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Optimization of Fluoride Removal on Carbon Sphere Using 1-pK Surface Complexation Modelling

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Abstract: Over 2 billion people in the world experience acute drinking water stress due to excess salinity. In most cases, water salinity and fluoride in water occur together. Water desalination is achieved by pressure-driven membranes technology that requires activated carbon pre-filtration to reduce turbidity. The water flow often follows a torturous route due to the uneven distribution of pores in activated carbon. In this research, we proposed using carbon spheres (CSs) in lieu of activated carbon for the concurrent removal of turbidity and fluoride at the pre-filtration level. Fluoride and proton absorption on the carbon sphere were examined. The pH_{zpc} of CSs in $NaNO_3$ was 8.29 as determined by the basic stern-layer model (BSM). The optimized electrolytic binding constants were coupled with the charge-distribution multi-site ion complexation (CD-MUSIC) model for fluoride adsorption. These all-equilibrium constants were determined by numeric optimization. The site density of CSs was reduced after adding fluoride due to the covering of additional sites on CSs. Development of CSs pre-filtration unit process at laboratory scale is underway presently.

Keywords: **Carbon sphere, Fluoride, Pre-filtration, CD-MUSIC model**

1. Introduction

Excessive fluoride in drinking water is a major problem in the world. The fluoride pollution in groundwater is higher than in surface water due to the dissolution of fluoride enrich minerals like fluorspar (CaF_2), cryolite (Na_3AlFPO_6), fluorapatite $Ca(PO)_2.Ca(FCl)_2$ (Meenakshi & Maheshwari, 2006). The high amount of fluoride is harmful to human health. Various type of health problems is occurring such as dental and skeleton fluorosis and neurotoxicity risks (Grandjean, 2019). The World Health Organization (WHO) recommended fluoride in drinking water is 1.5 mg/l (WHO, 2019). There are several fluoride remediation methods used such as precipitation-coagulation, membrane-based process, ion-exchange method, and adsorption(Jagtap et al., 2012; Meenakshi & Maheshwari, 2006) Salinity and fluoride effects are combined (Mor et al., 2009). The membrane technology is used for the desalination of water that the pre-Filtration process to reduce turbidity. This research process fabricated the pre-

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filter unit using carbon spheres.

Carbon spheres (CSs) are novel spheroidal carbon structures. CSs are presently attractive research areas in a multitude of fields due to their unique characteristics such as size controllability, adjustable porosity, high surface area, low weight, surface functionality, and outstanding electronic and chemical properties (Chen et al., 2019; Xu et al., 2018).

When comparing other carbon nanomaterials, the chemistry of CSs strongly depends on the reactivity of opened-edge graphitic flakes. In the nucleation mechanism, graphitic flakes are constructed on the surface presence of combined pentagonal, hexagonal, and heptagonal carbon rings (Song et al., 2011). These valence sp2 carbon atoms at the edge and defects of the flakes are linked to other atoms typically O atoms or H atoms to fulfill requirements. Further, suitable surface functional groups on carbon spheres can improve the removal capacity of pollutants .1 But, there has been less evidence for the water treatment process using CSs. Moreover, few studies have demonstrated for removal of harmful heavy metals from water(Pol et al., 2006). However, carbon spheres may be promising nanomaterials for water treatment not only at the lab scale but also industrial scale due to their cost-effectiveness and biocompatibility when compared to the other nanomaterials(Miao et al., 2004; Pol et al., 2004; Purohit et al., 2014).

2. Experimental

2.1 Materials

Sodium fluoride was from Fluke (Switzerland), other all chemicals were from Sigma-Aldrich (USA), and ultra-pure water was used in all experiments

2.2 Synthesis of carbon spheres

The ceramic boat was mounted at the center of the CVD furnace setup containing a quartz tube. In a typical experiment, high-purity N_2 (99.99%) was purged into the tube while the furnace was heated to the desired temperature (1000 °C) at a heating rate of 10 °C.min^{-1} under atmospheric conditions. Then the production of NCS was initiated using C_2H_2: N_2(500:600) gases under constant flow rates for 1 h. Afterward, the supply of C_2H_2 was stopped and the N_2 supply was continued until the reactor reached ambient temperature conditions.

2.3 Surface titration

The experiments were carried out as a function of $NaNO_3$ concentration to the determined point of zero charge and electrolytic binding constants of Na^+ and NO_3 $^-$ on CSs. A 1 g/l CSs suspension was equilibrated at a desired ionic strength for 20 min the initial pH was 5 after 20 min of equilibration. The pH was raised to 10 with 0.98 M NaOH soon after, surface titration was started with 0.09 M HNO_3 using auto-titration.

2.3 Fluoride adsorption

The fluoride removal by 0.15±0.01 g/L CSs was determined using a simulated water sample with the 5 mg/L fluorides at 298 K. The 20 mL of fluoride and CSs suspensions were equilibrated in 50 mL centrifuge tubes using end to end shaker (MS-RD-Pro Rotor, HINOTEK China). The particulate separation from the solution was carried out using 0.22 um syringe filters. The supernatant and 0.094 mol/dm^{-3} HOAc/ 0.005 mol/dm^{-3} NaOAc buffer solutions were mixed at a 1:1 ratio to determine the total fluoride activity. the suspension pH was varied between 4 and 10 at 298 K using 1.00 mol/dm^{-3} NaOH or 1.00 mol/dm^{-3} HNO_3.

2.4 Surface complexation Modeling

The reactivity of CSs was modeled with a 1-pK CD-MUSIC and basic Stern electrostatic model. The assumption made that CSs have one active surface site namely $\equiv GOH^{-0.5}$. All surface complexation reactions and other input data were indicated in table 1. Optimized electrolyte and fluoride binding constants were determined by the FIT-ECOSAT utility

Table 1 – Physico-chemical data of carbon nono sphere and formation constants of various solute species used in BSM and CD-MUSIC modeling

Parameter	Value
Surface area, m^2g^{-1}	1000
Site density sites nm^{-2}	6-10
Stern layer capacitance	2.58
pH_{zpc} (in $NaNO_3$)	8.29
Ion-pair formation	Log K
$\equiv GOH^{-0.5} + H^+ = \equiv GOH_2^{+0.5}$	8.29
$\equiv GOH^{-0.5} + Na^+ = \equiv GOH^{-0.5} Na^+$	-9.01
$\equiv GOH_2^{+0.5} + NO_3^- = \equiv GOH_2^{+0.5}NO_3^-$	-4.9
$\equiv GOH_2^{+0.5} + F^- = \equiv GOF^{-0.5} + H_2O$	8.58

`3. Result and Discussion

3.1 Proton titration

The surface charge density of CSs as a function of pH was determined by a rapid proton titration in 0.01M6 $NaNO_3$ and the result are shown in figure 1. In the experimental condition working pH range is 7.5 to 9.5. Electro neutrality condition is applied to the particles in the aquatic suspension. The surface charge due to the proton adsorption is calculated using the following equation,

$$\sigma_H = (\Delta C_A - \Delta C_B)FS/a$$

Where, σ_H charge attribution due to proton, ΔC_A and ΔC_B represent the acid and base concentration added. F is Faraday's constant. The a and S represent the solid content and specific surface area.

When any absorbed ions are absent, the surface and the diffuse double layer do not contain any other ions. Therefore, it can be applied, the basic stern model. Proton titration data can be used to calculate an ion-pair formation constant of sodium and nitrate on the CSs surface. Here CSs has a defects edge of $GOH^{-0.5}$ reactive sites.

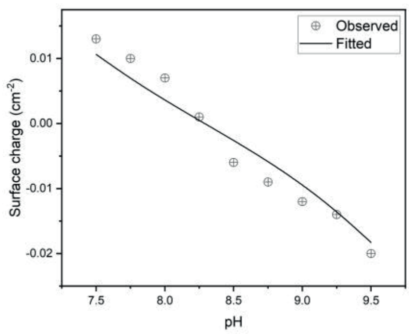

Figure 1 – Proton titration curve of CSs as a function of 0.01M $NaNO_3$ concentration

3.3 Fluoride adsorption

The effect of Adsorption density on CS function as a pH in 0.01 M $NaNO_3$ at 278 K was determined. The initial Fluoride concentration was always kept at 2.3 mg/l. Fluoride adsorption density rapidly increased pH > 7. The maximum removal efficiency was observed at pH 7.5. During the Fluoride adoption the results are shown in figure 2.

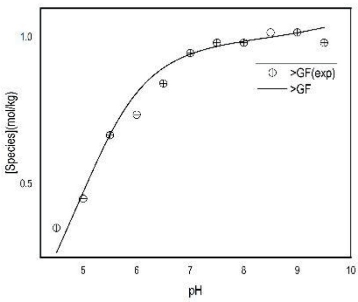

Figure 2 – Fluoride abruption density curve of CS as a function of 0.01M $NaNO_3$ concentration

5. Conclusions

The CSs surface sites readily hydroxylate forming conducive environments for fluoride adsorption according to 1-pK Stern layer model formulations. The pH_{zpc} of CSs in $NaNO_3$ was 8.29 and the binding constant of Fluoride was 8.58. CSs can concurrently remove fluoride in water. Therefore, it has the potential as a starting material to be used in the pre-filtration in the drinking water treatment industry.

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