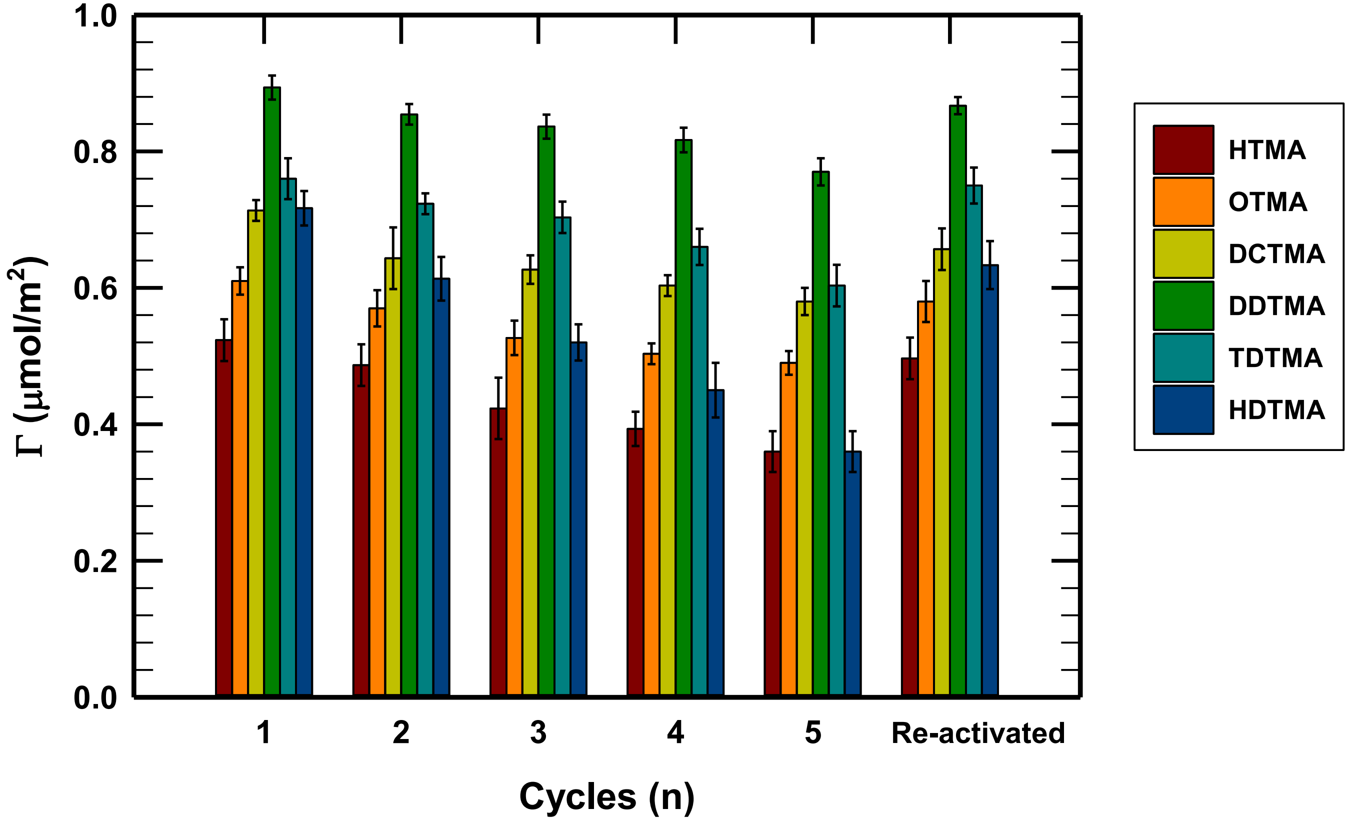
Effect of DDTMA loading





Effect of DDTMA surface loading on fluoride adsorption.
Experimental conditions: $[F^-]_o$ = 20 mM, pH = 3, I = 10^{-2} M NaCl, [FAC] = 2.0 g/L.

Reusability of Quat-KAC



Performance of reusability of KAC functionalized with Quats.
Experimental conditions: [FAC] = 2.0 g/L, I = 10^{-2} M NaCl, [NaOH] = 10^{-2} M, KAC modified with 10 mM of Quats, solution pH = 3.

Conclusions

- Ash content of untreated activated carbon plays an important role on fluoride adsorption
- Fluoride removal increases at acidic pH
- DDTMA-KAC exhibits the best fluoride removal
- Fluoride removal increases with increase in carbon number at Quats concentration < CMC
- DDTMA-KAC shows at lease five cycles of reusability

Acknowledge

- Mr. Michael Davidson
- Members of UD Aquatic Chemistry Lab
- KDE Company, S. Korea
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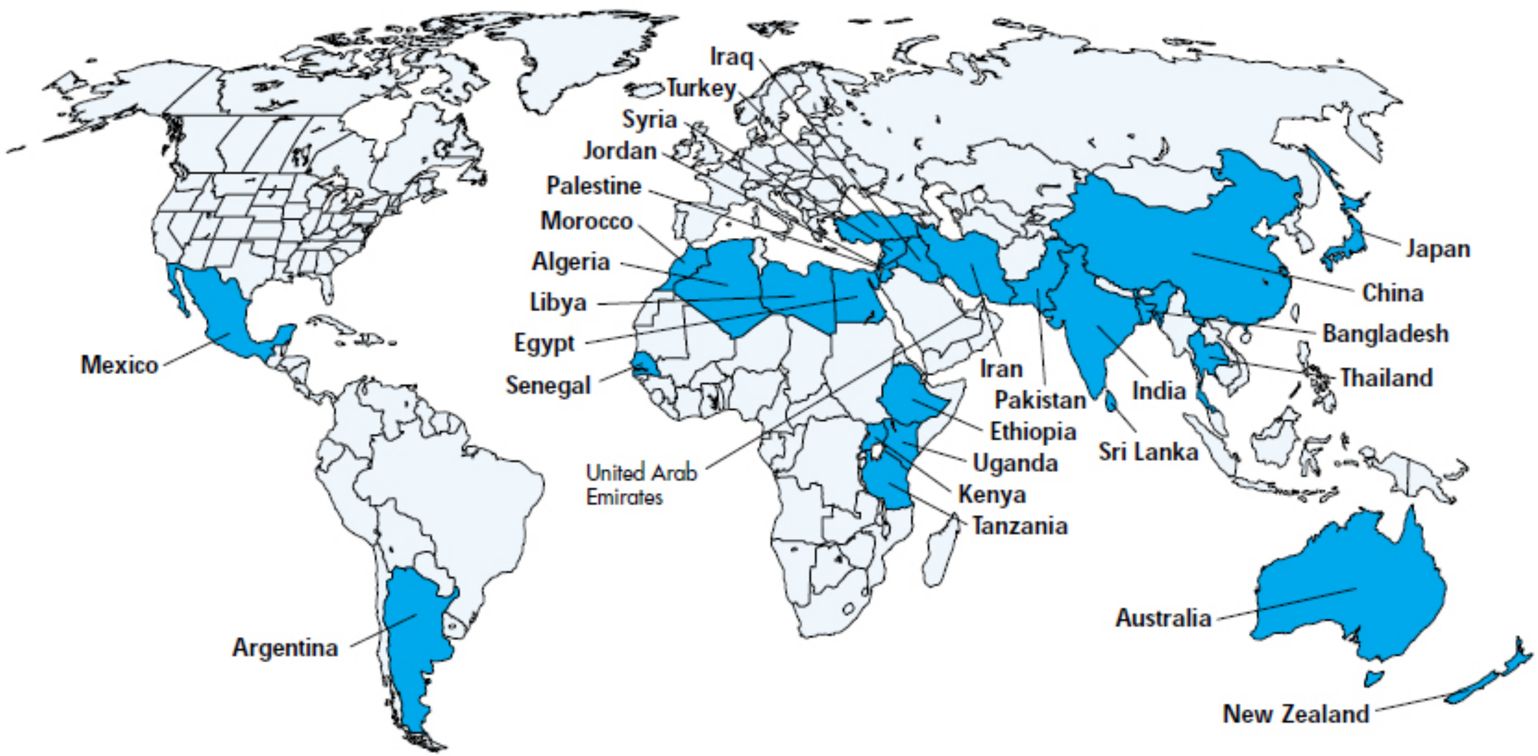
Thank you

Back up



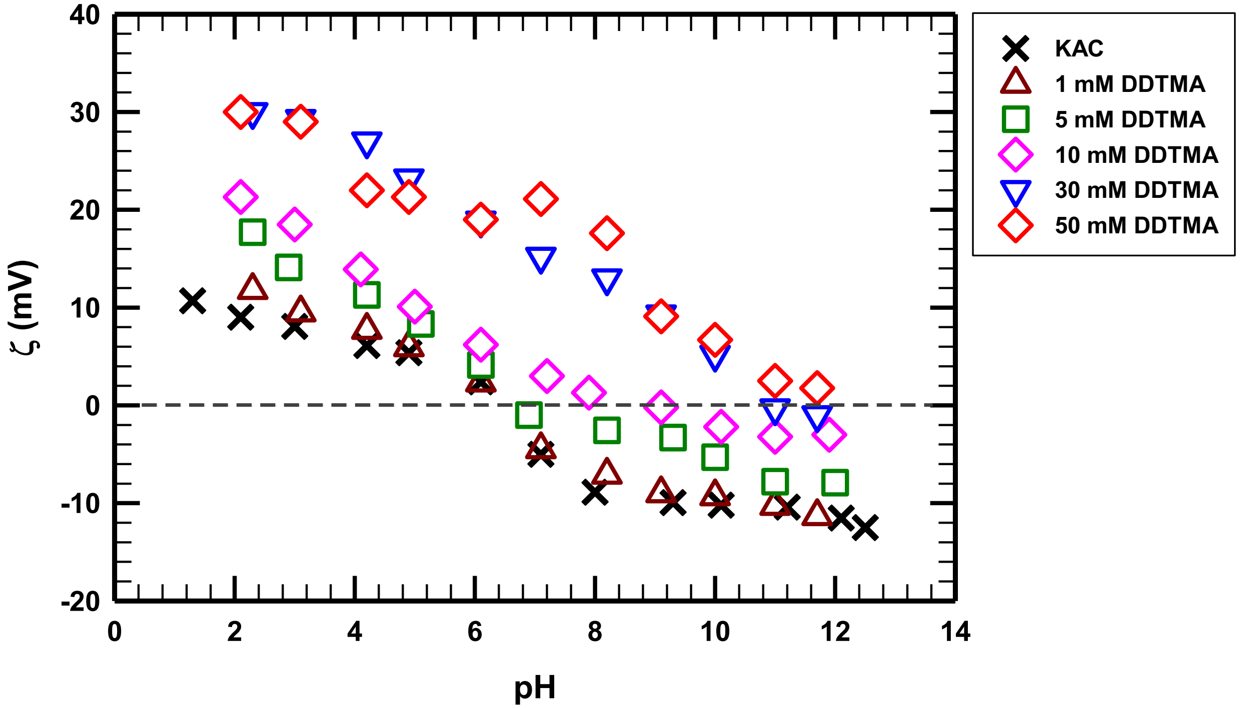
Countries with endemic fluorosis due to excess fluoride in drinking water

http://www.nofluoride.com/unicef_fluor.htm

Current Remediation Technology

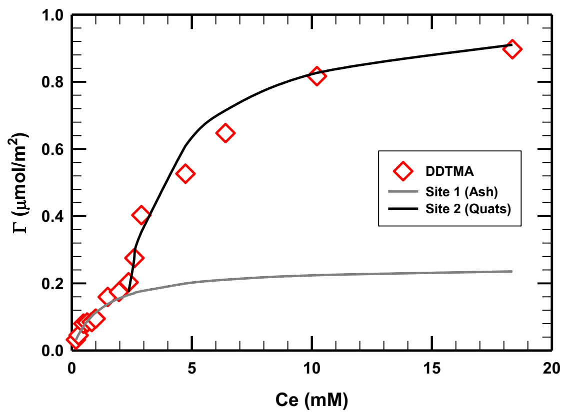
Technology	Advantages	Disadvantages
Precipitation	Commercially available	Expensive; waste disposal
Filtration	Commercially available	Expensive; fouling
Electrodialysis	Easy implementation; fast	Energy costs; nonselective
Adsorption	Low cost; Simple operation	Ions competition; pH adjustment

Zeta potential



Zeta potential of functionalized KAC functionalized with HTMA, OTMA, DCTMA, DDTMA, TDTMA, and HDTMA.
Experimental conditions: [FAC] = 2 g/L, I = 10^{-2} M NaCl. AC modified with 10 mM of Quats.

Adsorption isotherm



$$\Gamma = \sum_{i=1}^{n} \frac{\Gamma_{m,i} K_{L,i} C_e}{1 + K_{L,i} C_e}$$

	$\Gamma_{m,1}$ ($\mu mol/m^2$)	$K_{L,1}$ (L/mmol)	$\Gamma_{m,2}$ ($\mu mol/m^2$)	$K_{L,2}$ (L/mmol)	$\Gamma_{m,total}$ ($\mu mol/m^2$)
Plain KAC	0.15	2.67	0.41	0.10	0.56
HTMA-KAC	0.17	1.69	0.68	0.45	0.85
OTMA-KAC	0.16	1.87	0.74	0.19	0.90
DCTMA-KAC	0.19	0.87	0.81	0.17	1.00
DDTMA-KAC	0.24	0.82	0.91	0.19	1.15
TDTMA-KAC	0.22	0.96	0.90	0.23	1.12
HDTMA-KAC	0.21	0.85	0.86	0.17	1.07