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Fish scale waste: Potential low-cost adsorbent for fluoride removal

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Wastes generated at fish industry are considered as an important pollutant having a serious impact on the environment. Fish waste generally has high biological oxygen demand (BOD) and typically possesses strong offensive smell. Fish scales constitute major part of fishery waste and usually be disposed as a waste with no commercial value. The feasibility of using fish scale derived biochar is investigated as a low-cost adsorbent for defluoridation. A batch removal and kinetic study was performed to examine the efficiency of fluoride removal from simulated spiked water sample. Some influencing parameters such as adsorbent dose contact time, agitation speed etc. on the fluoride removal kinetics are also evaluated. Experimental outcome reveals that fish scale biochar (FSB) can successfully be used as an effective adsorbent in water environment for fluoride removal.

Keywords: Fishery waste, fish scales, adsorption, biochar, fluoride removal.

Introduction

Consumption of fish and shrimp worldwide is increased over the last decade. As an outcome of these activities a huge production of fish scale is salvaged globally. In India, this waste is discarded as garbage and indiscriminately disposed without recovery of any useful product¹. About 18–30 million tons of fish wastes is generated at fish processing industry of which 4% are fish scales². Depending on the fish species, the yield of scales from fish is around 4–10%³. In last few decades, variety of low-cost adsorbents were derived from different types of waste/by-products of agricultural, municipal and industrial sources which were reported as effective pollutant removal from water and wastewaters⁴. Many conventional methods like membrane filtration, precipitation, ion-exchange, electro-coagulation, reverse osmosis, nanofiltration and adsorption are widely used for defluoridation. These methods so far are either not sustainable or economical for various unfavorable factors.

In past few decades, many biosorbents from various trees and animal sources have been tried as defluoridation agents. leaf powder^{5–7}, activated rice husk^{8,9}, barks^{10,11}, tamarind seeds¹², seed extracts of *Moringa oleifera*¹³, tea ash^{14,15}, egg shell powder¹⁶, treated powdered corn cob¹⁷, chitin, chitosan¹⁸ are few among them. In recent times, adsorbent

produced from industrial waste have attracted many researchers for using as relatively less costly, renewable and abundantly available materials. Similarly, many studies have reported biochar as a universal sorbent for the removal of pollutants from soil and water environment. Biochar possesses relatively large specific surface area, high porosity and stable carbon matrix structure which make it a material of choice as an adsorbent¹⁹. A few studies have shown fish scales are used as effective biosorbent for removal of lead, chromium, arsenic and many such heavy metals. Table 1 shows recent studies made on fish scale as an adsorbent for removal of heavy metals from water environment.

This study is conducted to examine the use of Rohu Fish (*Labeo Rohita*) scales (FS) waste collected from fish market as a raw material to produce fish scale biochar (FSB) as a novel inexpensive adsorbent for defluoridation of drinking water and industrial wastewater. The primary emphasis of this present investigation was to reduce the high amount environmental burden related to fish waste disposal. This will also result in value addition of usages of waste materials. Few researchers have evaluated the potential of fish scale to remove heavy metals from water environment as listed in Table 1. The existing literature reveals that, no previous study has been done to explore the potential of fish scale biochar (FSB) for fluoride removal from water environment which

Table 1. Heavy metal removal efficiency of fish scales as reported in the literature

Metal	Heavy metal removal efficiency (%)	Ref.
As ^{III} and As ^V	94%	20
	99.83	21
Fe ^{III}	80.00	22
	90.00	23
	64.20	24
Cd ^{II}	98.00	22
	86.00	23
Zn	91.00	24
	84.00	23
Mn ^{II}	84.00	23
	60.89	24
Cr ^{VI}	60.12	25
	86.00	24
Pb	Almost 100	26

motivated the authors to undertake the present investigation.

Experimental

Materials and methods:

Analytical grade (AR) sodium fluoride (NaF, Merck, India) with a purity of 98% was used to prepare Fluoride Stock solution of 1000 mg/L. Labeo Rohita (Rohu) scales used were collected from the local fish market of Kolkata (India). The dust, dirt and soluble impurities from the surface of fish scales were removed by washing them thoroughly with tap water and distilled water. Then the scales were sun dried for 2 days and carbonized in muffle furnace at 600°C for 3 h. The resulting fish scale biochar was pulverized to biochar powder using a grinder. The grinded powder was sieved to obtain particle size of 125–250 µm and was used as adsorbent without any chemical modification. The schematic representation of used material is exhibited in Fig. 1 and Fig. 2.

**Fig. 1.** Fish Scales (FS).**Fig. 2.** Fish Scale Biochar (FSB).

Thermo Scientific Orion Fluoride Ion Selective Electrode (Orion Star™ A214 pH/ISE Bench top Meter) was employed for the determination of fluoride ions. EPA-approved ISE test procedures for fluoride in drinking water and waste water (ASTM D1179-B) and Standard Methods (4500-F-C) was used for measurement of fluoride. The ISE instrument was calibrated daily before measurement of fluoride from aqueous solution and operated as and as recommended by the manufacturers.

Batch adsorption studies:

All adsorption batch study experiments were performed in triplicate. The effect of influencing parameters i.e. adsorbent dose, pH, contact time, initial concentration and agitation speed on fluoride removal is evaluated through different sets of batch adsorption studies.

Data analysis:

The amount of fluoride ion adsorbed per unit fish scales biochar (FSB) was calculated using eq. (1):

$$q_e = \frac{(C_i - C_e) V}{m} \quad (1)$$

where q is the fluoride uptake capacity (mg/g), C_i is the initial fluoride ion concentrations in solution (mg/L), C_e is the final fluoride ion concentrations in solution (mg/L), V is the volume of solution (L), and m is the mass of fish scale biochar (g).

The sorption percentage (%) of fluoride was calculated using the following equation

$$\text{Sorption \%} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

where, C_i is the initial fluoride ion concentrations in solution (mg/L), C_e is the final fluoride ion concentrations in solution (mg/L).

Adsorption isotherm modelling:

The Langmuir and Freundlich isotherms models are expressed in linearized equation forms as eq. (3) and eq. (4) respectively.

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \tag{3}$$

where, q_e (mg/g) and C_e (mg/L) are the amount of fluoride adsorbed per unit mass of fish scale biochar (FSB) and equilibrium concentration of fluoride, respectively. q_{max} is the maximum amount of the fluoride ions per unit mass of FSB to form a complete monolayer on the surface bound at high C_e , K_L is a Langmuir constant expressing the affinity of the binding sites (L/mg).

The Freundlich isotherm model is expressed as:

$$\ln q_e = \ln K_f + \ln C_e \tag{4}$$

where, K_f ((mg g⁻¹)(L mg⁻¹)^{1/n}) is a parameter of relative adsorption capacity of the adsorbent and $1/n$ gives an indication of the favorability of adsorption. Values of $n > 1$ represent favorable adsorption condition²⁷.

In the present study only two-parameter isotherm equations are used for analyzing experimental equilibrium data. Linear form of two well-known isotherm models i.e. Langmuir and Freundlich are used to calculate isotherm constants.

Kinetic modelling:

The sorption kinetics provides insight into mechanism of adsorption reaction, pseudo-first order kinetic model and pseudo-second order were used in the present study. The pseudo-first order kinetic model assumes that at the specific time, solute sorption process is first order in nature and it is only dependent on number of fluoride ions present in the solution²⁸⁻³⁰.

Pseudo-first order kinetic model is expressed as:

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{5}$$

where, q_e and q_t are uptake capacity (mg/g) at equilibrium and at any time t , respectively. k_1 is first order kinetic rate constant (min⁻¹). Pseudo-second order kinetic model as-

sumes that the fluoride adsorption process is dependent on the number of fluoride ions present in the solution as well as available adsorption sites on the adsorbent surface^{27,31}. The pseudo-second order equation is expressed as

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_t} \tag{6}$$

where K_2 is rate constant, q_t is uptake capacity at any time t .

Results and discussion

Batch equilibrium adsorption experiments were conducted under differing operating conditions to evaluate the adsorption potential of fluoride on FSB. The effect of process parameter i.e. contact time, adsorbent dose, pH of solution and initial. Fluoride concentrations are further discussed in the following section.

Effect of contact time:

The Fig. 3 shows the effect of contact time on adsorption of fluoride onto FSB. The batch studies illustrate that, the adsorption dynamics is greatly influenced by contact time. As shown in Fig. 3 the adsorption rate of fluoride on FSB increases with time and eventually reaches to equilibrium after 180 min. At the start of FSB and F⁻ interaction initial more number of active sites are available favorably for adsorption but with progress of time active adsorption sites was decreased and hence after equilibrium time no significant increase in removal of fluoride is observed. Similar trend of adsorptive removal were observed by Rout *et al.*³² and Marrakchi *et al.*³³.

Effect of adsorbent dose:

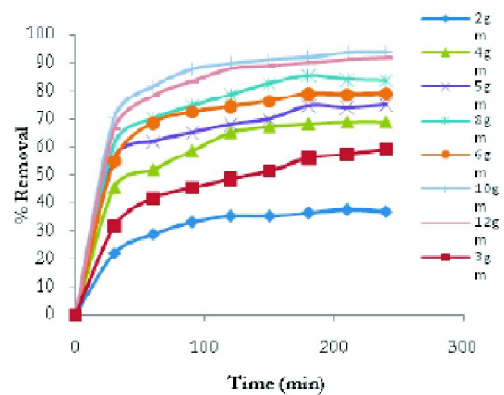


Fig. 3. Effect of contact time.

Fig. 4 shows the effect of adsorbent dose on the fluoride removal on FSB. The adsorbent doses were varied in the range of 2 to 12 g/L. It is observed that the percentage fluoride removal increased with increase in adsorbent dose. The maximum of removal was 97.41% at 10 g/L. At higher concentration of the sorbent amount percentage removal is increased as exchangeable sites present are more and remained constant as it reached towards equilibrium as reported in literature^{24,34}.

The effect of initial pH:

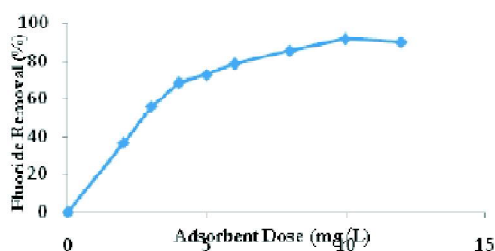


Fig. 4. Effect of adsorbent dose.

The pH of the solution is one of the major influencing process parameter in adsorptions as discussed in some literatures³⁴. The effect of pH on fluoride removal from water by FSB is plotted in Fig. 5. The effects of initial pH on adsorption capacity of FSB was observed for pH range of 2.0–12.0 with 10 g/L of adsorbent dose at initial fluoride concentration at 5 mg/L for a contact time of 180 min. The 0.5 N HCl/0.1 N NaOH was used to maintain desired value of pH within ± 0.2 . The adsorption percentages decreased approximately from 92 to 80% with increasing initial pH from 5.0 to 12.0. The anions are better absorbed at a low pH in presence of H^+ . At a high pH, because of competition with OH^- the fluoride surface by FSB found to be decreased due to

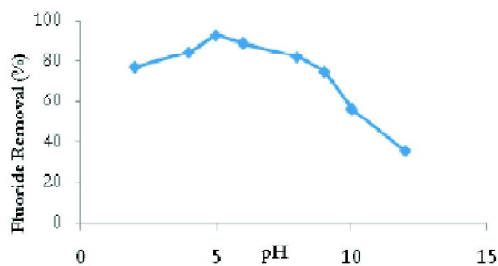


Fig. 5. Effect of initial pH.

electrostatic repulsion. A similar observation was recorded by Nabilah Zayadi *et al.*²⁴.

Effect of initial concentration of fluoride:

The Fig. 6 shows the effect of initial fluoride ion concentration on its removal efficiency by FSB. The fluoride ion concentration was varied in the range of 2–14 mg/L with 10 g/L adsorbent dose and contact time of 180 min it was observed that as fluoride concentration increases, the percentage removal of fluoride increased too. This is due to higher ratio of surface active sites to fluoride ions at lower concentrations^{26,34}.

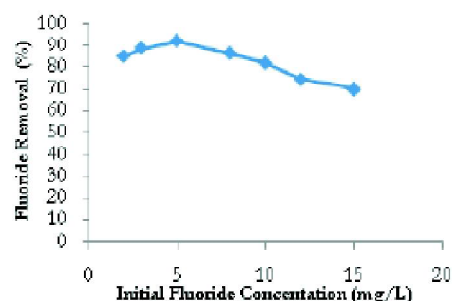


Fig. 6. Effect of initial concentration of fluoride.

Effect of agitation speed:

The Fig. 7 shows the effect of agitation speed on removal efficiency of fluoride removal by FSB. The effect of agitation was observed by varying stirring speeds from 60 to 180 rpm with optimum adsorbent dose of 10.0 g/L, pH of 5 with, contact time of 180 min and initial concentration of 5 mg/L. Maximum removal achieved was about 91.67% above boundary

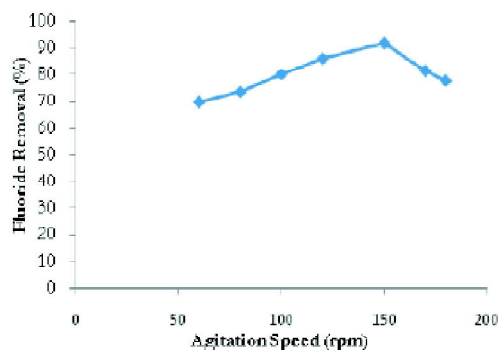


Fig. 7. Effect of agitation speed.

conditions with initial F^- concentration of 5 mg/L at 150 rpm. It was observed that at a given time, fluoride removal increases with the increase in the speed of agitation. This is because; at higher agitation speed adsorbate can make proper contact with adsorbent surface³⁵⁻³⁷.

Adsorption isotherm:

Analysis of adsorption data is needed for developing equilibrium and evaluating the kinetic parameters. The data obtained from equilibrium modeling is basically used to explain the interaction of fluoride ions with the fish scale biochar which can further be used in optimizing the design parameters.

Fig. 8 shows the linearized Langmuir isotherm plot of specific adsorption (C_e/q_e) against the equilibrium concentration (C_e). The slope and intercept have been used to calculate the q_{max} and K_L respectively. The high correlation coefficient (R^2) ≥ 0.98 shows that adsorption of fluoride by FSB follows the Langmuir isotherm model of monolayer adsorption^{38,39}.

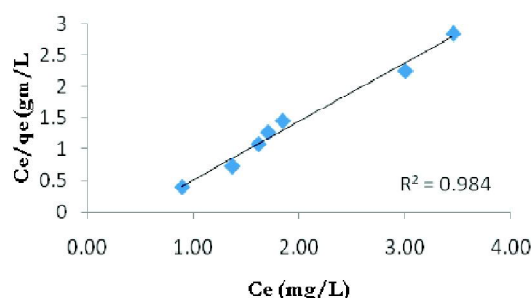


Fig. 8. Langmuir isotherm plot.

Similarly, Fig. 9 shows the linearized Freundlich isotherm plot of $\log q_e$ against $\log C_e$ which gives a straight line, and the slope and intercept correspond to $1/n$ and $\log K_F$, respectively. The constant parameters of the isotherm equations and the correlation coefficient (R^2) are summarized in Table 2.

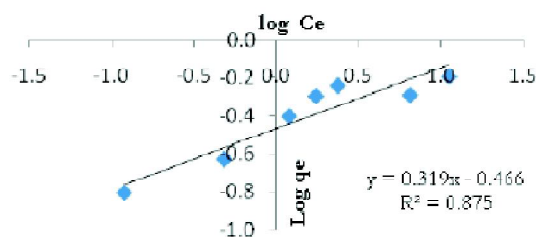


Fig. 9. Freundlich isotherm plot.

Table 2. Adsorption isotherm constants on fluoride removal by fish scale biochar (FSB)

Langmuir isotherm		Freundlich isotherm	
q_{max} (mg/g)	2.16	K_F	2.92
K_L (L/mg)	0.437	$1/n$	0.319
R_L	0.320	n	3.135
R^2	0.984	R^2	0.875

Kinetic order studies:

The pseudo-first order kinetic model and pseudo-second order were applied to the batch experimental data. The correlation results for adsorption of fluoride by FSB are summarized in Table 3. The values of R^2 and closeness of experimental and theoretical adsorption capacity (q_e) shows that the first order model is well fitted and more applicable to explain and interpret the experimental data. The R^2 value for pseudo-first order kinetic model was found to be higher (≥ 0.95) and also the calculated adsorption capacity (q_e) of FSB is found to be closer to the experimental adsorption capacity.

Table 3. Kinetic parameter for adsorption of fluoride on FSB

Pseudo-first order		Pseudo-second order	
Experimental q_e (mg/g)	2.91	Experimental q_e (mg/g)	2.91
Calculated q_e (mg/g)	3.21	Calculated q_e (mg/g)	1.961
K_1 (1/min)	0.021	K_2 (g/mg min)	0.0041
R^2	0.954	R^2	0.771

Conclusions

The fish scale biochar (FSB) used in the present study showed a cheaper and non-conventional adsorbent for fluoride removal from water environment. Fluoride adsorption capacity is dependent on the pH, initial concentration and agitation time. Compared with Freundlich isotherm, Langmuir isotherm model is found to be more suitable to describe removal of fluoride by FSB. The adsorption capacity of Fluoride onto fish scale biochar is found to be not very high but be improved through surface modification. Transforming the fish scale waste into a biochar as an adsorbent would be a promising approach to come up with innovative way for reducing the burden of environmental pollution. However, des-

orption kinetics and regeneration aspects of using the noble material to be explored as future investigation work along with characterization of FSB to explain the research in more convincing and scientific way.

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