



The adsorption characteristics of fluoride on commercial activated carbon treated with quaternary ammonium salts (Quats)

Ching-Lung Chen^a, Sang-Won Park^b, Jenn Feng Su^a, Yu-Han Yu^a, Jae-eun Heo^c,
Kyung-duk Kim^c, C.P. Huang^{a,*}

^a Department of Civil and Environmental Engineering, University of Delaware, Newark, DE 19716, USA

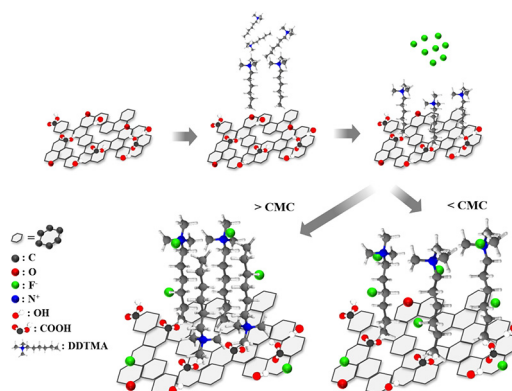
^b Department of Environmental Science, Keimyung University, Daegu, South Korea

^c Center for Green & Convergence Technology, Keimyung University, Daegu, South Korea

HIGHLIGHTS

- Quaternary ammonium salts enhanced fluoride adsorption capacity.
- Hydrogen bond formation and electrostatic force controlled fluoride adsorption.
- DDTMA surface modification increased fluoride adsorption by two folds.
- Quats modified activated carbons can be regenerated effectively in multiple cycles.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 1 May 2019

Received in revised form 24 July 2019

Accepted 25 July 2019

Available online 26 July 2019

Keywords:

Fluoride

Activated carbon

Surface treatment

Quaternary ammonium salts

Multi-site Langmuir equation

ABSTRACT

Commercial activated carbon was treated with six quaternary ammonium salts (Quats), namely, hexyltrimethylammonium (HTMA), octyltrimethylammonium (OTMA), decyltrimethylammonium (DCTMA), dodecyltrimethylammonium (DDTMA), Tetradecyltrimethylammonium (TDTMA), and hexadecyltrimethylammonium (HDTMA) as to enhance the fluoride adsorption capacity. In batch mode experiments, fluoride adsorption onto the Quats-treated activated carbon decreased dramatically with increase in solution pH. Fluoride removal by the Quats-treated activated carbons was closely related to the Quats chain length at less-than critical micelle concentration (CMC). Multi-site adsorption isotherm described fluoride adsorption characteristics well. Results showed that activated carbon treated with DDTMA exhibited the best fluoride adsorption density among all Quats investigated. DDTMA-treated activated carbons exhibited two-fold increase in the fluoride adsorption capacity compared to the untreated activated carbon. Results of regeneration, by alkaline desorption and/or Quats re-loading, showed fluoride-laden activated carbons have high reusability. DDTMA increased the positive surface charge of the activated carbon that enhanced fluoride adsorption. DDTMA-treated activated carbon was promising for fluoride removal from water with much enhanced removal capacity.

© 2019 Elsevier B.V. All rights reserved.

* Corresponding author.

E-mail address: huang@udel.edu (C.P. Huang).

1. Introduction

High fluoride concentration has impacted the drinking water quality in numerous regions of the world. Fluoride in drinking water at concentration higher than 4 mg/L may cause denser bones and skeletal damage (Dissanayake, 1991). Generally, fluoride concentration of surface water is less than that of groundwater water (~ 0.2 mg/L versus 0.02–1.5 mg/L). However, some areas in southwest United States, the fluoride concentration in surface water often exceeds 1.5 mg/L (USEPA (Environmental Protection Agency), 2003). Many regions worldwide have excessive fluoride in the groundwater. Numeral wells in north-central Mexico, for example, have fluoride concentration >6 mg/L (Díaz-Nava et al., 2002). The maximum contaminant level (MCL) and the maximum acceptable fluoride concentration detected in drinking water is 4.0 mg/L and 1.5 mg/L, respectively, according to the US Environmental Protection Agency and the World Health Organization (Díaz-Nava et al., 2002).

There are several water treatment processes for fluoride removal from drinking water, including chemical precipitation, membrane processes, ion-exchange, and adsorption (Meenakshi and Maheshwari, 2006; Srimurali et al., 1998). Although chemical precipitation is a simple practice, the separation and ultimate disposal of fluoride sludge remain a technical and economical challenge (Ayoob et al., 2008; Warmadewanthi and Liu, 2009). Many efforts on fluoride removal by membrane separations, such as reverse osmosis (Greenlee et al., 2009; Owusu-Agyeman et al., 2019), nanofiltration (Yu et al., 2018; He et al., 2016; Bouhadjar et al., 2019; Dolar et al., 2011), and electrodialysis have been made (Kabay et al., 2008; Arahman, 2019). However, fouling, scaling, membrane degradation, and high maintenance cost makes the technology relatively unaffordable over other separation processes (Ayoob et al., 2008; Judd, 2017; Meng et al., 2017). Ion exchange and adsorption methods have been extensively used, and are more effective than chemical precipitation especially in dealing with dilute fluoride concentration (Ayoob et al., 2008; Cai et al., 2016; Robshaw et al., 2019). Moreover, adsorption is a rapid and inexpensive water purification process (Bhatnagar et al., 2011; Habuda-Stanić et al., 2014; Loganathan et al., 2013; Mohanta and Ahmaruzzaman, 2018; Kang et al., 2018; Kang et al., 2017).

Modifying the surface of solid absorbents to increase the removal capacity of specific impurities from water has been attempted (Asgari et al., 2012; Ding and Shang, 2010; Pan et al., 2013; Bombuwala et al., 2018; Mohan et al., 2014; Saikia et al., 2017; Wang et al., 2018; Tang and Zhang, 2016; Wu et al., 2016). Surfactants have been reported to be ideal surface modifiers for the adsorption of inorganic and organic chemicals from waters (Bors, 1990; Bowman et al., 1994; Celik et al., 2000; Dentel et al., 1998; Li and Bowman, 2001; Mahmudov et al., 2015; Stapleton et al., 1994; Yildiz et al., 2005; Mobarak et al., 2018; Mobarak et al., 2019). In general, a solid surface can be rendered negatively charged by anionic surfactants to enhance the adsorption of cationic species from aqueous solution, and vice versa (Liu and Zhang, 2007; Ghiaci et al., 2004). Basar et al. reported that loading cationic surfactants such as cetyltrimethylammonium bromide (CTAB) on powder activated carbon increased the positive zeta potential of the absorbent, whereas adsorbing anionic surfactants such as linear alkylbenzene sulfonate (LABS) renders the activated carbon surface charge negative (Basar et al., 2003). Mahmudov and Huang (Mahmudov et al., 2015) studied two kinds of activated carbon (Filtrisorb 400 and Nuchar SA) tailored with straight chain cationic surfactants of bromide salts such as hexyltrimethylammonium, octyltrimethylammonium, dodecyltrimethylammonium, and hexadecyltrimethylammonium and reported improved perchlorate removal from dilute aqueous solutions. The alkyl chain length of the fabricating surfactants directly controlled the perchlorate removal efficiency (or adsorption capacity). HDTMA (the one with the longest chain length) enhanced perchlorate removal by 10 and 2 folds on Nuchar SA and Filtrasorb 400, respectively.

Several studies have suggested that the critical micelle concentration (CMC) of the surfactants and the hydrophobicity of the solid surface affect the ion adsorption characteristics of surfactant-modified solids (Rennie et al., 1990; Fragneto et al., 1996; Hasan and Huang, 1997; Turner et al., 1999; Parette and Cannon, 2005; Mahmudov (2007); Pitakteeratham et al., 2013; Mahmudov et al., 2015). Activated carbon has unique surface consisting of both hydrophobic and hydrophilic sites thereby making its surface structure ideal for modification by surfactants as to enhance ion adsorption.

There are investigations on modification of solid substrates by surfactants as to enhance the adsorption of chemical contaminants from water (Mobarak et al., 2018; Mobarak et al., 2019). However, much information on the mode of surfactants adsorption and its relation to ions adsorption from water and its regeneration is still needed. The objectives of this work were 1) to study the mode of fluoride adsorption on activated carbon treated with cationic surfactants, 2) to understand the characteristics of surfactants modification of activated carbon and its relation to fluoride adsorption, and 3) to assess the feasibility and the regeneration of Quats-treated activated carbons in terms of fluoride removal. This research was to test the hypothesis that the chain length of quaternary salts (Quats) could affect the mode and thus the extent of fluoride adsorption onto the Quats-modified activated carbon.

2. Materials and methods

2.1. Materials

A commercial Korean activated carbon (KAC) from Shin Ki Chemical, Korea was selected in this work. Table S1 shows the general physical and chemical characteristics of activated carbon studied. Based on the manufacturing process (i.e., temperature and gas), activated carbons can be classified as L or H type (Steenberg, 1944). The L type carbons are more hydrophilic and upon dispersing in water exhibit acidic pH and predominantly negative surface charge under ambient conditions. In contrast, the H type carbons are more hydrophobic, elevate solution pH, and have positive surface charge at ambient aquatic conditions. KAC is a typical H type activated carbon and is a granular with 20 mesh grain size (0.85 mm) and pH_{zpc} of 6.8 (Corapcioglu and Huang, 1987; Mahmudov and Huang, 2010).

Before batch adsorption experiments, activated carbon was washed with 1 L of dilute strong acid then base (0.1 mM HCl and 0.1 mM NaOH), respectively. The procedure follows that reported by Mahmudov and Huang (Mahmudov and Huang, 2010). Dilute HCl and NaOH might remove ash minerals such as Al_2O_3 , Fe_2O_3 and CaO from the activated carbon (Wang et al., 2008).

The cationic surfactants were acquired from Alfa Aesar Corporation (US) and utilized without further purification. Table 1 and Table S2, respectively, lists the general properties and structure of the surfactants studied, including, hexyltrimethylammonium (HTMA), octyltrimethylammonium (OTMA), decyltrimethylammonium (DCTMA), dodecyltrimethylammonium (DDTMA), tetradecyltrimethylammonium (TDTMA), and hexadecyltrimethylammonium (HDTMA). These six quaternary ammonium salts (Quats) were all straight chain with positive head and are employed in this study. The Quats chain length, L_c , is determined by the semi-empirical equation below (Eq. (1)) (Nevskaia and Guerrero-Ruiz, 2001):

$$L_c \leq L_{\text{max}} = (0.154 + 0.1265n) \quad (1)$$

where L_{max} is the fully extended alkyl chain length (nm) and n is the amount of carbon atoms of the saturated hydrocarbon chain.

Table 1
Cationic surfactants used in this study.

	Moiety	Chain length (Å)	CMC (mM) ^a	Reference
Hexyltrimethylammonium (HTMA)	CH ₃ -(CH ₂) ₅ N ⁺ (CH ₃) ₃	9.13	495.0	(Mosquera et al., 1998)
Octyltrimethylammonium (OTMA)	CH ₃ -(CH ₂) ₇ N ⁺ (CH ₃) ₃	11.66	140.0	(Sanyo et al., 2006; Li et al., 2002)
Decyltrimethylammonium (DCTMA)	CH ₃ -(CH ₂) ₉ N ⁺ (CH ₃) ₃	14.19	64.6	(Tuddenham and Alexander, 1962)
Dodecyltrimethylammonium (DDTMA)	CH ₃ -(CH ₂) ₁₁ N ⁺ (CH ₃) ₃	16.72	15.0	(Milton and Kunjappu, 2012; Bijsterbosch, 1974)
Tetradecyltrimethylammonium (TDTMA)	CH ₃ -(CH ₂) ₁₃ N ⁺ (CH ₃) ₃	19.25	1.6	(Lin, 2009)
Hexadecyltrimethylammonium (HDTMA)	CH ₃ -(CH ₂) ₁₅ N ⁺ (CH ₃) ₃	21.78	0.9	(Milton and Kunjappu, 2012; Bijsterbosch, 1974)

^a For pure water at 25 °C.

2.2. Characterization of the activated carbon

The specific surface area and surface charge, two of the most important properties on ion adsorption, were measured. The zeta potential of activated carbons was determined by Zetasizer 3000 HSA, Malvern Co. USA. After Quats functionalization, the grinded KAC (75 µm) was dispersed in 10 mM of NaCl solution for zeta potential measurement. It must be noted that in the absence of other surface analyses, since the activated carbon KAE used in this study was made from bituminous material and had surface charge characteristics same as that of Filtrasorb 400, it stands to reason that other surface characteristics of KAE such as XPS and FTIR will be close to that of Filtrasorb 400 (Castillejos-López et al., 2008). S4 (Supporting Information) gives the surface analysis of commercial activated carbons exemplified by Filtrasorb 400 and Nuchar SA.

2.3. Adsorption of Quats on activated carbon

Twenty milliliter of DDW (distilled deionized water) were first placed in plastic bottles followed by the addition of 0.5 mL of 1.0 M NaCl solution to give an ionic strength of 10⁻² M. Pre-weighted activated carbon sample (0.1 g) was then placed in the plastic bottles and hydrated for 1 h. A pre-calculated amount of stock Quats solution was added to the plastic bottles to reach desired concentrations. The samples were agitated on a reciprocal shaker and mixed for 10 h, after which 10 mL of the surfactant were sampled for the analysis of residual surfactant concentration expressed as TOC. The characteristics and mode of surfactants adsorption onto commercial activated carbons have been reported previously (Mahmudov et al., 2015). Mahmudov et al. reported that the quaternary ammonium salts adsorb strongly onto the activated carbon surface by hydrophobic forces (Mahmudov et al., 2015).

2.4. Fluoride adsorption onto activated carbons

Preliminary adsorption run showed that fluoride adsorption reached equilibrium state rapidly in <4 h (results not shown). All adsorption experiments were run overnight, which was adequate to attain equilibrium adsorption. Plain or Quats-treated activated carbon, 0.1 g by weight, was placed in 50 mL of solution containing fluoride at various concentrations and ionic strength of 10⁻² M NaCl, and then shaken for 10 h on a reciprocal shaker. Afterward the activated carbon was separated by filtration. The fluoride adsorption capacity of the activated carbon was calculated from the difference between the initial and the final concentrations divided by the mass (g) or surface area (m²) of the activated carbon. The concentration of fluoride was determined by DIONEX 500 Ion Chromatograph (IC) equipped with AS50 thermostat for temperature control, a GP50 gradient pump, and Dionex IonPac AC20 column.

Since all fluoride adsorption experiments were conducted under well-controlled conditions, namely, in synthetic solutions with pH, ionic strength, and temperature controlled, data were reasonably reproducible, within 5–10% errors. Nonetheless, all fluoride adsorption

experiments were conducted in duplicate and results were reported as averages of two separate runs.

2.5. Regeneration of fluoride-laden activated carbons

The regeneration experiments were conducted in five adsorption-desorption cycles. The fluoride-loaded activated carbons were added to a 100 mL of 10⁻² M NaOH solution and agitated on a reciprocal shaker for 10 h. After regeneration, the surface-treated KAC was rinsed with 2 L of DDW and dried in air at 37 °C overnight. The regenerated KAC was stored in a desiccator for reuse in the next adsorption cycle. The Quats-treated KAC, after the fifth adsorption/desorption cycle was re-loaded with Quats following the above surface modification procedures and the fluoride adsorption capacity determined. All regeneration experiments were conducted in triplicate.

3. Result and discussion

3.1. The effect of pH on fluoride adsorption

Fig. 1 shows the fluoride adsorption capacity as a function of equilibrium pH on KAC pre-treated with 10 mM each of HTMA, OTMA, DCTMA, DDTMA, TDTMA, and HDTMA. The fluoride adsorption capacity was markedly affected by the solution pH. Furthermore, the influence of pH on fluoride adsorption, onto Quats-treated KAC, was similar to that of the untreated activated carbon. The adsorption of fluoride onto KAC pre-treated with 10 mM of Quats in the pH range from 3 to 11 followed the following increasing order: DDTMA-KAC > TDTMA-KAC > HDTMA-KAC > DCTMA-KAC > OTMA-KAC > HTMA-KAC. The fluoride adsorption capacity was the greatest at pH 3 then decreased dramatically with increase in solution pH, similar to that of the plain KAC.

The fluoride removal capacity was less pH independent at low (e.g., 1 mM) than high (>5 mM) initial fluoride concentration. At low pH, the surface of Quats-pretreated KAC was protonated and positively charged, which tended to enhance the adsorption of the anionic fluoride ions. Note that in the pH range from 3.1 to 11 (HF: pK_a 3.18), fluoride ion (F⁻) is the predominant specie (Fig. S1). Fluoride adsorption capacity decreased dramatically with increase in pH due in part to hydroxide (OH⁻) competition for adsorption sites. The acidity constant of hydrofluoric acid is 3.18 ± 0.02 (Hefter, 1984). Therefore, at pH < 3.1, fluorine acid, HF, became a predominant species, competition for the activated carbon surface with proton decreased the total fluoride removal capacity of KAC. Obviously, electrostatic interaction plays an important role on fluoride ion adsorption onto the Quats-pretreated activated carbon.

Additionally, Fig. 1 shows that fluoride adsorption capacity increases with increase in carbon chain length of Quats (except HDTMA-KAC) in the pH range from 3 to 11. The DDTMA-KAC exhibited markedly enhanced adsorption capacity at pH 3, which indicated that hydrogen atoms on the tail of DDTMA also contributed to fluoride adsorption. Our results agreed well with those reported previously on fluoride adsorption onto pumice stone pretreated with HDTMA (Asgari et al., 2012) and KMnO₄-modified activated carbons (Daifullah et al., 2007). The above authors reported that low pH enhanced and high pH

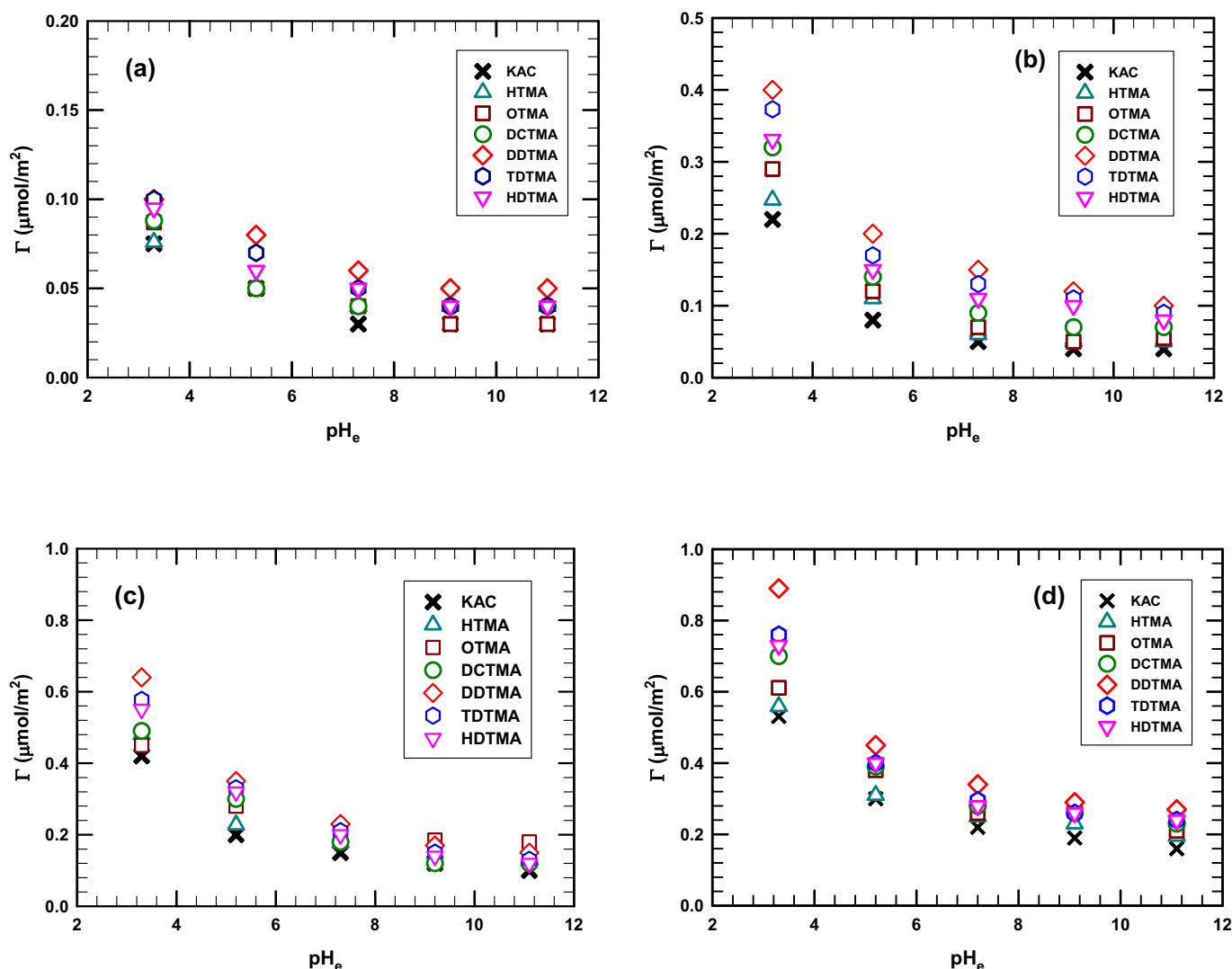


Fig. 1. Effect of pH on fluoride removal by functionalized KAC at fluoride concentration of (a) 1 mM, (b) 5 mM, (c) 10 mM, and (d) 20 mM. $[FAC] = 2 \text{ g/L}$, $I = 10^{-2} \text{ M NaCl}$. AC modified with 10 mM of Quats. The reported values were the average of two individual measurements.

impeded fluoride adsorption, respectively, which was in agreement with our findings above.

Results clearly showed that fluoride adsorption capacity was closely related to the alkyl chain length of Quats, especially at concentration lower than the critical micelle concentration (CMC). Although HDTMA has the longest carbon chain, it has the lowest CMC, the fluoride removal of HDTMA-KAC is less than that of DDTMA-KAC. Therefore, to some extent, CMC also contributes to fluoride adsorption capacity.

3.2. Adsorption isotherm

Fig. 2a shows the fluoride adsorption isotherms of Quats-pretreated KAC at pH 3. Results showed two distinct adsorption steps. The fluoride adsorption capacity of the first step was the same for all Quats pretreated activated carbons. Adsorption capacity of the second step was significantly different among all modified KACs, which reflected the effect of Quats and the intrinsic carbon surface properties. Results revealed that DDTMA-KAC exhibited the most remarkable improvement on fluoride removal with nearly 2-fold increase in adsorption capacity versus the plain KAC at initial fluoride concentration of 20 mM. With only a 6-C chain length and the lowest CMC, HTMA-KAC exhibited no significant enhancement in fluoride removal compared to plain activated carbon.

To further quantify the type of Quats affecting fluoride adsorption, we used the multi-site Langmuir adsorption model, i.e., Eq. (2).

$$\Gamma = \sum_{i=1}^n \frac{\Gamma_{m,i} \times K_{L,i} \times C_e}{1 + K_{L,i} \times C_e} \quad (2)$$

where Γ is the total adsorption density ($\mu\text{mol/m}^2$), $\Gamma_{m,i}$ is the monolayer adsorption density ($\mu\text{mol/m}^2$) at the i th site, n is the set of surface site, $K_{L,i}$ is the equilibrium constant (L/mmol) of the i th site, and C_e is the equilibrium fluoride concentration in solution (mmol/L). The adsorption data in Fig. 2b are fitted by Eq. (2) and Fig. S2 (solid lines) shows the fitted results. Table 2 lists the fitted monolayer adsorption density ($\Gamma_{m,1}$, $\Gamma_{m,2}$) and equilibrium constants, $K_{L,1}$, the first, and $K_{L,2}$, the second-(Quats plus virgin AC sites), respectively, and the total monolayer adsorption density, Γ_m , of all Quats-pretreated KACs. Note that the $\Gamma_{m,1}$ of all Quats-KACs and plain KAC were of the same order of magnitude. There was no significant difference in $K_{L,1}$ for all Quats-KACs, except that $K_{L,1}$ was generally larger than $K_{L,2}$ (the Quats sites). In conclusion, the Quats modified KACs, especially, DDTMA-KAC, had larger adsorption capacity but weaker adsorption energy toward fluoride than the plain KAC, which clearly showed the merits of Quats pretreatment of activated carbons, especially KAC, for fluoride removal from water. Quats pretreated KAC exhibited much improved fluoride

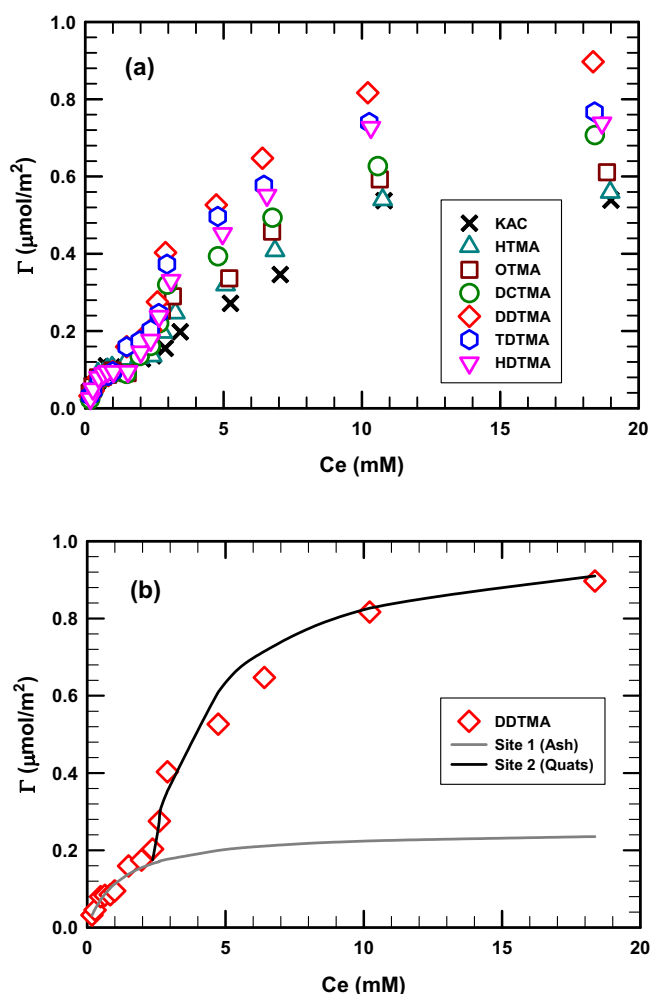


Fig. 2. (a) Adsorption of Fluoride onto functionalized KAC. (b) Lines represent the fit by the multi-surface Langmuir model. $[FAC] = 2.0 \text{ g/L}$, $I = 10^{-2} \text{ M NaCl}$, KAC modified with 10 mM of Quats, $\text{pH} = 3$. The reported values were the average of two individual measurements.

adsorption capacity but small $K_{L,2}$, i.e., adsorption energy, which would make it easy to be regenerated for reuse.

3.3. Optimization of surface surfactant loading

Fig. 3 shows the relationship between carbon number of Quats and fluoride adsorption capacity on KAC pretreated 10 mM of Quats. At 10 mM, the Quats concentration of HTMA (C6), OTMA (C8), DCTMA (C10), and DDTMA (C12) were below the individual CMC value, and that of TDTMA (C14) and HDTMA (C16) exceeded the corresponding CMC. The first group of adsorption sites, the linear correlations ($R^2 =$

0.13) between the carbon number of Quats and fluoride adsorption capacity was low, which indicated that fluoride adsorption was independent of the carbon chain number. However, there was strong linear correlation between fluoride adsorption capacity and C number for the second group of adsorption sites, i.e., the Quats-occupied surface. Adsorption on the second group of sites, the fluoride adsorption capacity increased with carbon number, from C6 to C10 ($R^2 = 0.95$) then decreased from C14 to C16 ($R^2 = 0.91$). Results indicated possible involvement of hydrogen atoms (with abundant localized positive charges) in fluoride adsorption. Therefore, it is likely that electrostatic interaction (positive N^+ head) and hydrogen bonding (related to chain length) are major forces responsible for the enhanced fluoride adsorption of Quats pretreated KAC (Paul and Raj, 1997; Loganathan et al., 2013; Aktaş and Çeçen, 2007). The fluoride adsorption capacity decreased from C6 (HTMA) to C12 (DDTMA) to C14 (TDTMA) then decreased from C12 to C16 (HDTMA) when the Quats concentration used to treat the activated carbon was greater than CMC. Results suggested that formation of micelle could hinder fluoride adsorption onto the second sites (hydrogen bonding formation) due to steric hindrance and increase in interfacial entropy.

3.4. Mode of fluoride adsorption on DDTMA-KAC

By subtracting the fluoride adsorption density ($0.53 \mu\text{mol}/\text{m}^2$) contributed from the plain KAC from the total fluoride adsorption capacity, one has the fluoride adsorption capacity contributed solely from the DDTMA (C12) sites (open diamonds in Fig. 5). Interestingly, the slope of the line connecting the open diamonds was two, which gave the surface molar ratio of fluoride to DDTMA. That is, 1 mol of DDTMA was responsible for the adsorption of 2 mol of fluoride anion. Results from Fig. 4 also showed enhancement of fluoride adsorption capacity with increase in carbon number (below CMC) indicating hydrogen atoms on the tail of DDTMA contribute to fluoride adsorption. Fluoride adsorption was not brought by electrostatic force alone. The surface molar ratio of F^- to DDTMA clearly implied that fluoride adsorption was brought by the positive N^+ (electrostatic) and the hydrogen atom on the chain (hydrogen bonding) of DDTMA (Deshmukh et al., 2006).

Fluoride adsorption with regard to carbon number could be divided into two regions: (i) $< \text{CMC}$ and (ii) $> \text{CMC}$. At Quats concentration $< \text{CMC}$, Quats formed a monolayer via the hydrophobic chain attaching to the activated carbon surface and the hydrophilic head at an upright position with respect to the activated carbon surface. The hydrogen atoms on the Quats chain contributed to the attachment of fluoride ions that increased with increase in carbon number (Fig. S3a). However, at concentration $> \text{CMC}$, Quats formed lamellar layer (admicelle) on the surface of activated carbon. The lamellar micelle significantly hindered fluoride adsorption onto the second site (hydrogen sites of Quats) and consequently decreased fluoride adsorption as shown in Fig. S3b.

Based on the above argument, fluoride adsorption occurring on DDTMA sites could be described by the following equilibrium equation also:



where $[S - F_a]$ is the fluoride-occupied DDTMA-KAC surface site ($\mu\text{mol}/\text{m}^2$), $[S]$ is the unoccupied DDTMA-KAC sites ($\mu\text{mol}/\text{m}^2$), and $[F^-]$ is the free fluoride bulk concentration (M). K is the equilibrium adsorption constant expressed as the following:

$$K = \frac{[S - F_a]}{[S][F^-]^a} \quad (4)$$

A plot of $\log \{[S - F_a]/[S]\}$ versus $\log [F^-]$ (not shown) gives K and “ a ” from the intercept and the slope, respectively. The K value was 0.18 (L/mmole) and the “ a ” value was 2.0. Note that K value was of the same order of magnitude as $K_{L,2}$ value (Table 2) and the “ a ” value was same

Table 2
Isotherm fit parameters for adsorption of fluoride on Korean activated carbon at pH 3.

	$\Gamma_{m,1}$ ($\mu\text{mol}/\text{m}^2$)	$K_{L,1}$ (L/mmole)	$\Gamma_{m,2}$ ($\mu\text{mol}/\text{m}^2$)	$K_{L,2}$ (L/mmole)	$\Gamma_{m,\text{total}}$ ($\mu\text{mol}/\text{m}^2$)
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

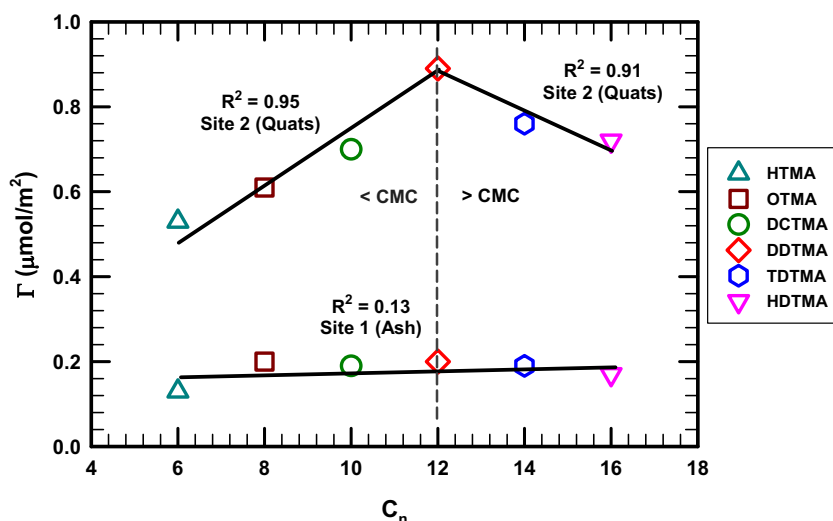


Fig. 3. Effect of carbon numbers on fluoride adsorption. $[FAC] = 2.0 \text{ g/L}$, $[F^-]_0 = 20 \text{ mM}$, $I = 10^{-2} \text{ M NaCl}$, KAC modified with 10 mM of Quats, $\text{pH} = 3$. The reported values were the average of two individual measurements.

as the surface molar ratio of adsorbed DDTMA to fluoride as shown in Fig. 4 above. The Gibbs free energy of adsorption, ΔG° can be determined according to the following equation:

$$\Delta G^\circ = -2.303 RT \log K \quad (5)$$

The Gibbs free energy of fluoride adsorption on KAC was -12.83 kJ/mol , which indicated that fluoride adsorption on the DDTMA-sites of KAC was thermodynamically favorable and spontaneous. In general, intramolecular hydrogen bonding can be considered weak (4 to 16 kJ/mol), moderate (16 to 60 kJ/mol), and strong (60 to 160 kJ/mol) (Ng et al., 2009). Based on the Gibbs free energy of fluoride on the functionalized KAC, result indicated that the formation of weak hydrogen bonds took place during fluoride adsorption on the Quats sites.

Table 3 compares the adsorption capacity of fluoride adsorption on Quats-treated activated carbon with other reported carbon based adsorbents. It is interesting to note that our Quats-treated activated carbon

exhibited a fluoride adsorption capacity that was competitive compared to other activated carbon materials.

3.5. Effect of Quats loading on surface charge of activated carbon

Fig. S4 shows the zeta potential of plain KAC and DDTMA-KAC as a function of pH. Results showed that DDTMA adsorption rendered the surface of KAC positive. Surface charge reversal on DDTMA-KAC indicated the presence of specific chemical adsorption of DDTMA on KAC. The degree of charge reversal was remarkable for KAC modified with 50 mM of DDTMA. The zeta potential increased from $+10$ to $+30 \text{ mV}$ at $\text{pH} 2$ when KAC was modified with none and 50 mM of DDTMA, respectively. As the initial DDTMA concentration was increased from 30 to 50 mM , the zeta potential of KAC remained unchanged. This observation was the same as the results shown in Fig. 4 that the KAC surface loading became constant ($0.53 \mu\text{mol/m}^2$) as the DDTMA concentration was increased (from 30 to 50 mM). The pH dependent nature of the zeta potential of the Quats-treated KAC suggested incomplete surface coverage by DDTMA under which circumstance the surface properties of KAC were partially covered by the adsorbed DDTMA. Our results agree well with observations from our previous study (Mahmudov et al., 2015).

Although the zeta potential increased with increasing DDTMA concentration, it did not increase fluoride removal when the DDTMA concentration was increased from 30 to 50 mM . Since the CMC of DDTMA is 15 mM , the formation of micelle can structurally hinder the fluoride ions from being in contact with the hydrogen on carbon chain. The impact of surfactant loading affecting zeta potential on fluoride adsorption was consistent with the observation on TDTMA- and HDTMA-KACs.

Upon hydration, surface hydrous species develop on the activated carbon surface. These hydrous species are Bronsted acids/bases that undergo proton transfer to endow surface charges to the activated carbon surfaces (Supporting information, S7). Table S2 lists the calculated surface intrinsic constants of activated carbon used in this study. Since $\text{pH}_{\text{zpc}} = \frac{1}{2} (\text{p}K_{\text{a1}}^{\text{int}} + \text{p}K_{\text{a2}}^{\text{int}})$, the pH_{zpc} value of KAC was calculated as 6.86 (at $I = 10^{-2} \text{ M}$). Fig. S8 shows the surface speciation for KAC, HTMA/KAC, and DDTMA-KAC. Results indicated that all three KACs exhibited nearly 100% positive surface charge at low pH, and that the positive surface charge on DDTMA-KAC (Fig. S7) was retained at higher pH value compared to that on KAC and HTMA-KAC. The results indicated that DDTMA-KAC contained relatively more positive surface charges

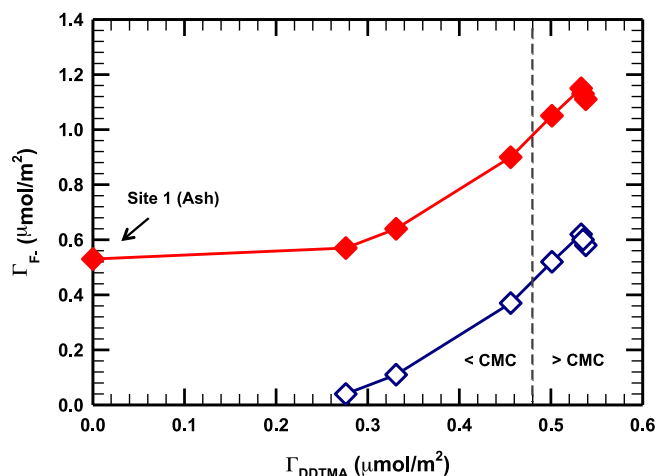


Fig. 4. Effect of DDTMA surface loading on fluoride adsorption. Solid diamond represents fluoride adsorption via carbon and surfactant. Open diamond indicates fluoride removal solely by surfactant. $[F^-]_0 = 20 \text{ mM}$, $\text{pH} = 3$, $I = 10^{-2} \text{ M NaCl}$, $[AC] = 2.0 \text{ g/L}$, $[DDTMA] \text{ CMC} = 15 \text{ mM}$. The reported values were the average of two individual measurements.

Table 3

Comparison of fluoride adsorption capacities of reported carbon based adsorbents.

Adsorbent	Asp (m ² /g)	pH	Γ_m ($\mu\text{mol}/\text{m}^2$)	Reference
Quats-treated activated carbon	1000.0	3.0	1.15	This study
Graphite	571.0	7.0	0.01	(Karthikeyan and Elango, 2008)
Activated carbon (coconut shell)	358.0	2.0	0.05	(Aragá et al., 2019)
Zr impregnated activated carbon	1103.9	4.0	0.25	(Mullick and Neogi, 2018)
Carbon nanotubes	687.0	7.0	0.34	(Li et al., 2003)
Carbon slurry	629.0	7.5	0.41	(Gupta et al., 2007)
Activated carbon fiber	1400	6.5	0.64	(Gupta et al., 2009)
Mg-Mn-Zr impregnated activated carbon	843.3	6.0	1.65	(Mullick and Neogi, 2019)

than HTMA-KAE and thus a much promising adsorbent for fluoride adsorption from water.

3.6. Reusability of DDTMA-KAC

Disposal of spent activated by incineration or landfilling, without regeneration, seldom is an acceptable option (Berenguer et al., 2010). It is known that the feasibility and applicability of activated carbon adsorption technology at industrial scale greatly relies on the degree of reactivation and reuse of the exhausted AC (Hutchins, 1973; Liu et al., 2018). Thermal (Nevskaia and Guerrero-Ruiz, 2001), chemical (Özkaya, 2006; Ferro-García, 1993), and biological (Aktaş and Çeçen, 2007; Ng et al., 2009; ElGamal et al., 2018) regeneration are common practices. Since fluoride adsorption on Quats modified activated carbon was highly pH-dependent, it will be possible to regenerate the spent activated carbon chemically.

Fig. 5 shows the performance of DDTMA-KAC in five consecutive adsorption/desorption cycles. The fluoride adsorption decreased, dependent on the type of Quats modified KAC, due in part to loss of surface Quats. The results indicated that the adsorption capacity was 67.9, 78.7, 83.9, 85.9, 80.3, and 50% that of the freshly modified activated carbons, for HTMA-KAC, OTMA-KAC, DCTMA-KAC, DDTMA-KAC, TDTMA-KAC, and HDTMA-KAC, respectively after five adsorption/desorption cycles. At the end of the 5th adsorption cycle, the fluoride loaded activated carbons were first washed with NaOH (0.01 M for 10 h) and then re-loaded with Quats (initial concentration = 10 mM). Re-loading of Quats totally restored the fluoride adsorption capacity (see fluoride adsorption at cycle $N = 1$). Results clearly showed that washing at alkaline pH using strong base such as NaOH or reloading Quats completely restored the fluoride adsorption capacity of the Quats-pretreated activated carbon.

4. Conclusion

The adsorption characteristics of fluoride onto activated carbon, hydrophilic wood-based KAC, modified by Quats, were studied. Results showed that the carbon number of Quats exhibited a dual role on fluoride adsorption. Electrostatic interaction between F^- and the N^+ head due to electrostatic interaction and hydrogen bonding formation between F^- and the hydrogen atoms on the Quats chain were responsible for the enhanced fluoride adsorption. In addition, pH also affected the removal of fluoride by both plain and Quats treated activated carbons. Competition between fluoride ions and hydroxide (OH^-) for the positively charged surface sites or electrostatic repulsion between fluoride ions and negatively charged surface sites decreased fluoride adsorption dramatically with increase in pH.

Six Quats, namely, HTMA, OTMA, DCTMA, DDTMA, TDTMA, and HDTMA were used to pretreat activated carbons. Results showed remarkable improvement in fluoride uptake over the plain activated carbon. Treating the activated carbon at low Quats concentration (10 mM of treatment dose) and below CMC, the fluoride removal was closely related to the alkyl chain length of the Quats. DDTMA (a longer and more hydrophobic Quats) exhibited the highest degree of enhancement in fluoride removal among all Quats studied. Overall, the fluoride adsorption capacity of the DDTMA-KAC (at 30 mM of treatment concentration) was increased by two-fold over the plain KAC. The DDTMA-KAC was effective in fluoride removal in multiple adsorption/desorption cycles. Increase in DDTMA surface loading increased the positive surface charge (based on zeta potential measurements); the zeta potential increased from +10 mV (the plain activated carbon) to +30 mV when the activated carbon was treated with 50 mM of DDTMA. However, as the zeta potential increased, the fluoride removal remained constant. The formation of bilayered micelles structurally hindered fluoride ions from accessing to the hydrogen atoms on the carbon chains.

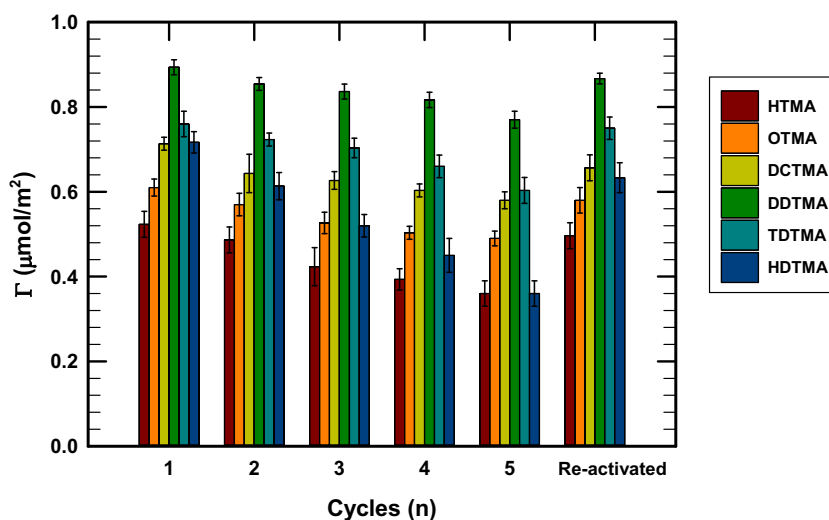


Fig. 5. Performance of reusability of KAC functionalized with Quats. $[\text{AC}] = 2 \text{ g/L}$, $[\text{F}^-]_0 = 20 \text{ mM}$, $\text{pH} = 3$, $I = 10^{-2} \text{ M NaCl}$, $[\text{NaOH}] = 0.01 \text{ M}$, KAC modified with 10 mM Quats. Results reported were mean values. The vertical error bars represent the range of standard deviation.

Overall, the DDTMA-KAC exhibited high fluoride adsorption capacity compared to other similar adsorbents. Results clearly showed that surface modification increased (positive) surface charge and fluoride adsorption capacity. The DDTMA-KAC was a promising adsorbent for enhanced fluoride removal from aqueous solutions.

Acknowledgement

Results presented in this manuscript are based on a research project supported by KDE Company, South Korea. Addition support was provided by US NSF IOA (1632899).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2019.133605>.

References

- Aktaş, Ö., Çeçen, F., 2007. Adsorption, desorption and bioregeneration in the treatment of 2-chlorophenol with activated carbon. *J. Hazard. Mater.* 141, 769–777.
- Arago, R., Kali, S., Sharma, C.S., 2019. Coconut-shell-derived carbon/carbon nanotube composite for fluoride adsorption from aqueous solution. *Clean-Soil, Air, Water* 47.
- Arahman, N., 2019. Effect of salt composition on the separation profile of contaminated groundwater ions by electrodialysis. *Int. J. GEOMATE*. 16, 76–83.
- Asgari, G., Roshani, B., Ghanizadeh, G., 2012. The investigation of kinetic and isotherm of fluoride adsorption onto functionalize pumice stone. *J. Hazard. Mater.* 217–218, 123–132.
- Ayoo, S., Gupta, A.K., Bhat, V.T., 2008. A Conceptual Overview on Sustainable Technologies for the Defluoridation of Drinking Water.
- Basar, C., Karagunduz, A., Keskinler, B., Cakici, A., 2003. Effect of presence of ions on surface characteristics of surfactant modified powdered activated carbon (PAC). *Appl. Surf. Sci.* 218, 169–174.
- Berenguer, R., Marco-Lozar, J.P., Quijada, C., Cazorla-Amorós, D., Morallón, E., 2010. Comparison among chemical, thermal, and electrochemical regeneration of phenol-saturated activated carbon. *Energy and Fuels* 24, 3366–3372.
- Bhatnagar, A., Kumar, E., Sillanpää, M., 2011. Fluoride removal from water by adsorption—a review. *Chem. Eng. J.* 171, 811–840.
- Bijsterbosch, B.H., 1974. Characterization of silica surfaces by adsorption from solution. Investigations into the mechanism of adsorption of cationic surfactants. *J. Colloid Interface Sci.* 47, 186–198.
- Bombuwalla, D.N., Liyanage, A.S., Pittman, C.U., Mohan, D., Mlsna, T., 2018. Fast nitrate and fluoride adsorption and magnetic separation from water on A-Fe₂O₃ and Fe₃O₄ dispersed on Douglas fir biochar. *Bioresour. Technol.* 263, 258–265.
- Bors, J., 1990. Sorption of radioiodine in organo-clays and -soils. *Radiochim. Acta* 51, 139–143.
- Bouhadjar, S.I., Kopp, H., Britsch, P., Deowan, S.A., Hoinkis, J., Bundschuh, J., 2019. Solar powered nanofiltration for drinking water production from fluoride-containing groundwater – a pilot study towards developing a sustainable and low-cost treatment plant. *J. Environ. Manag.* 231, 1263–1269.
- Bowman, R., Sullivan, E., Haggerty, G., 1994. Sorption of inorganic oxyanions by surfactant-modified zeolites. *Abstr. Pap. Am. Chem. Soc.* 207, 178.
- Cai, J., Zhang, Y., Pan, B., Zhang, W., Lv, L., Zhang, Q., 2016. Efficient defluoridation of water using reusable nanocrystalline layered double hydroxides impregnated polystyrene anion exchanger. *Water Res.* 102, 109–116.
- Castillejos-López, E., Nevskaja, D.M., Muñoz, V., Guerrero-Ruiz, A., 2008. On the interactions of phenol, aniline and p-nitrophenol on activated carbon surfaces as detected by TPD. *Carbon N. Y.* 46, 870–875.
- Celik, A., Yildiz, N., Calimli, A., 2000. Adsorption of some organic compounds by hexadecyltrimethylammonium-bentonite. *Rev. Chem. Eng.* 16, 301–309.
- Corapcioglu, M.O., Huang, C.P., 1987. The surface acidity and characterization of some commercial activated carbons. *Carbon N. Y.* 25, 569–578.
- Daifullah, A.A.M., Yakout, S.M., Elreedy, S.A., 2007. Adsorption of fluoride in aqueous solutions using KMnO₄ modified activated carbon derived from steam pyrolysis of rice straw. *J. Hazard. Mater.* 147, 633–643.
- Dentel, S.K., Jamrah, A.L., Sparks, D.L., 1998. Sorption and cosorption of 1, 2, 4-trichlorobenzene and tannic acid by organo-clays. *Water Res.* 32, 3689–3697.
- Deshmukh, M.M., Gadre, S.R., Bartolotti, L.J., 2006. Estimation of intramolecular hydrogen bond energy via molecular tailoring approach. *J. Phys. Chem. A* 110, 12519–12523.
- Díaz-Navá, C., Olguín, M.T., Solache-Ríos, M., 2002. Water defluoridation by Mexican heulandite-clinoptilolite. *Sep. Sci. Technol.* 37, 3109–3128.
- Ding, C., Shang, C., 2010. Mechanisms controlling adsorption of natural organic matter on surfactant-modified iron oxide-coated sand. *Water Res.* 44, 3651–3658.
- Dissanayake, C., 1991. The fluoride problem in the groundwater of Sri Lanka – environmental management and health. *Int. J. Environ. Stud.* 38, 137–155.
- Dolar, D., Košutić, K., Vučić, B., 2011. RO/NF treatment of wastewater from fertilizer factory – removal of fluoride and phosphate. *Desalination* 265, 237–241.
- ElGamal, M., Mousa, H.A., El-Naas, M.H., Zacharia, R., Judd, S., 2018. Bio-regeneration of activated carbon: a comprehensive review. *Sep. Purif. Technol.* 197, 345–359.
- Ferro-García, M.A., Utrera-Hidalgo, E., Rivera-Utrilla, J., Moreno-Castilla, C., Joly, J.P., 1993. Regeneration of activated carbons exhausted with chlorophenols. *Carbon N. Y.* 31, 857–863.
- Fragneto, G., Thomas, R.K., Rennie, A.R., Penfold, J., 1996. Neutron reflection from hexadecyltrimethylammonium bromide adsorbed on smooth and rough silicon surfaces. *Langmuir* 12, 6036–6043.
- Ghiaci, M., Kia, R., Abbaspur, A., Seyedeyn-Azad, F., 2004. Adsorption of chromate by surfactant-modified zeolites and MCM-41 molecular sieve. *Sep. Purif. Technol.* 40, 285–295.
- Greenlee, L.F., Lawler, D.F., Freeman, B.D., Marrot, B., Moulin, P., 2009. Reverse osmosis desalination: water sources, technology, and today's challenges. *Water Res.* 43, 2317–2348.
- Gupta, A.K., Deva, D., Sharma, A., Verma, N., 2009. Adsorptive removal of fluoride by micro-nano-hierarchical web of activated carbon fibers. *Ind. Eng. Chem. Res.* 48, 9697–9707.
- Gupta, V.K., Ali, I., Saini, V.K., 2007. Defluoridation of wastewaters using waste carbon slurry. *Water Res.* 41, 3307–3316.
- Habuda-Stanić, M., Ravančić, M.E., Flanagan, A., 2014. A review on adsorption of fluoride from aqueous solution. *Materials (Basel)* 7, 6317–6366.
- Hasan, F.B., Huang, D.D., 1997. Characterization of colloidal silica and its adsorption phenomenon with silicon-base surfactants with relation to film strength. *J. Colloid Interface Sci.* 190, 161–170.
- He, J., Zhang, K., Wu, S., Cai, X., Chen, K., Li, Y., Sun, B., Jia, Y., Meng, F., Jin, Z., Kong, L., Liu, J., 2016. Performance of novel hydroxyapatite nanowires in treatment of fluoride contaminated water. *J. Hazard. Mater.* 303, 119–130.
- Hefter, G.T., 1984. Acidity constant of hydrofluoric acid. *J. Solution Chemistry* 13, 457–470.
- Hutchins, R., 1973. Economic factors in granular carbon thermal regeneration. *Chem. Eng. Prog.* 69, 48–55.
- Judd, S.J., 2017. Membrane technology costs and me. *Water Res.* 122, 1–9.
- Kabay, N., Arar, Ö., Samatya, S., Yüksel, Ü., Yüksel, M., 2008. Separation of fluoride from aqueous solution by electrodialysis: effect of process parameters and other ionic species. *J. Hazard. Mater.* 153, 107–113.
- Kang, D., Yu, X., Ge, M., 2017. Morphology-dependent properties and adsorption performance of CeO₂ for fluoride removal. *Chem. Eng. J.* 330, 36–43.
- Kang, D., Yu, X., Ge, M., Lin, M., Yang, X., Jing, Y., 2018. Insights into adsorption mechanism for fluoride on cactus-like amorphous alumina oxide microspheres. *Chem. Eng. J.* 345, 252–259.
- Karthikeyan, M., Elango, K.P., 2008. Removal of fluoride from aqueous solution using graphite: a kinetic and thermodynamic study. *Indian J. Chem. Technol.* 15, 525–532.
- Li, Y.H., Wang, S., Zhang, X., Wei, J., Xu, C., Luan, Z., Wu, D., 2003. Adsorption of fluoride from water by aligned carbon nanotubes. *Mater. Res. Bull.* 38, 469–476.
- Li, Z., Bowman, R.S., 2001. Retention of inorganic oxyanions by organo-kaolinite. *Water Res.* 35, 3771–3776.
- Li, Z., Alessi, D., Zhang, P., Bowman, R., 2002. Organo-illite as a low permeability sorbent to retard migration of anionic contaminants. *J. Environ. Eng.* 128, 583–587.
- Lin, C.E., 2004. Determination of critical micelle concentration of surfactant by capillary electrophoresis. *J. Chromatogr.* 1037 (1–2), 467–478.
- Liu, D., Deng, S., Maimaiti, A., Wang, B., Huang, J., Wang, Y., Yu, G., 2018. As (III) and As (V) adsorption on nanocomposite of hydrated zirconium oxide coated carbon nanotubes. *J. Colloid Interface Sci.* 511, 277–284.
- Liu, P., Zhang, L., 2007. Adsorption of dyes from aqueous solutions or suspensions with clay nano-adsorbents. *Sep. Purif. Technol.* 58, 32–39.
- Loganathan, P., Vigneswaran, S., Kandasamy, J., Naidu, R., 2013. Defluoridation of drinking water using adsorption processes. *J. Hazard. Mater.* 248–249, 1–19.
- Mahmudov, R., 2007. Removal and Destruction of Perchlorate by Activated Carbon Based Processes. Doctoral Dissertation. University of Delaware, Newark DE 19716 (327 pp).
- Mahmudov, R., Huang, C.P., 2010. Perchlorate removal by activated carbon adsorption. *Sep. Purif. Technol.* 70, 329–337.
- Mahmudov, R., Chen, C., Huang, C.P., 2015. Functionalized activated carbon for the adsorptive removal of perchlorate from water solutions. *Front. Chem. Sci. Eng.* 9, 194–208.
- Meenakshi, Maheshwari, R.C., 2006. Fluoride in drinking water and its removal. *J. Hazard. Mater.* 137, 456–463.
- Meng, F., Zhang, S., Oh, Y., Zhou, Z., Shin, H.S., Chae, S.R., 2017. Fouling in membrane bioreactors: an updated review. *Water Res.* 114, 151–180.
- Milton, R., Kunjappu, J.T., 2012. *Surfactants and Interfacial Phenomena*. 4th ed. Wiley, Hoboken, New Jersey.
- Mobarak, M., Selim, A.Q., Mohamed, E.A., Selim, M.K., 2018. Modification of organic matter-rich clay by a solution of cationic surfactant/H₂O₂: a new product for fluoride adsorption from solutions. *J. Clean. Prod.* 192, 712–721.
- Mobarak, M., Mohamed, E.A., Selim, A.Q., Sellaiou, L., Ben Lamine, A., Erto, A., Bonilla-Petriciolet, A., Selim, M.K., 2019. Surfactant-modified serpentine for fluoride and Cr (VI) adsorption in single and binary systems: experimental studies and theoretical modeling. *Chem. Eng. J.* 369, 333–343.
- Mohan, D., Kumar, S., Srivastava, A., 2014. Fluoride removal from ground water using magnetic and nonmagnetic corn stover biochars. *Ecol. Eng.* 73, 798–808.
- Mohanta, D., Ahmaruzzaman, M., 2018. Bio-inspired adsorption of arsenite and fluoride from aqueous solutions using activated carbon@SnO₂ nanocomposites: isotherms, kinetics, thermodynamics, cost estimation and regeneration studies. *J. Environ. Chem. Eng.* 6, 356–366.
- Mosquera, V., del Río, J.M., Attwood, D., García, M., Jones, M.N., Prieto, G., Suarez, M.J., Sarmiento, F., 1998. A study of the aggregation behavior of hexyltrimethylammonium bromide in aqueous solution. *J. Colloid Interface Sci.* 206, 66–76.
- Mullick, A., Neogi, S., 2018. Acoustic cavitation induced synthesis of zirconium impregnated activated carbon for effective fluoride scavenging from water by adsorption. *Ultrason. Sonochem.* 45, 65–77.

- Mullick, A., Neogi, S., 2019. Ultrasound assisted synthesis of Mg-Mn-Zr impregnated activated carbon for effective fluoride adsorption from water. *Ultrason. Sonochem.* 50, 126–137.
- Nevskaia, D.M., Guerrero-Ruiz, A., 2001. Comparative study of the adsorption from aqueous solutions and the desorption of phenol and nonylphenol substrates on activated carbons. *J. Colloid Interface Sci.* 234, 316–321.
- Ng, S.L., Seng, C.E., Lim, P.E., 2009. Quantification of bioregeneration of activated carbon and activated rice husk loaded with phenolic compounds. *Chemosphere* 75, 1392–1400.
- Owusu-Agyeman, I., Reinwald, M., Jeihipour, A., Schäfer, A.I., 2019. Removal of fluoride and natural organic matter removal from natural tropical brackish waters by nanofiltration/reverse osmosis with varying water chemistry. *Chemosphere* 217, 47–58.
- Özkaya, B., 2006. Adsorption and desorption of phenol on activated carbon and a comparison of isotherm models. *J. Hazard. Mater.* 129, 158–163.
- Pan, B., Xu, J., Wu, B., Li, Z., Liu, X., 2013. Enhanced removal of fluoride by polystyrene anion exchanger supported hydrous zirconium oxide nanoparticles. *Environ. Sci. Technol.* 47, 9347–9354.
- Parette, R., Cannon, F.S., 2005. The removal of perchlorate from groundwater by activated carbon tailored with cationic surfactants. *Water Res.* 39, 4020–4028.
- Paul, H., Raj, R., 1997. *Principles of Colloid and Surface Chemistry*. 3rd ed. Marcel Dekker, New York.
- Pitakteeratham, N., Hafuka, A., Satoh, H., Watanabe, Y., 2013. High efficiency removal of phosphate from water by zirconium sulfate-surfactant micelle mesostructure immobilized on polymer matrix. *Water Res.* 47, 3583–3590.
- Rennie, A.R., Lee, E.M., Simister, E.A., Thomas, R.K., 1990. Structure of a cationic surfactant layer at the silica-water interface. *Langmuir* 6, 1031–1034.
- Robshaw, T.J., Dawson, R., Bonser, K., Ogden, M.D., 2019. Towards the implementation of an ion-exchange system for recovery of fluoride commodity chemicals. *Kinetic and dynamic studies. Chem. Eng. J.* 367, 149–159.
- Saikia, R., Goswami, R., Bordoloi, N., Senapati, K.K., Pant, K.K., Kumar, M., Katak, R., 2017. Removal of arsenic and fluoride from aqueous solution by biomass based activated biochar: optimization through response surface methodology. *J. Environ. Chem. Eng.* 5, 5528–5539.
- Sanyo, H., Sasaki, Y., Takahiro, H., Aiko, T., 2006. Interactions of tetrakis (4-sulfonatophenyl) porphyrin with γ -cyclodextrin and alkyltrimethylammonium bromides in aqueous solutions. *J. Incl. Phenom. Macrocycl. Chem.* 54, 67–76.
- Srimurali, M., Pragathi, A., Karthikeyan, J., 1998. A study on removal of fluorides from drinking water by adsorption onto low-cost materials. *Environ. Pollut.* 99, 285–289.
- Stapleton, M.G., Sparks, D.L., Dentel, S.K., 1994. Sorption of pentachlorophenol to HDTMA-clay as a function of ionic strength and pH. *Environ. Sci. Technol.* 28, 2330–2335.
- Steenberg, B., 1944. Adsorption and Exchange of Ions on Activated Charcoal. *Almquist & Wiksells*.
- Tang, D., Zhang, G., 2016. Efficient removal of fluoride by hierarchical Ce-Fe bimetal oxides adsorbent: thermodynamics, kinetics and mechanism. *Chem. Eng. J.* 283, 721–729.
- Tuddenham, R.F., Alexander, A.E., 1962. The effect of pressure on micell formation in soap solutions. *J. Phys. Chem.* 66, 1839–1842.
- Turner, S.F., Clarke, S.M., Rennie, A.R., 1999. Adsorption of sodium dodecyl sulfate to a polystyrene/water interface studied by neutron reflection and attenuated total reflection infrared spectroscopy. *Langmuir* 15, 1017–1023.
- USEPA (Environmental Protection Agency), 2003. *Toxicological Profile for Fluorides, Hydrogen Fluoride and Fluorine*.
- Wang, J., Wang, T., Burken, J.G., Chusuei, C.C., Ban, H., Ladwig, K., Huang, C.P., 2008. Adsorption of arsenic (V) onto fly ash: a speciation-based approach. *Chemosphere* 72, 381–388.
- Wang, J., Wu, L., Li, J., Tang, D., Zhang, G., 2018. Simultaneous and efficient removal of fluoride and phosphate by Fe-La composite: adsorption kinetics and mechanism. *J. Alloys Compd.* 753, 422–432.
- Warmadewanthi, B., Liu, J.C., 2009. Selective separation of phosphate and fluoride from semiconductor wastewater. *Water Sci. Technol.* 59, 2047–2053.
- Wu, L., Zhang, G., Tang, D., 2016. A novel high efficient Mg-Ce-La adsorbent for fluoride removal: kinetics, thermodynamics and reusability. *Desalin. Water Treat.* 57, 23844–23855.
- Yildiz, N., Gönülşen, R., Koyuncu, H., Çalimli, A., 2005. Adsorption of benzoic acid and hydroquinone by organically modified bentonites. *Colloids Surfaces A Physicochem. Eng. Asp.* 260, 87–94.
- Yu, Z., Xu, C., Yuan, K., Gan, X., Feng, C., Wang, X., Zhu, L., Zhang, G., Xu, D., 2018. Characterization and adsorption mechanism of ZrO₂ mesoporous fibers for health-hazardous fluoride removal. *J. Hazard. Mater.* 346, 82–92.