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Novel Anionic Clay Adsorbents for Boiler-Blow Down Waters Reclaim and Reuse – Phase II

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INTRODUCTION

U.S. Electric Utilities are a large user of water. New regulations to diminish the effect of power generation on aquatic life will mean, that Utilities will have to retrofit from the once-through cooling technology, to recirculating cooling towers, and to reclaim/reuse discharged water throughout the power-plant (e.g., boiler blow-down water). Concerns exist today, in particular, about heavy metals, such as Hg, As and Se, found in many of the power-plant effluents. Most of these streams fall today under the category of high volume, "too clean to clean" effluents. They require highly efficient treatment techniques, particularly for the removal of trace-level metal contaminants. Little emphasis, so far, has been placed on such discharges. The focus of the project is on treating and reusing such effluents, particularly on dealing with Se and As impacted boiler blow-down streams. In this project we study the utilization of novel anionic clay sorbents for treating and reclaiming/reusing power-plant effluents, in particular, boiler blow-down waters containing heavy metals, such as As and Se. Developing and using novel materials for such application is dictated by the challenge posed by reclaiming and recycling these "too clean to clean" effluent streams, generated during electricity production, whose contaminant levels are in the ppm/ppb (or even less) trace levels.

Contaminants of Concern

Arsenic (As): MCL of 0.01 ppm

- Oxidation states: As(III) (arsenite) and As(V) (arsenate)
- Considered carcinogenic to humans, protracted contact causes arsenicosis, a form of poisoning in humans.

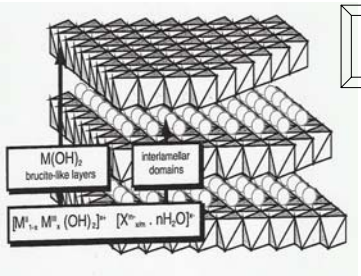
Selenium (Se): MCL of 0.01 ppm

- Oxidation states: Se(IV) (selenite) and Se(VI) (selenate)
- Acute exposure leads to severe respiratory problems and neurological effects

Techniques Available

- PRECIPITATION - FILTRATION
- ADSORPTION
- ION EXCHANGE
- REVERSE OSMOSIS

Layered Double Hydroxides



$$[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[A_{x/n}^{n-}.yH_2O]$$

$$0.17 \le x \left(= \frac{M^{(III)}}{M^{(II)} + M^{(III)}} \right) \le 0.33$$

M^{II}: Mg, Fe, Co, Cu, Zn

M^{III}: Al, Cr, Mn, Co, Ni

A: CO_3^{2-}, OH^-, NO_3^-

- It has significant number of exchangeable ions
- Large interlayer spaces
- Requires a simple thermal regeneration procedure

Coprecipitation Method

$NaOH + Na_2CO_3$

↓

$Mg(NO_3)_2.6H_2O + Al(NO_3)_3.\ 9H_2O$

↓ 333K, Vigorous stirring; Thick gel aged for 24 h

Filtration, Washing (Deionised water) & Drying (333K)

↓

Mg-Al-CO_3-LDH

↓ Heat; 500 °C for 4 h

Calcined LDH

↓ Wash; 24 h

Conditined LDH

CONDITIONING

- Significantly reduces the Mg and Al dissolution
- Tempers the solution pH change

Packed-Bed Column Equations

$$u\frac{\partial C}{\partial z} + \frac{\partial C}{\partial t} + \frac{1-\varepsilon}{\varepsilon}\frac{\partial \bar{\bar{q}}}{\partial t}\cdot\rho = 0 \qquad \begin{cases} C = 0,\ \bar{\bar{q}} = 0 & @\ t = 0 \\ C = C_0 & @\ z = 0 \end{cases}$$

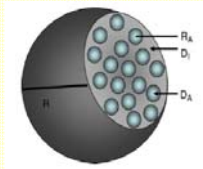
Homogeneous Surface Diffusion Model

$$\frac{\partial q}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_i \frac{\partial q}{\partial r}\right) \qquad \begin{cases} q = 0, t = 0 \\ \frac{\partial q}{\partial r} = 0, r = 0 \\ \rho D_i \left.\frac{\partial q}{\partial r}\right|_{r=R} = k_f(C - C_s), r = R \end{cases}$$

$$q = \frac{Kq_s C_s^{\,n}}{1 + KC_s^{\,n}}, r = R$$

$$\bar{\bar{q}} = \frac{3}{R^3}\int_0^R q\, r^2 dr$$

Bidisperse Model



MACROPARTICLE

$$\varepsilon_M \frac{\partial C_M}{\partial t} + (1-\varepsilon_M)\rho_s \frac{\partial \bar{q}_\mu}{\partial t} = \varepsilon_M \frac{D_M}{r_M^2}\frac{\partial}{\partial r_M}\left[r_M^2 \frac{\partial C_M}{\partial r_M}\right] \qquad \begin{cases} C_M = 0, t = 0 \\ \frac{\partial C_M}{\partial r_M} = 0, r_M = 0 \\ \varepsilon_M D_M \left.\frac{\partial C_M}{\partial r_M}\right|_{r_M = R_M} = k_f(C - C_{MS}), r_M = R_M \end{cases}$$

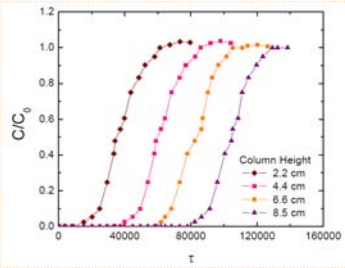
MICROPARTICLE

$$\frac{\partial q_\mu}{\partial t} = \frac{D_\mu}{r_\mu^2}\frac{\partial}{\partial r_\mu}\left(r_\mu^2 \frac{\partial q_\mu}{\partial r_\mu}\right) \qquad \begin{cases} q_\mu = 0, t = 0 \\ \frac{\partial q_\mu}{\partial r_\mu} = 0, r_\mu = 0 \\ q_\mu = \frac{Kq_s C_M^{\,n}(r_M, t)}{1 + KC_M^{\,n}(r_M, t)}, r_\mu = R_\mu \end{cases}$$

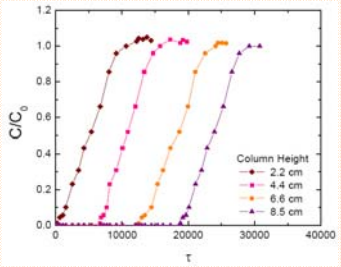
$$\bar{\bar{q}} = \frac{3}{\rho R_M^3}\int_0^{R_M} r_M^2\left[(1-\varepsilon_M)\rho_s \bar{q}_\mu + \varepsilon_M C_M\right] dr_M \qquad \bar{q}_\mu = \frac{3}{R_\mu^3}\int_0^{R_\mu} q_\mu r_\mu^2 dr_\mu$$

Multi Solute Experiments (Arsenic & Selenium)

Arsenic

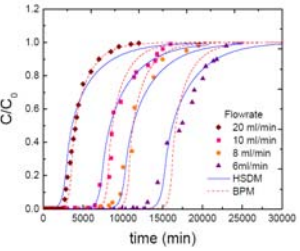


Selenium

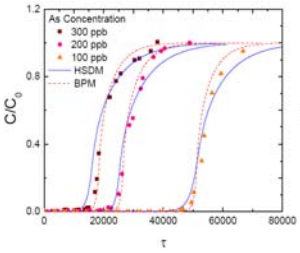


Simulation Results

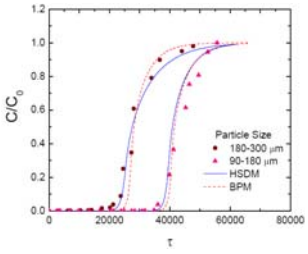
Flowrate Effect



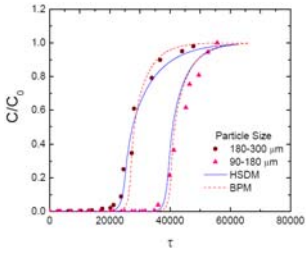
Concentration Effect



Particle Size Effect



pH Effect



Summary

- Mg-Al-CO_3-LDH shows promising capacity for the removal of trace levels of As and Se from aqueous solutions.
- In packed-bed columns, breakthrough time increases upon decreasing stream flow rate, feed concentration, solution pH, and particle size.
- Both HSDM and BPM models predict the experimental data quite well.

Future Work

- Studies with real power-plant effluents.
- Safe disposal of the spent adsorbents.
- Preliminary estimation of capital and operating costs.
- Completion of the project and Final Report preparation.

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