ADSORPTIVE REMOVAL OF FLUORIDE UPDATE FROM AQUEOUS MEDIA BY USING THERMALLY TREATED MARBLE POWDER

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ABSTRACT

The impacts on the mechanistic feature of marble powder in fluoride extraction were explored by various operating factors. Operating conditions like Initial solute concentration, adsorbent doses and pH of the solution determine the extent of fluoride removal. A model equation from which a percentage removal according to each fluoride removal is determined for a fixed set of experimental conditions. For the maximum fluoride absorption, the contact time, pH & dose respectively were 97.1, 3 hr,7 and 3g respectively at initial concentration 10ppm. Kinetics study showed that marble powder absorbent follows Pseudo second order (R2=0.9701). Itshows good result with intra-particle diffusion (R2=0.6614) kinetics. Marble powder is absorption uses Freundlich isotherm (R2=0.9253) with pH 7 at temp. 305 K and Langmuir, Freundlich, DR-isotherm fits well with R2=0.981, R2=0.9253 and R2=0.9156 respectively. The Freundlich, Langmuir, DR-isotherm are traced for the marble powder. However, the Esvalue of the D-R isotherm 3.535 kJ/mol (mean energy adsorption or bonding energy) is still good fit, indicating physical adsorption.

KEYWORDS: Adsorption, Fluoride Removal, Groundwater, Thermally Marble Powder, Pseudo Second Order

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1. INTRODUCTION

Fluoride contamination in groundwater poses severe health risks, including dental and skeletal fluorosis. According to the World Health Organization (WHO) 1984 and Indian standard drinking water specification 1991, the maximum permissible limit of fluoride in drinking water is 1.5 mg/L [1]. In many regions, especially in developing countries like India, groundwater is the primary source of drinking water, and elevated fluoride levels significantly impact the public health [2]. This study aims to evaluate the effectiveness of Marble powder in removing fluoride from groundwater through adsorption processes.

Numerous studies have investigated various methods for fluoride removal, including electro-coagulation, reverse osmosis, and adsorption using various materials such as activated alumina, bone char, activated carbon and natural clays[3]. Adsorption is preferred due to its simplicity, cost-effectiveness, and removal efficiency. Recent research has shown that geo-materials like laterite and modified clays are effective in fluoride removal due to their high surface area and ion exchange properties [4]. This study builds on this knowledge by examining the use of Marble powder, which is abundant and cost effective which is a better approach for sustainable development [5].

The aim of1the study was1to evaluate the feasibility of adsorption to remove fluoride from groundwater by analyzing effect of parameters such as Contacttime, pH, adsorbent doses and initial fluoride Concentration by locally available, cost effective adsorbent like marble powder.

2. Materials

2.1 Chemicals

Chemical used sodium hydroxide, sodium fluoride, nitric acid. The entire chemicals are analytic grade.

2.2 Water

Distilled water was used for washing of bio agriculture waste which is preparation of adsorbent. And milli-Q water was used preparation of stock solution which is used by ion selective electrode.

2.2 Equipment

Various type of equipment which are listed below were used for determining different parameter and carrying out various test are Whatman No-42 filter paper, Thermo scientific ion selective fluoride electrode, Incubator shaker, Muffle furnace, pH meter, Electric Oven, weighing machine, IS 75-micron sieve and Conical flask

Research Paper

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3. METHODOLOGY

3.1 Preparation of Adsorbent

Marble powder was obtained locally from the Bihar region of India. Initially, the marble pieces were thoroughly washed multiple times with water to remove unwanted dust and solid particles. After cleaning, the pieces were oven-dried at a temperature of 372 K to eliminate any moisture content. Once dried, the marble pieces were crushed using an impact loading machine. The resulting material was then sieved through an IS 75 µm sieve. Particles larger than 75 µm were repeatedly crushed and sieved to ensure the majority of the sample met the desired particle size. Finally, the processed marble powderas placed in an oven and heated at 878 K for 3.5 hours to complete the preparation process.

Fig. 1: Marble Powder Adsorbent

3.2 Preparation of Fluoride Stock Solution

A stock solution containing 1000 ppm of fluoride was prepared by dissolving 2.21 grams of sodium fluoride (NaF) in one liter of distilled water. To obtain a 10 ppm fluoride solution, 10 milliliters of the 1000 ppm stock solution were measured and diluted with distilled water to make up a total volume of 1000 milliliters.

3.3 Batch Adsorption Experiment

Adsorption studies using treated marble waste powder were carried out through batch experiments to evaluate its de-fluoridation capacity. The experiments examined the effects of various parameters, including adsorbent dosage, contact time, initial fluoride concentration, pH, and the presence of other ions. All batch experiments were performed in 250 ml conical flasks containing 100 ml of solution. A known amount of the sorbent was added to the fluoride-containing water, and the flasks were placed on an incubator shaker at a temperature of 303 K for a specified duration. After equilibrium was reached, the solutions were filtered using Whatman filter paper No. 42, and the residual fluoride concentration was determined using a selective ion electrode method. To eliminate interference from polyvalent cations that could form complexes with fluoride ions and affect measurement accuracy, TISAB-II (Total Ionic Strength Adjustment Buffer) was added to the filtrate. Determined marble waste adsorption capacity(q_e) and % removal using Eq^n 1 &2.

$q_e = (c_i - c_e)v/w$……….(1)   % fluoride Removal $= \left(\frac{(c_i - c_e)}{c_i}\right) * 100$……….(2)

3.4 ADSORBENTION IOSTHERM MODEL

Different adsorption isotherms link the amount of solvents adsorbed by adsorbent unit weight with the amount of solvents at equilibrium. This prediction for the adsorbent's capacity to develop a Sorption scheme is one of the main parameters. The current research described the equilibrium results using Langmuir, Freundlich and Dubinin-Radushkevich isothermic designs.

In calculation of the Langmuir adsorption isothermal model the Langmuir constant (K_a) and maximum Q_m (mg/g) monolayer adsorption capacities were used in connection with the affinity of the binding sites (L /mg).Experimental data show that the Langmuir model was not acceptable with regard to fluoride adsorption in TTA dust, showing the bad regression coefficient (R^2= 0.981).It indicated that monolayer adsorption in this system may take place; instead the adsorbate diffusion in several layers of the adsorbent may take place.

$$\frac{C_e}{q_e} = \frac{1}{k_a Q_m} + \frac{C_e}{Q_m} \quad \text{……………..(Eq}^n\text{. 3)}$$

Where, C_e is the equilibrium concentration (mg/L), q_e is the amount of solute adsorbed per unit of adsorbent at equilibrium (mg/g). Q_m and K_a are the monolayer adsorption capacity(mg/g) and energy of adsorption respectively.The Q_m and K_a constant of Langmuir can be determined by the C_e/ $q_e$compared with the Ce linear plot.

Freundlich isothermal system shows that a heterogeneous interface adsorption mechanism can be described in Eq^n (4)

$$\log(q_e) = \frac{1}{n}\log(C_e) + \log(k_f) \quad \text{……..(Eq}^n\text{. 4)}$$

where, K_f and 1/n are empirical constants related to bonding energy or as an indicator of adsorption capacity and measureof intensity of adsorption respectively.A regression coefficient of 0.922 shows that heterogonous areas are formed on the solid surface in a Freundlich model. The value of n from 1 to 10 shows a positive adsorption situation (Huang et al. 2012) and small n value shows a weaker bond between the adsorbate and the adsorbent.). Lower value for K_f indicates that the rate of adsorbate removal is low.When the maximum capacity of adsorption is increased, the higher the K_f and the 1/n value higher, adsorption is better.

Dubinin-Radushkevich model is expressed as (Eq^n. 5):

$$q_e = q_m \exp(-K\varepsilon^2) \quad \text{……………………..(Eq}^n\text{. 5)}$$

Where, q_e is the adsorption capacity at equilibrium condition, qm is the maximum adsorption capacity, the constant K gives an idea about the mean free energy. 'ε' is the Polanyi potential which is defined as (Eq^n. 6),

$$\varepsilon = RT\ln(1+1/C_e) \quad \text{…………………..…(Eq}^n\text{. 6)}$$

Where, R is universal gas constant (8.314 J mol- K) and T is absolute temperature

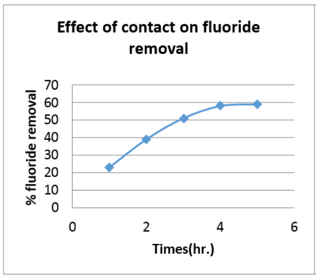
4. RESULTS AND DISCUSSION

4.1 Effect of contact time on fluoride removal

It is observed that with increasing contact time, there is increase in fluoride removal efficiency from 23% to 59%. From the Fig. (2), Optimum contact time is observed to be 180 minutes.

4.2 Effect of pH on adsorption of fluoride

Study of adsorption1of fluoride onto marble powder was done at different1pH from 2-12. Fluoride adsorption was maximum in neutral range and as pH increases adsorption decreases and becomes nearly constant at pH of 7.5. At pH of 7.5 removals efficiency was 59% but fluoride conc. was 4.1 which were not within permissible limit. Adsorption of fluoride within pH range of 6-8 showed good results shown in Fig. (3).



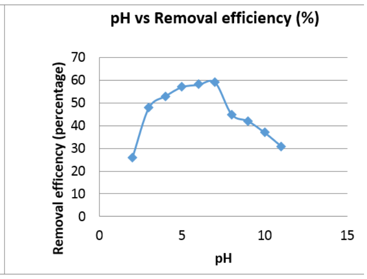


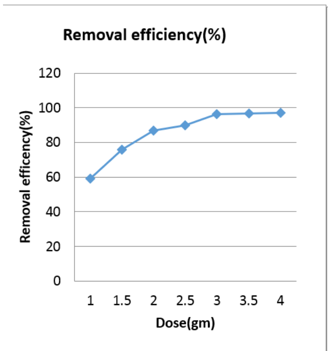
Fig. 2. Plot of effect of contact time vs % removal
Fig. 3. Plot of effect of pH vs % removal

4.3 Effect of adsorbent dose on fluoride removal

It is observed that with increasing adsorbent dose, there is increase in fluoride removal % and from the Fig. (4), adsorbent dose is observed to be 3gm

4.4 Effect of initial conc. on fluoride removal

It is observed that with increasing initial fluoride concn., there is decrease in fluoride removal % shown in the Fig. (5).



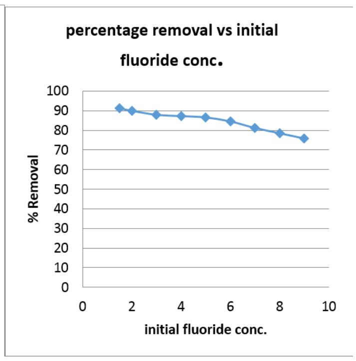
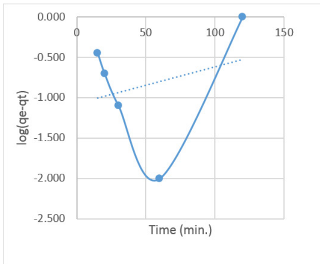


Fig. 4. Plot of effect of Dose vs % removal
Fig. 5. Plot of effect of initial F-Concevs % removal

4.5 Adsorption Kinetics and isotherms on marble powder

To estimate the kinetics of fluoride adsorption on the particle, we matched the experimental data using two types of kinetic models: pseudo-first order and pseudo-second order models. We explain the solid/liquid adsorption using these two models. The fit of the two models for the kinetic data obtained from the experiment of fluoride adsorption is shown in Fig. 6 and 7. Table 1 summarizes the kinetic data for fluoride adsorption onto the adsorbent based on the two models. A linear connection is shown in Fig. Fig. 6 and 7, with an excellent correlation value. The adsorption rate constant k1 shows rapid fluoride removal, presumably suggesting the presence of a significant number of binding sites on the adsorbent surface. The experimental data for the adsorbent could be fitted to a pseudo-first order kinetic model, but the pseudo-second order kinetic model (R2 = 0.9701) provides the best fit. Therefore, pseudo-second order kinetics were followed by fluoride adsorption onto the adsorbent throughout the adsorption process. It is believed that this model assumes that rate-limiting step is absorption of electrons, valence bonding or exchange between adsorbent and the adsorbate substance. Therefore, electron sharing or an exchange on the adsorbent surface may help with the development of the adsorption process.



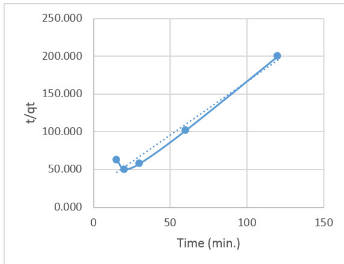


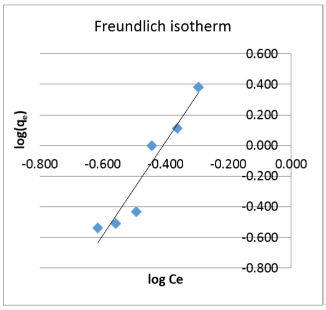
Fig. 6. Plot of Pseudo First Order
Fig. 7. Plot of Pseudo Second Order

Adsorption Kinetics	Equation	R2
Pseudo first order	y = 0.0045x - 1.0707	0.7455
Pseudo second order	y = 1.4159x + 24.999	0.9701

Table 1. Kinetic parameters for the adsorption of fluoride onto an adsorbent

4.6 Adsorption Isotherm

Isotherm data analysis is critical for predicting an adsorbent's adsorption capability, which is one of the most significant criteria to consider when designing an adsorption system. In this investigation, Langmuir and Freundlich isotherm models were used. The equilibrium isotherm of fluoride adsorption experimental findings was found to be consistent with the Langmuir and Freundlich isotherm models. Fig.8 and 9 show the results of fitting Langmuir and Freundlich isotherm curves as listed in Table 2. The 'n' value falls within the range of 1–10, indicating suitable fluoride adsorption conditions and when the value of 'n' lies between 0 to 1 shows weaker bond between adsorbent and adsorbate. The Langmuir isotherm model effectively described fluoride adsorption when calculating the correlation coefficient 'R^2.' It was postulated that all adsorption sites exhibited comparable accessibility, with a monolayer surface covering and no discernible interaction among the adsorbed species.



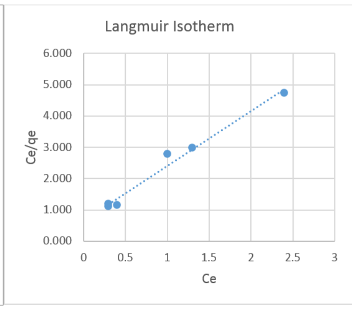


Fig. 8. Plot of Freundlich isotherm
Fig. 9. Plot of Langmuir isotherm

Models	Isotherm parameter	Isotherm value
Freundlich Isotherm	K^f	17.83
	n	0.3258
	R^2	0.9253
Langmuir Isotherm	q_m(mg/g)	0.5706
	ka (L/mg)	2.641
	R^2	0.981
Dubinin-Radushkevich Isotherm	q_m (mg/g)	0.4748
	K_a	4×10^{-8}
	R^2	0.9156
	E_s(KJ/mol)	3.535

Table 2. Calculated adsorption isotherm parameters by the different linear method.

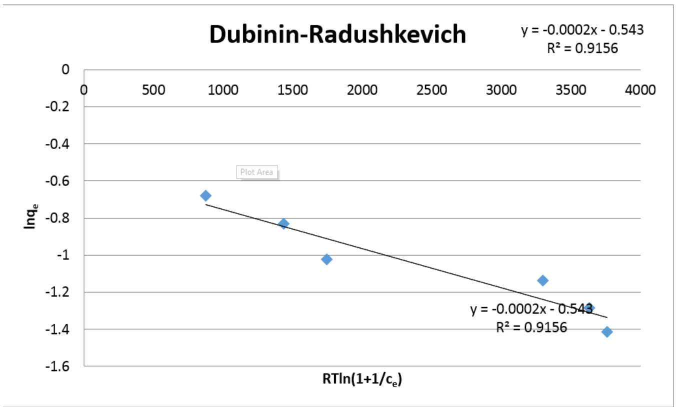


Fig. 10. Plot of D-R isotherm

The typical adsorption bonding energy range of chemisorptions through ion-exchange mechanism is 8 and 16 kJ/ mol. When value of Es is less than 8kJ/mol shows significant physical adsorption. Since, the Esvalue of the D-R isotherm is 3.535 kJ/ mol (mean energy adsorption or bonding energy) is still good fit, indicating physical adsorption.

5. CONCLUSION

It has been observed that marble powder removes the fluoride from drinking water. Marble powder reduces the fluoride concentration up to the WHO guideline. The equilibrium time for adsorbent was approximately 3 hrs. with 97% fluoride removal from 10ppm to 0.3ppm. The change in pH of the marble powder indicates that it works best in the pH range of 7 and is suitable for removing fluoride from groundwater and tube wells in rural areas. The batch adsorption kinetics show that it follows pseudo second order reaction (R2=0.9701) means adsorption is chemisorption. Adsorbent follows Langmuir Isotherm with R2=0.981 means it is monolayer adsorption (occurs only at specific homogeneous sites on the surface, and once a site is filled, no further adsorption can occur at that site).

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