Biomass as a Sustainable Alternative for Defluoridation of Water: An Understanding on the Biosorption Mechanism

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Abstract **--Consumption of Water with excessive fluoride concentration above 1.5 mg/L can cause severe health issues including skeletal and dental fluorosis. In the present context, utilization of biosorbents from waste biomass would be sustainable and economic option for removal of fluoride ions from water compared to other alternatives. The present paper discusses the summary of various processes used biomasses for defluoridation of water. The theoretical and instrumental methods utilized by the researchers till date to understand the defluoridation mechanisms were also discussed in brief. Literature survey carried out suggested that theoretical models such as Freundlich and Langmuir isotherms, pseudo-first order and second order kinetic models, and different thermodynamic parameters were also used to explain the defluoridation process by biomasses. In addition to various theoretical models, advanced instrumentation facilities like FESEM, FTIR, EDX etc., have been also utilized to study the defluoridation mechanism by biomasses.**

Keywords: Defluoridation, Biomass, Biosorption, Mechanism, Instrumentation

I. INTRODUCTION

Water containing high fluoride is serious concern and is usually unusable for drinking and even cooking purpose to evade health tribulations. Removal of fluoride from contaminated drinking water is inevitable, to avoid ingestion of excess fluoride as an anticipatory measure, until alternative water sources with low fluoride content is available. The reported tolerance limit of fluoride concentration in drinking water is 1.5 mg/L (WHO, 1994). However, continuous consumption of high concentrations of fluorides in excess of 0.5-1.0 mg/L may also lead to accumulation in body tissues capable of causing dental and skeletal fluorosis. To surmount the negative health effects, numerous defluoridation techniques are being attempted around the globe. The most common being membrane separation, chemical coagulation, ion-exchange, contact precipitation and chemical additive methods. However, each of them have some limitations which in general make their use unsustainable under most given conditions, particularly in remote areas in developing countries. Among the defluoridation processes, the adsorption process is reported to be effectiveness of removing fluoride. Adsorption technique has been the most extensively applied method for defluoridation of water because of its low cost, the simplicity of design and ease of operation. Commercial activated carbon was commonly used as an adsorbent for removing fluoride from water. But, this is expensive and high-tech produced material. Therefore, excessive fluoride is removed from water using a cost effective and eco-friendly alternative.

Indian almond is a large deciduous tree, a hard endocarp enclosing edible seeds and whorled branches. Indian almond leaves contain many functional groups which exhibits affinity to Fluoride ion. These two materials were chosen as biosorbents as they are easily available, natural and low cost.

II. ADSORBENTS FOR FLOURIDE REMOVAL

The different types of biomass used for fluoride removal are seaweeds, algae, fungal mycelia, and lignocellulosic plants. Surfaces of biomasses contain amine, carboxyl, hydroxyl, sulfhydryl, and phosphate functional groups which help in the fluoride removal. The efficiency of any adsorbent is known to depend on their affinity toward fluoride ions and the capacity of the functional groups present within the adsorbent. In the following sections of this article, waste biomass-based fluoride removal processes are reviewed.

III. LIGNOCELLULOSIC PLANT MATTERS

Lignocellulosic plant matters have hemicelluloses, cellulose, and lignin. This biomaterial can adsorb fluoride from water if they have functional groups. They are inexpensive and easily available. In the following subsection, different treatment methods of lignocellulosic plant materials are discussed that are needed for improving the fluoride removal efficacy of lignocellulosic biomatters.

IV. TREATMENT OF ADSORBENTS

Lignocellulosic biomass are modified by physical and/or chemical treatments to exhibit higher fluoride removal and regeneration. Removal efficiencies depend on their particle size, surface area, and functionality on their surface.

Lignocellulosic biomasses can be converted to activated charcoal for enhancing specific surface area and pore characteristics so that more fluoride adsorption will take place. Surface area and functionality of lignocellulosic plant matters can also be improved by treating chemically. Chemical treatment includes acid and/or alkali treatment. During chemical treatment amorphous cellulose, hemicellulose and

lignin will be removed from the surface of biomass which will enhance the amount of pores on the biomatters surface. These pores will adsorb fluoride ions present in the water. Acid treatment is done for protonation, removal of metal traces and formation of COOH group. Alkali treatment is done for decomposition of surface walls, cellulose, lignin and formation of functional groups.

V. BATCHSTUDIES OF ADSORBENTS

Batch adsorption studies are conducted for determination of optimum conditions required for removal of fluoride from water. For determination of optimum pH for adsorption, water samples of 5g/L fluoride concentration was taken in five beakers with pH varying from 2-10, and was agitated for one hour at 50rpm with adsorbent dosage of 5g/l. On determination of optimum pH, for optimum adsorbent dosage determination, batch study is done at obtained optimum pH with varying adsorbent dosage from 5g/l-25g/L for a time period of one hour. For determination of optimum contact time, fluoride contaminated water sample are taken in five beakers at optimum pH, at best adsorbent dosage and is stirred at 50 rpm for time periods of 30 mins, 1 hour, 1.5 hrs, 2 hrs, 2.5 hrs etc. Similarly, test is done for determination of removal at different fluoride dosages. Amount of adsorbed fluoride was determined by the equation-

$$q=\frac{(C_0-C_e)V}{M_S} \quad (1)$$

Percentage removal of fluoride is given by-

$$R\% = \frac{(C_0-C_e)}{C_0} * 100 \quad (2)$$

Where C_0=initial concentration of fluoride, Ce=equilibrium concentration of fluoride, V=Volume of sample and MS= mass of adsorbent used.

A. *Equilibrium studies*

Equilibrium studies are useful for evaluating if the sorption processes is appropriate to termed as a unit operation. Langmuir and Freundlich models are the mostly used models for biosorption experimental data evaluation, probably due to the simplicity of these models.

Langmuir isotherm is valid for single layer adsorption. The general form of Langmuir isotherm as follows:

$$1/qe = (1/a) + (1/abCe) \quad (3)$$

where, '*a*' is number of moles of solute sorbed per unit mass of sorbent in forming a monolayer on the surface, b is a constant related to energy. A plot of *1/qe* against *1/Ce* gives a straight line, slope of which gives the value of *b* and the intercept gives the value of '*a*'. To predict whether the sorption process is favourableor unfavourable for the Langmuir type of sorption, the isotherm can be further tested by the values of 'RL', the dimensionless separation factor, given by;

$$RL = 1/ (1 + bCo) \quad (4)$$

For a favourable sorption process the value of *RL* lies in the range $0 < RL < 1$

Freundlich isotherm is applicable to physico-chemical adsorption on heterogeneous surfaces. Freundlich isotherm equation is given by:

$$\log qe = (1/n) \log Ce + \log Kf \quad (5)$$

where, *Ce* is the equilibrium sorbate concentration in the liquid phase and Kf and 1/n are Freundlich coefficients, which represent the sorption capacity and intensity of the sorption respectively. These coefficients can be obtained from the slope and intercept of Freundlich plots of '*log qe*' vs. '*log Ce*'.

Apart from these two isotherm models, many other isotherm Models are also there like Temkin, Elovich, Redlich, and Peterson isotherms

B. *Kinetic studies*

The data obtained from kinetic evaluation provide a detail description of the sorbate transport mechanisms within the adsorbent. The three main kinetic models are the pseudo first order, the second order and the intra-particle diffusion model. When adsorption is preceded by diffusion through a boundary, the sorption kinetics generally follows the pseudo first order rate equation given by Lagergren,

$$Log (qe - qt) = log\ qe - (k1/2.303) \times t \quad (6)$$

where, k1 is the first order rate coefficient, *qe* and *qt* are the amount sorbed per unit mass of the sorbent at equilibrium and at time '*t*' respectively.

The linear form of the second order kinetic equation is given by:

$$t/qt = 1/h + (1/qe) \times t \quad (7)$$

where, h is equal to k2qe2 and can be considered as the initial rate of interaction

The intraparticle diffusion rate constant (Ki) is given by the equation,

$$qt = Ki.t0.5 + C \quad (8)$$

where, C is a constant, given by the intercept of the Weber–Morris plots of '*qt*' vs. '*t0.5*'.

C. Thermodynamic studies

In addition to the isotherm and kinetic data, thermodynamic data are also essential to understand an adsorption process. The important thermodynamic parameters, namely, entropy change (ΔS), enthalpy change (ΔH) and Gibbs energy change (ΔG) for the sorption process can be calculated from the Van't Hoff equation, which is given by,

$$log (qe/Ce) = \Delta S/(2.303R) - \Delta H/2.303RT \quad (9)$$

ΔH and ΔS can be calculated from the van't Hoff plots of *log (qe/Ce)* vs. *1/T* and ΔG can be obtained by using the following relationship,

$$\Delta Go = \Delta Ho - T\Delta So \quad (10)$$

where, ΔGo, ΔHo and ΔSo are standard Gibbs energy change, standard enthalpy change and standard entropy change for the sorption process respectively.

VI.CONCLUSION AND FUTURE PERSPECTIVES

Extensive laboratory investigations were conducted to evaluate the adsorptive capability of low cost adsorbents prepared from biomass for adsorption of fluoride. Surface characterization and determination of surface ligands present helps identify processes involved in adsorption of flouride onto active sites. Further study of the same helps in in-depth understanding of complex redox reactions involved hence paving scope for future works.

REFERENCES

[1] Yangzhong Zhang(2019), "Grape pomace as a biosorbent for fluoride removal from groundwater". *RSC Advances Journal*, Volume 9, pp.7767-7776.

[2] Aju Mathew George, A.R. Tembhurkar (2018), "Analysis of equilibrium, kinetic, and thermodynamic parameters for biosorption of fluoride from water onto coconut (Cocos nucifera Linn) root developed adsorbent". *Chinese Journal of Chemical Engineering*, Volume 27, pp. 92-99.

[3] Nayan J. Khound, Ranjan Kr. Bharali (2018), "Biosorption of Fluoride from Aqueous Medium by Indian Sandalwood (*Santalum Album)* Leaf Powder". *Journal of Environmental Chemical Engineering*, Volume 6, Issue 2 pp.1726-1735.

[4] Shabnam Dan, Amit Chattree (2018), " Sorption of fluoride using chemically modified Moringa oleifera leaves".*Applied Water Science*, Volume 8, pp. 76- 84.

[5] N.B. Singh et.al (2018), "Water purification by using Adsorbents: A Review". *Journal of Environmental Chemical Engineering*, Volume 11, pp.187-240.

[6] PoonamTirkey, Tanushree Bhattacharya (2017), "Optimization of fluoride removal from aqueous solution using Jamun (*Syzygiumcumini*) leaf ash". *Process Safety and Environmental Protection*, Volume 115, pp.125-135.

[7] PranjalSaikiaet.al (2017), "Kinetic and thermodynamic studies for fluoride removal using a novel bio-adsorbent from possotia (Vitex negundo) leaf". *Journal of Analytical Science and Technology*, Volume 8, pp. 23-28.

[8] Jagvir Singh et.al (2016), "Fluoride ions vs removal technologies: A study". *Arabian Journal of Chemistry*, Volume 9, pp. 815-824.

[9] Ramya Araga, Shantanu Soni, Chandra S. Sharma(2017), "Fluoride Adsorption from Aqueous Solution using Activated Carbon Obtained from KOH-treated Jamun (Syzygiumcumini) Seed". *Journal of Environmental Chemical Engineering*, Volume 5, Issue 6 pp. 5608-5616.

[10] PoonamTirkey, TanushreeBhattacharya (2017), "Optimization of fluoride removal from aqueous solution using Jamun (*Syzygiumcumini*) leaf ash". *Process Safety and Environmental Protection*, Volume 115, pp.125-135.