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Defluoridation of Groundwater Using Formaldehyde-Treated Agricultural Waste - Wheat, Oats, And Pea Straw

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Abstract
The present study investigates the potential of acid-treated agricultural waste (Wheat, Oat, and Pea straw) for the defluoridation of groundwater following the chemical treatment using formaldehyde in 1:5 w/v ratio at 50°C. The effects of operational parameters (pH, dose, time, and initial fluoride concentration) were investigated in the batch mode. Response surface methodology (RSM) was employed to predicted and validated the experimental findings. The efficiency of developed adsorbents was compared with commercially available activated carbon (CAC) and found suitable for working at neutral pH conditions. The better applicability of Langmuir isotherm on adsorption data reflects monolayer adsorption over the homogeneous surface of adsorbents. Further, the experimental data can better be modeled by the pseudo-second-order kinetics ($R^2 = 0.996$). The simple synthesis technique and massive raw material availability made these adsorbents a promising and cost-effective tecnhiqe for removing the fluoride from groundwater.

Keywords: Fluoride; Agricultural waste; Adsorption, Kinetics, Isotherms, RSM

Introduction

Fluoride ions in the groundwater were wholly dissociated from the parent rocks, occurring either naturally or in the form of added salts [1]. The gound and surface water bodies were highly susceptible to fluoride contamination (Ramanaiah et al., 2006; Abugri and Ba, 2011). Approx. two hundred million peoples in the world are at risk of fluorosis [2, 3]. Fluoride is essential for the human body; however, the high exposure results in structural defects in teeth, bones, and skeleton and may also damage the tissue and cells of the human [4]. In addition, the excess levels of fluoride in surface water may possess toxic effects on aquatic species [4]. The sporadic incidence of high fluoride contents was reported in the drinking water of countries like India, China, Sri Lanka, West Indies, Spain, Holland, Italy, Mexico, and North and South American (Suttie, 1969; Mella et al., 1994; Grimaldo et al., 1995; Li et al., 1995). According to a report of World Bank, 2012, nearly 85% of the Indian population relies on groundwater for drinking purposes. Hence it becomes a crucial concern to be tackled separately. The prevalence of fluorosis is one of the major issues with the groundwater of India, especially in the states of Rajasthan, Gujarat, Haryana, and Andhra Pradesh [3, 5]. Besides these stats, more than 30 mg/L concentration level of fluoride was monitored in the groundwater of Agra city, Uttar Pradesh (UP) [6]. Thus, the defluoridation of groundwater is the need for time to ensure public safety. Various methods such as ion exchange, precipitation, electrodialysis, and Donnan dialysis were already investigated for the removal of fluoride from groundwater. Still, due to their high cost and practical in-feasibility, they did not find their application to the water industry [7,8,9]. Among these techniques, the adsorption process could prove to be the most widely used method for removing fluoride from water [10]. A wide array of adsorbents were already developed by the various researchers for the defluoridation of groundwater like activated charcoal, Mn-Ce oxide, rice husk, leaf biomass, algal biomass, biochar, etc. [11-14]. However, the applicability of these adsorbents was restricted to the ground, especially in rural villages, due to their efficiency on alkaline pH and need for a higher dose [4, 6]. The growing evidence suggested that agricultural waste is not put to any use, and it contains plenty of carbon which can serve as a cheap and effective sorbent for adsorption [15]. In addition, the presence of various chemical functional groups (hydroxyl, carbonyl, carboxyl, sulfhydryl, sulfonate, amino amide, imidazole, phosphonate, and phosphodiester) over the surface of adsorbent based on agricultural waste provide support to the biosorption [16, 17].

Hence the present study was undertaken to develop the low-cost adsorbent using agricultural waste viz. Wheat straw raw (WSR), Oats straw raw (OSR), and Pea straw raw (PSR). The literature review confirmed that no adsorbent was developed using these agricultural waste for the removal of fluoride except WSR. The efficiency of developed adsorbents was tested in groundwater with particular reference to the rural areas of Agri City, UP. Moreover, the study also focused on the development RSM model for predicting fluoride, especially for rural areas.

Materials and Methods
Synthesis of adsorbent
The raw straws of all the agricultural waste (WSR, OSR, and PSR) were collected from the local mills and dried into the sunlight. The dried samples were powdered and impregnated with one percent formaldehyde (1:5) ratio w/v at 50°C for 4 hours. The chemical activation of formaldehyde results in the removal of water-soluble substances and colors that adhere to the adsorbate surface. After the chemical activation, the obtained powder material was washed with double distilled water several times. Further, it was dried in an oven at 80°C for 24 h and stored in a moisture-free container for further use.

Batch Adsorption Study
All the batch adsorption studies were performed using synthetic water. Initially, the 100 ppm of stock fluoride solution was prepared by adding 221 mg of sodium fluoride salt in 1 liter of deionized water. Further, the adsorption study was carried out with 100 ml of synthetic water having a concentration of 5 ppm. The pH of the solution was adjusted using 0.1 M HCl/NaOH. The batch experiment was conducted in various doses and times with 150 rpm speed at room temperature using a digital magnetic stirrer (Negation, HP 550, India). The sample was then filtered by Whatman filter paper (No.42) for further analysis. The fluoride concentration was examined by SPADNS method (Standard Methods of Examination of Water and Wastewater [18].

Adsorption isotherms
In adsorption, isotherms models are invaluable tools to describe how the adsorbent interacts with adsorbate and evaluate the performance of the adsorption process. Although several isotherms models have been reported in the literature, only three (Langmuir, Freundlich, and Temkin isotherm models) are analyzed in the present study. The Langmuir isotherm is applicable to describe monolayer adsorption on the homogenous surface without any interaction between adsorbed ions. The Langmuir isotherm model is commonly represented as (Worku et al., 2007; Arami et al., 2007)

$$\frac{qe}{qm} = \frac{bCe}{1+bCe}$$

and can be rewritten in linear form by following equation:

$$\frac{1}{qe} = \frac{1}{qm} + \frac{1}{qmbCe}$$

Where Ce is the equilibrium concentration of the adsorbate (mg/L), qe is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), b is the Langmuir constant (L/mg), and qm is the maximum adsorption capacity (mg/g).

The dimensionless separation factor (R_L) can be used to express the favorable nature of adsorption, is calculated by using the Langmuir parameter by following equation:

$$R_L = \frac{1}{1+bCo}$$

If value of R_L > 1 adsorption is unfavorable, R_L = 0 adsorption is irreversible; $0 < R_L < 1$, adsorption is favorable, and if R_L = 1 adsorption is linear.

The Freundlich isotherm model assumes the physical adsorption on both homogeneous and heterogeneous surfaces and also describes the exponential distribution of active site, commonly represented by the following equation [19].

$$q_e = KC_e^{1/n}$$

Linear equation of Freundlich isotherm can be represented as:

$$\log qe = \log K + \left(\frac{1}{n}\log Ce\right)$$

Where K is the Freundlich constant ($mg1^{-(1/n)} L^{1/ng-1}$), and 1/n adsorption intensity, which values less than unity, specifies favorability of adsorption.

Temkin isotherm is applicable for the chemisorptions on the heterogeneous solid adsorbent. It also assumes that the heat of adsorption decreases linearly with the coverage of the adsorbent surface due to adsorbate–adsorbent interactions. It is given by the following equation:

$$qe = \frac{RT}{bT} \ln KTce$$

A linear form of the Temkin equation can be written as:

$$qe = \frac{RT}{bT} \ln KT + \left(\frac{RT}{bT}\right) \ln Ce$$

Where R is the universal gas constant (8.314 J/mol/K), T is the temperature at 298K, KT (L/g) andbT (kJ/mol) are Temkin equilibrium binding constants related to maximum binding energy and heat of adsorption, respectively.

Adsorption Kinetics
Application of adsorption kinetics models is vital in the determination of rate-controlling step and explication of adsorption mechanism. Experimental data obtained from the batch study were tested by using three kinetics models, including the pseudo-first-order, pseudo-second-order, and intra-particle diffusion model.

Lagergren gives the pseudo-first-order equation is generally expressed by the following equation (linearised form).

$$\ln(qe - qt) = \ln qe - k_1 t$$

Where qe and qt (mg/g) are adsorption capacity at equilibrium and time t (min), respectively, k1 (min⁻¹) is pseudo-first-order adsorption rate constant.

The linear form of the pseudo-second-order equation is expressed

as:

$$\frac{t}{qt} = \left[\frac{1}{k_2 qe^2}\right] + \frac{t}{qe}$$

Where k_2 (g/mg/min) is adsorption rate constant.

Intra-particle diffusion model given by Weber and Morris can be expressed as:

$$qt = K_{id}t^{\frac{1}{2}} + Ci$$

Where, k_{id} (mg/g/min$^{0.5}$) intra-particle rate constant, and C_i is the intercept.

Results and Discussion
Effect of Operational Parameters
The effects of pH (4-10) on percentage fluoride removal using WSR, OSR, PSR, and CAC are shown in Fig.1a. No significant impact of pH was observed in the removal efficiencies of WSR, OSR, PSR. However, CAC showed the highest adsorption of fluoride in acidic pH (4) conditions. The performance of WSR (46%), OSR (43%), and PSR (31%) were observed well in neutral pH (7) because of protonation and deprotonation of functional group adsorbents [15]. The pH of the solution also affects the ionic form of fluoride and the electrical charge of adsorbent over the surface [17]. The phenomenon of the present study good supported by the findings of [20-22].

The effect of adsorbent dose on percentage removal of fluoride was investigated by varying the dose from 1 to 10 gm/L at neutral pH conditions (Fig.1b). The percentage removal efficiency was observed to be increased with increasing the adsorbent dose, but after a dose of 6gm/L, it remained almost constant. This occurred phenomenon was most likely because of high adsorbent dose expected to owe greater availability of surface area support the high adsorption [23]. Based on the result of Fig. 1b, an optimum dose of 6 gm/L was chosen.

The study of contact time is vital in determining the equilibrium era required for maximum fluoride adsorption. Fig. 1c illustrated that fluoride uptake was rapid initially for the first 30 min, and after that, the rate of adsorption increases gradually with the time until it attained the equilibrium at 70 min. Further, no significant improvement in fluoride removal was noticed beyond this time. All through the adsorption process, initially, more active sites were available on the exterior surface of the adsorbent, which enhances the rate of fluoride uptake. Later the time it attains a level saturation due to the gradual occupancy of these sites. The present result is well in line with the study of [24, 12].
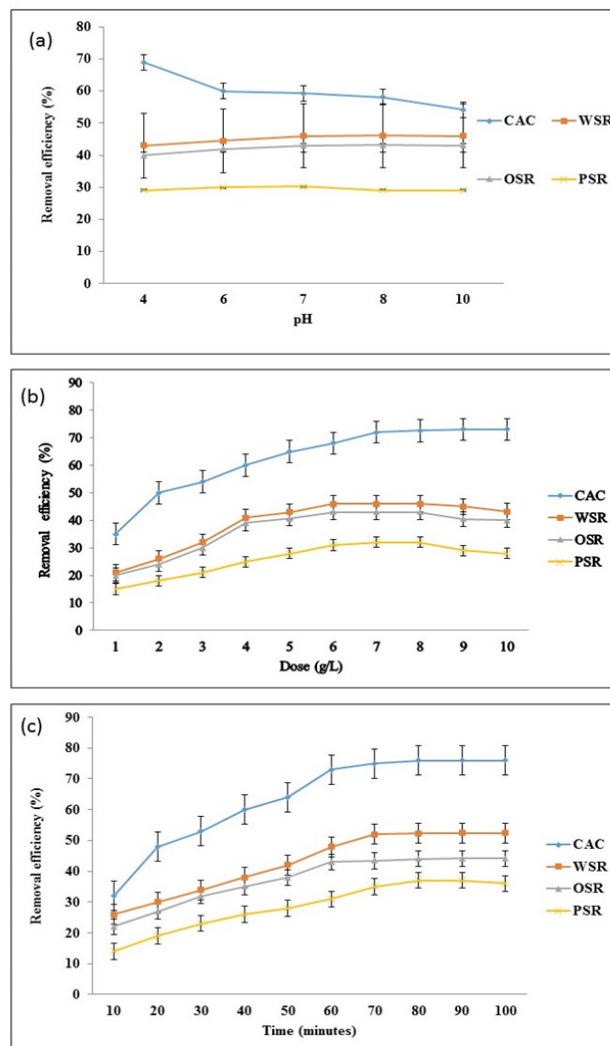
Figure 1: Effect of operational parameters (a) pH (b) Time and (c) Dose

Adsorption isotherms
The adsorption isotherms describe how the adsorbate interacts with an adsorbent in an equilibrium state and is vital for the design and optimizing the efficiency of the adsorption column. The isotherm study revealed better compliance of Langmuir than other isotherms and reflect monolayer adsorption having the homogenous distribution of active adsorption sites on the surface of the adsorbent (Fig. 2a-d - 4a-d). The obtained maximum adsorption capacity (qm) was 0.13, 0.07, 0.06, and 0.06 mg/g for CAC, WSR,

OSR, and PSR, respectively. The computed value of RL lying between unity and zero indicated that the adsorption of fluoride is favorable (Table 1). The high correlation observed in the Freundlich model plot described the heterogeneous characteristics of surface and an exponential distribution of active sites; and assumed that it initially attains complete monolayer coverage and then multilayer adsorption begins. The value of n is between 2 to 10, concluding that adsorption is also favorable and hence Freundlich isotherms also equally describe the adsorption process (Table 1). The adsorption through chemisorptions is ruled out as the qe versus ln Ce plot did not show good linearity (Fig. 4) signify non-compliance of Temkin isotherm. Analysis of isotherm had a clear indication of monolayer adsorption of NOM followed by multilayer physical adsorption.
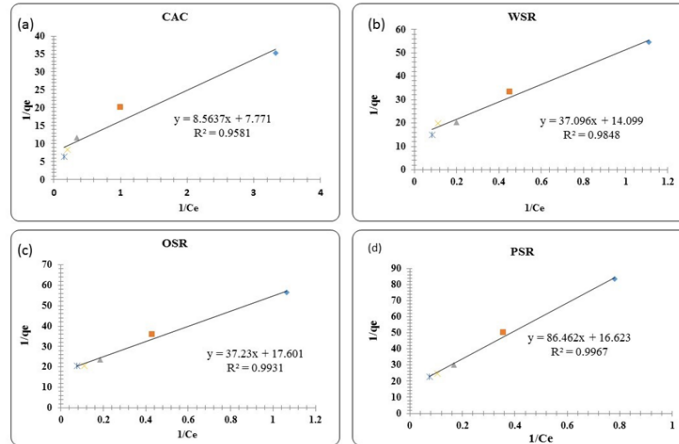

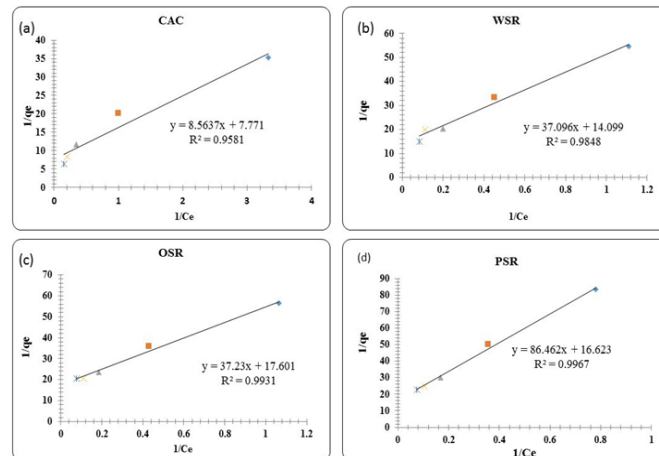**Figure 2:** Langmuir isotherm for fluoride adsorption (a) CAC (b) WSR (c) OSR (d) PSR

Figure 3: Freundlich isotherm for fluoride adsorption on (a) CAC, (b) WSR, (c) OSR and (d) PSR
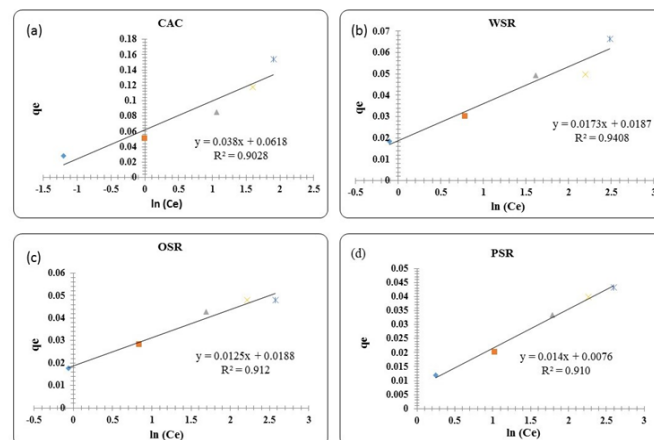

Figure 4: Temkin isotherm for fluoride adsorption for (a) CAC (b) WSR (c) OSR and (d) PSR

Table 1: Isotherm parameter

| Adsorbent	Langmuir				Freundlich			Temkin		
	B	qm	RL	R2	Kf	n	R2	AT	bT	R2
CAC	0.90	0.13	0.18	0.958	0.052	1.876	0.992	4.98	65855	0.902
WSR	0.38	0.07	0.34	0.984	0.02	2.118	0.964	2.88	147206	0.94
OSR	0.473	0.06	0.29	0.993	0.019	2.518	0.955	4.48	208542	0.912
PSR	0.192	0.06	0.50	0.996	0.01	1.87	0.981	1.648	178751	0.910

Adsorption kinetics

The adsorption kinetics of fluoride on CAC, WSR, OSR, and PSR were tested using the pseudo-first-order, pseudo-second-order, and intra-particle diffusion models (Fig. 5a-c). The summary of kinetics parameters and rate constant were illustrated in Table.2. The Lagergren plot of pseudo-first-order and Weber and Morris's intra-particle diffusion showed poor correlation and linearity with the experimental data. Also, there is no good agreement establish between experimental (qe) and calculated value (qecal), indicating that the adsorption of fluoride did not follow first-order kinetics. The plot for pseudo-second-order yield showed a better correlation (R2 = 0.996) than the other two applied kinetics models. Moreover, the calculated value of qe is also very close to the experiment value suggesting better applicability of pseudo-second-order to the adsorption of fluoride on CAC, WSR, OSR, and PSR. A similar type of adsorption kinetics is generally observed for fluoride adsorption, as reported by other researchers [25, 26].

Table 2: Summary of kinetics parameters and rate constant

Adsorbents	Pseudo first order			Pseudo-second order			Intra particular diffusion	
	K1(min-1)	qecal (mg gm-1)	R2	K2(gm mg-1 min-1)	qecal (mg gm-1)	R2	Kp(mg gm-1 min-0.5)	R2
CAC	0.055	0.118	0.933	0.740	0.070	0.996	0.005	0.932
WSR	0.027	0.035	0.910	0.704	0.058	0.972	0.003	0.958
OSR	0.032	0.033	0.927	0.990	0.048	0.985	0.003	0.952
PSR	0.041	0.040	0.879	0.821	0.039	0.980	0.002	0.975
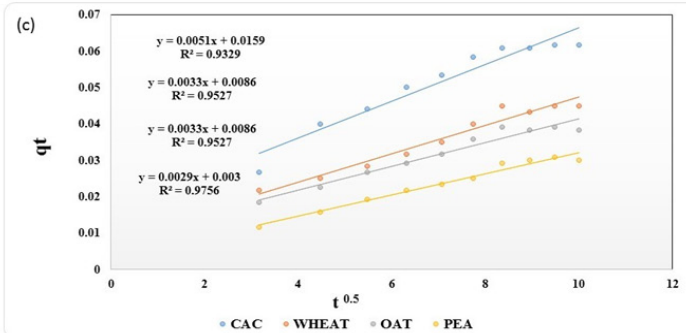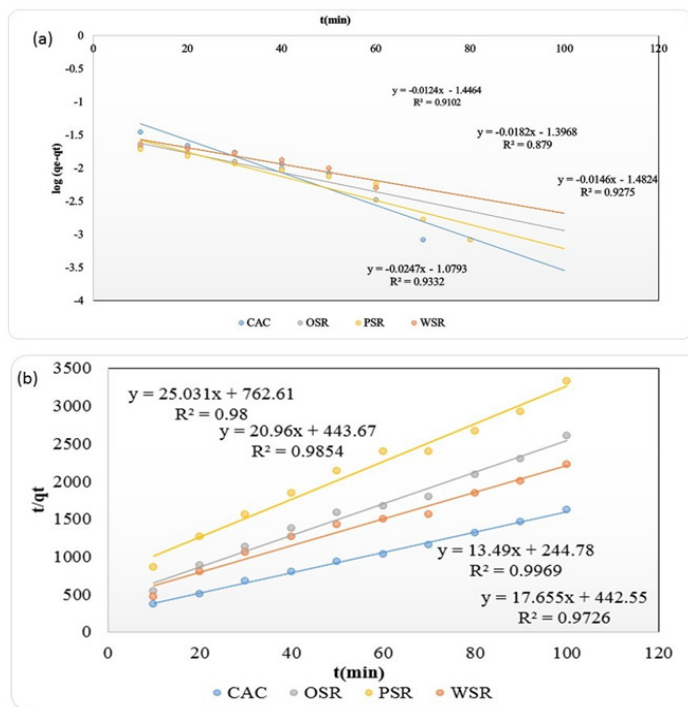
Figure 5: Kinetics plot (a) pseudo-first-order (b) pseudo-second-order and (c) intra-particular diffusion model

RSM for The Prediction of Percentage Fluoride Adsorption

RSM was applied using Design Expert 7.0.0 as a part for the prediction of percentage fluoride adsorption. The Central composite design (CCD) of this model was implemented to analyze the data, which led to the development of mathematical equations in terms of coded factors (Eq. 11). Accordingly, the predicted response (% fluoride removal) was calculated as :

% Fluoride removal = -2.49683 + 8.81746*A + 0.69048*B + 0.69048*D - 0.15873*A*B -0.012698*B*D - 0.48485*(A2)- 1.2682 - 003*(D2).   (11)

Where A, B, and D represent input variables like adsorbent dosage, initial fluoride concentration, and contact time, respectively. The data of analysis of variance (ANOVA) indicated that the equation adequately represented the relationship between significant variables and response factors (Table.3). The value of F also implied that the model is significant, and there is only 0.01% chance that the model F-value deviates from the experimental values. In addition, the closeness between R2 (0.9396) and R2adj.(0.9294) confirmed the better applicability of the RSM model.

Table 3: ANOVA results of the quadratic model for % Desorption

Response	Source	Sum of Squares	DF	Mean square	F-Value	P-Value Prob>F	Remarks
% fluoride adsorption	Model	2424.97	7	346.42	46.64	<0.0001	Significant
	Residual	155.99	21	7.43			
	Lack of Fit	143.99	17	8.47	2.82	0.1625	Not significant
	Pure Error	12.00	4	3.00			
	Cor Total	2580.97	28				
R^2 = 0.9396	R2Adj. = 0.9294	R2Pred. = 0.8935		SD = 2.73		Adequate Precision = 24.55	
R^2: correlation coefficient; R^2_{adj}: adjusted R2; R^2_{Pred}: predicted R^2; SD: standard deviation.							

Conclusion

In the present study, agricultural waste was used for the development of low-cost adsorbents. The experimental results showed that the WSR (46%), OSR (43%), and PSR (31%) have promising potential for the removal of fluoride from groundwater even at neutral pH (7) conditions. However, CAC resulted in the highest fluoride adsorption (73%) under acidic pH (4) conditions, which may not be acceptable for drinking water treatment. The adsorption data followed the Langmuir isotherm demonstrated monolayer adsorption, and can be better modeled by the pseudo-second-order kinetics (R2 = 0.996). The applied RSM model was accurately predicted the percentage of fluoride removal with a very close value between R2 (0.9396) and R2adj.(0.9294) [27].

Data Availability

Data collected and analyzed in this study are available from the corresponding author upon request.

Authors' Contributions

Shahjad Ali1 (First and Corresponding Author): Investigation and Writing - original manuscript. Jaydev Kumar Mahato: Modeling and data analysis,
Sunil Kumar Gupta: Conceptualization and Supervision.
Alok Sinha - Conceived and designed the analysis
Raisul Islam - Performed the analysis

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