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Evaluating the effectiveness of the banana (*Musa* spp. ABB cv. Kluai Namwa) peel for the removal of fluoride from water



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PRESENTATION OUTLINE

INTRODUCTION

MATERIALS AND METHODS

RESULTS AND DISCUSSION

CONCLUSIONS

Introduction

Fluoride (F⁻): Simplest anion of fluorine persistent in all environmental components

Commonly encountered in the water resources

-Weathering of fluoride bearing minerals/leaching from soil into groundwater

-Community water fluoridation and dietary fluoride supplements



<image><image>

Fluoride containing minerals: Fluorite, Cryolite, Fluorapatite

Additive in municipal water supplies

• Optimum level of fluoride in drinking water (0.5 - 1 mg/L) : Effective reduction of dental caries







Continued consumption of >1.5 mg/L F⁻: Dental fluorosis and severe skeletal fluorosis



Very mild fluorosis



Mild fluorosis



Moderate fluorosis



Severe fluorosis



Introduction

- Defluoridation as the most feasible option in absence of alternate water sources
- *Limited use of conventional additive methods and sophisticated membrane technologies:
 - -Social, financial, cultural and environmental reasons
- Adsorption: Economic feasibility and simplicity in design and operation
- Exploration of novel low cost adsorbents
 - -Musa spp. ABB cv. Kluai Namwa (banana) peel
 - -Most widely disseminated ABB cultivar in Thailand
- -Banana Peel: Major horticultural by product (40 % of total weight of the fresh fruit) **OBJECTIVES**
- *Bioadsorption of fluoride in batch system by Kluai Namwa peel powder
- Elucidation of sorbent-sorbate interactions: Langmuir and Freundlich isotherm models

Materials and Methods

Preparation of Bioadsorbent

- Banana peels collected from fruit market, and washed thoroughly to remove fleshy residues
 Peels were dried in sunlight for 7-8 hours followed by hot air oven at 120±2 °C for 36 hours
 Dried peels crushed using mortar and pestle and sieved by 250 BSS, mesh size
- Screened banana peel powder (BP) stored in sterilized airtight container











Materials and Methods

Experimental Approach

- Preparation of 1000 mg/L stock fluoride solution and 10 mg/L test solution
- Batch mode experiment with 50 mL working solution at room temperature
 - -Optimization of influencing parameters: Adsorbent dose, pH, speed, contact time, initial fluoride concentration and effect of co-existing ions
- Filtrate analyzed using ExStik FL700 Fluoride meter
 - -Measurement procedure follows ASTM and EPA standard methodology, using total ionic strength adjustment buffer (TISAB) reagents
- FTIR spectra collected over 4000–500 cm⁻¹ at resolution of 4 cm⁻¹ in FTIR spectrometer
- ♦BP surface morphology studied with SEM at variable pressure (VP) mode accelerating voltage

SEM studies of BP at a resolution of $500 \times$ and 20 μ m particle size





(a) (b) Fig. SEM images for banana peel: (a) Before adsorption (b) After fluoride adsorption

- Before adsorption: BP exhibited irregular and rough porous surface with heterogeneous voids

 Reactive adsorption centers for fluoride adsorption
- * After adsorption: Peels appear to have smooth surface as pores were partially covered by fluoride

FTIR analysis

FTIR analysis of BP

Peaks	Functional groups			
Broad absorption band at 3447.7 cm⁻¹	O-H stretching of hydroxyl groups of alcohols and phenols			
Peaks at 2918.1 cm⁻¹	C-H stretching of alkane representing aliphatic nature of BP			
Peaks pertaining to 1758.2 cm⁻¹	Asymmetrical stretching of C=O bond of carboxylic acids or ester			
Adsorption peaks at 1636.4-962.6 cm⁻¹	Attributed to ester, polysaccharide or protein			
Peak at 1384.2 cm⁻¹	Stretching vibration of -COO			
Absorption bands at 1758.2 – 1384.2 cm⁻¹	Characteristics of C=C in aromatics rings			
Peaks at 1043.3 and 1089.9 cm⁻¹	Si-O stretching and Si-O bending indicating the presence of silica			
Peaks in the region of lower wave numbers	N containing bioligands and N-H deformation of amines			

Effect of adsorbent dose



- Better sorbate-sorbent interaction at higher dose
- Flattening of curve at higher doses of BP

-Shortage of F- ion in solution with respect to higher exchangeable sites on adsorbent

Reduction in the net surface area due to overlapping of active sites at higher doses
Further experiments carried out with 4 g/L as an optimum dose



✤ Increase in removal from acidic to neutral pH

-Higher columbic interaction between F⁻ and positively charged H⁺ along with some neutral charges

- Reduction of adsorption in acidic pH range
 - Conversion of fluoride into neutral HF, directly affecting the anion exchanging nature
- Reduction of adsorption in alkaline pH range
 - Presence of large number of OH⁻ ions causes increased hindrance to diffusion of F⁻ ions 11

Optimization of agitation speed



Maximum removal of 83 % at 300 rpm

-Proper contact between F⁻ ions in solution and binding sites at higher speed

- Decrease in removal efficiency at lower speeds
 - -Burial of active adsorption sites at lower speed
 - -Presence of liquid film thickness around particles decreases fluoride uptake rate

Damage in the physical structure of adsorbents at higher speed
 -200 rpm speed sufficient to assure all surface binding sites readily available for fluoride uptake

Optimization of contact time



- Simultaneous increase in removal until the attainment of equilibrium at 160 minutes
- * Rapid removal in early stage due to larger available surface area of adsorbent
- Decrease in adsorption efficiency at later stage
 - -Saturation of binding sites
 - -Existence of repulsive forces between solute molecules on the solid and bulk phases

Effect of Initial fluoride concentration



♦ Maximum removal at 5 mg/l F⁻ concentration which then decreased to 52 % for 40 mg/L

- Active interaction of F⁻ ions with the available binding sites at low concentration

- Increment in F⁻ /adsorbent ratio at higher concentrations resulting in faster saturation of sites

Similar trend was followed for fluoride removal using pumice and modified azolla filiculoides

Effect of Chloride and Sulfate ions on fluoride adsorption



♦ Defluoridation studies in presence of Cl⁻ and SO₄²⁻ ions at pH 7and optimized conditions

- No remarkable influence on the F⁻ removal in presence of monovalent Cl⁻ ions
 - Cl- ion: Low affinity ligand and outer sphere complex forming species

* Presence of divalent SO_4^{2-} ions at higher concentrations resulted in decrease of fluoride removal

- SO₄²⁻ ions: Partially inner and outer sphere complex forming species
- Competition between fluoride and sulfate ions for the sorption sites

Langmuir isotherm

Langmuir Isotherm Model



✤ Assume monolayer formation on adsorbent surface

Linearized form (Type I) is expressed as: $\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o}$

 $q_e = amount of fluoride adsorbed per unit weight of adsorbent (mg/g)$

 C_e = equilibrium concentration (mg/L) Qo and b = Langmuir constants related to measures of maximum adsorption capacity (mg/g) and adsorption affinity coefficient (L/mg)

Langmuir constants calculated from intercept and slope of the graph above

Adsorption capacity based on Langmuir model

Adsorbent	pН	Adsorption capacity (mg g ⁻¹)	Adsorbent	pН	Adsorption capacity (mg g ⁻¹)
Eichhormia crassipes Biomass	5.8	0.52	(Anacardium occidental) shell		
Carbon at 300 °C			carbon		
Biomass Carbon at 600 °C		1.54	Sugarcane bagasse carbon		
Moringa indica based activated	2.0	0.23	Phyllanthus embolic based	7.0	7.014
carbon			thermally activated carbon		
Used tea waste carbon			Pecan (carya illinoinensis)nut shell	7.0	1.61-2.51
Activated carbon derived from rice strand	2.0	15.90	carbon modified with egg shells calcium		
Pine wood biochar	2.0	7.66	Scandinavia spruce wood modified	6.9	7.92
Pine wood biochar	2.0	9.77	with aluminum and iron oxides		
Ammonium carbonate activated	7.05	22.33	carbonized at 500 °C		
carbon of Tamarindus indica fruit shell			Scandinavia spruce wood modified with aluminum and iron oxides	6.9	5.67
Zirconium(iv)-impregnated		2.23	carbonized at 650 °C		
groundnut (Anacardium			Scandinavia spruce wood modified	6.9	5.67
occidentale) shell carbon			with aluminum and iron oxides		
Cynodon dactylon-based activated	7.0	4.617	carbonized at 900 °C		
carbon			Activated bagasse carbon	6.0	1.15

Source: Mondal et al., Alexandria Engineering Journal (2015) 54, 1273–1284

Monolayer adsorption capacity (5.99 mg/g) is comparable with that of other

adsorbents and even greater than certain adsorbents reported earlier

Freundlich isotherm

Freundlich Isotherm Model



Sased on multilayer adsorption state and adsorption on heterogeneous surface

- Logarithmic form is expressed as: $\log q_e = \log K + \frac{1}{n} \log C_e$ K = Freundlich adsorption coefficient denoting the adsorption capacity n = Adsorption intensity
- \mathbf{K} and $\frac{1}{n}$ calculated from the linear correlations between the values of log q_e and log C_e

Freundlich isotherm

Table 1 : Calculated parameters of Langmuir and Freundlich Isotherms

Langmuir Isotherm			Freundlich Isotherm		
Monolayer adsorption capacity (Q _o ,mg/g)	Surface energy (b, L/mg)	Correlation coefficient (R ²)	Adsorption capacity (K)	(1/n)	Correlation coefficient (R ²⁾
5.99	0.283	0.990	1.46	0.44	0.991

✤ Values were calculated at an adsorbent dose of 4 g/L and neutral pH

- Data pertaining to adsorbent is statistically significant as evidenced by R² values close to unity
 -Indication of physicochemical adsorption process
- Calculated value of adsorption intensity (n) between 1 to 10
 Favorable conditions for adsorption due to increase in bond energies with increase in surface density

CONCLUSIONS

- * Banana Peel as an easily available agro-based adsorbent for treatment of fluoridated water
- Work optimally at pH 6 and 7, reducing the cost of post defluoridation pH adjustment
- ✤ Removal efficiency of 88 % for 5 mg/L F⁻ at optimum conditions
 - -Fluoride concentration of the treated water is below the regulated standard
- FTIR spectroscopy and scanning electron microscopy (SEM) techniques supported the results
- * Both Langmuir and Freundlich isotherm models fitted well to the experimental data
- * Adsorption process was favorable for all the tested adsorbent

THANK YOU !!!

