JOURNAL OF CRITICAL REVIEWS

ISSN- 2394-5125 VOL 06, ISSUE 04, 2019

BATCH ADSORPTION ANALYSIS AND EQUILIBRIUM STUDY OF A NOVEL VELVET BEAN SEED COAT (VBSC) ADSORBENT USED FOR DEFLUORIDATION

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Abstract

Fluoride contamination study analyzed the process of defluoridation of groundwater by using the Velvet Bean Seed Coat (VBSC). It is estimated and analyzed in batch experimental analysis. Different sets of adsorption parameters, such as effect of dose, pH, contact time, initial concentration and particle size were optimized for this study. The dose of adsorbent was observed 2.0 gm/L as a optimum dose for 15 mg/L initial concentration. At the optimum condition of pH 6.5. The percentage removal from synthetic sample was found to be 92.5 % for the contact time 6 hrs. The adsorption equilibrium data fitted well to Freundlich isotherm than Langmuir.

Keywords: Fluoride, Adsorption, Adsorbent, Fly ash.

INTRODUCTION

Worldwide the study reveals that a fluoride ion has toxicity for human and animals too. The quantity of fluoride ion matters the effect on living beings. Therefore its ingestion in food or drinking water must not exceed a narrow range of concentrations. Various organizations sets a limit of tolerance in this regards. WHO sets a limit of maximum acceptable concentration of fluoride ions in drinking water which is below of 1.5 mg/L (WHO, 2004). In the Indian context, Indian standards for drinking water recommended an acceptable fluoride concentration of 1.0 mg/L and the allowable fluoride concentration of 1.5 mg/L in potable waters depends on the availability and quality of fluoridated water (CPHEEO, 1984).

The National Environmental Engineering Research Institute (NEERI), Nagpur, India, developed a well known method i.e Nalgonda Technique (Bulusu et al., 1979). The Nalgonda technique of community defluoridation is based on precipitation process which is very efficient and cost effective. The major limitations of Nalgonda technique are daily addition of chemicals, large amount of sludge production, least effective with water having high total dissolved solids and high hardness. Besides, it converts a large portion of ionic fluoride (67–87%)

into soluble aluminum complex and practically, removes only a small portion of fluoride in the form of precipitate (18–33%). Therefore, this technique is erroneous. Drinking water standards for fluoride ions prescribed by various authorities refer Table 1 and for state wise details Table 2. In India many states are affected due to high concentration of fluoride, it has dual effect on health, if it is less than 0.5 and more than 1.5 ppm. India is one among 25 nations in the world where fluorosis problem is persisting due to consumption of excessive fluoride bearing drinking water. Recent findings indicates that more than 60 million people including children in India (in 16 out of 32 states) are suffering from dental, skeletal and non skeletal forms of fluorosis and other associated health problems. This study focuses on the Defluoridation of drinking water by using fly ash as a new, feasible, suitable and low-cost adsorbent. Fly ash is a waste material collected from the power plant near Nagpur, Maharashtra. This collected fly ash was tested in a laboratory for its chemical compositions. On the basis of its chemical compositions this fly ash is confirmed for the experimental study and used in the process of defluoridation. The collected Fly ash was washed by double distilled water and dried in oven under the temperature of 100 0C for 12 Hrs, and sieved through the sieves of 300 μ size then the material was used as an adsorbent for the removal of fluoride.

PLANT DESCRIPTION:

- **Shrub height**
  Up to 15 M
- **Flower color**
  Dark Purple
- **Beans**
  Black or Brown
- **Pod**
  Ribbed pod
- **Seed shape**
  Ellipsoid

Figure 1: Description of climbing shrub Velvet Bean [https://www.sciencephoto.com/media/428878/view/velvet-bean-mucuna-pruriens-]

MATERIAL AND METHODS

Chemical & Adsorbent

This study used all the (AR grade) chemicals and reagents in the experimental work and the solutions were prepared for the entire study using distilled water. Stock fluoride solution and other reagents were prepared in accordance with the 'Standard methods' (APHA, AWWA, and WPCF) (1989).

Laboratory setup & testing methodology

This experimental study required various testing's throughout the work and hence in this study stock solution of fluoride was prepared by dissolving 221 mg of anhydrous NaF in a required quantity of distilled water (Bhambulkar & Patil, 2020) . Test solution of 15.0 mg/L fluoride was prepared from fresh stock solution keeping in view that the maximum concentration of fluoride reported in groundwater of most of the fluoride affected area is around 10.0 -15.0 mg/L. All the experiments

were carried out in 200 ml plastic bottles containing 100 ml of fluoride test solution at room temperature. Samples were filtered using whatman 42 filter paper and filtrate samples were analyzed for residual fluoride concentration by SPADNS method. The filtered solution was analyzed for fluoride concentration and the standard graph of concentration versus absorbance was prepared by measuring the absorbance at 570 nm wavelength. Absorbance was found out by using the SYSTRONIC made Spectrophotometer (Patil, R. N., & Bhambulkar, A. V.,2020).

Preparation of Adsorbent

The Velvet Bean Seed Coats (VBSC) were collected from Nagpur Maharashtra. The collected Beans seed coat were first washed many times by the tab water so that it has no dust and particles retained over its surface and then again washed with distilled water. The washed VBSC then cut in to small pieces thoroughly and then sundried for 3 days at the average temperature 38 ^{0}C. Afterward the sundried seed coat was kept in oven for a period of 24 hours at a temperature of 105^{0}C. The completely dried VBSC cooled in a room temperature and then it was pulverized. The grounded VBSC were kept in muffle furnace at a temperature of 750 ^{0}C for 2 hours for activation. This physically activated VBSC charcoal was used in the process of defluoridation (Bhambulkar, 2011).

EXPERIMENTAL METHODS

The adsorption method is used for this study which has a low-cost effective method having easy and feasible approach. In this method of adsorption, the parameters such as dose, pH, initial concentration, particle size and time of contact were selected and studied.

The experimental batch study samples prepared and performed for the separate parameter study by using 200 ml sized plastic bottles which contained 100 ml of fluoride sample. The pH of bottled contained fluoride samples were adjusted by using 0.1 N HCl or 0.1 N NaOH solutions. The complete prepared samples after all process were tested for the quantity estimation by using spectrophotometer.

RESULTS AND DISCUSSION

Effect of Dose

In this experimental study dose of adsorbent was optimized by using different trial dosage ranging from 0.5 g/L to 5.0 g/L for the initial concentration of 15.0 mg/L. The percentage removal varies to ascertain the effect of dosage and to optimize the minimum dosage required for bringing down the fluoride level to its permissible limit. In fig. 2, it is clearly seen that the effects of percentage removal of fluoride with sorbent dosage. This figure shows the significant increased with increased in dose of adsorbent which happens with the increased of number of active sites as the dosage increased. It can also observe from the analysis that the % removal of

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fluoride gradually increases up to a certain limit and then it remains almost constant. The optimum level of dose was found 2.0 g/L for initial concentration 15.0 mg/L with the conditions of agitation 24 hours with a speed of 150 rpm for a neutral pH.

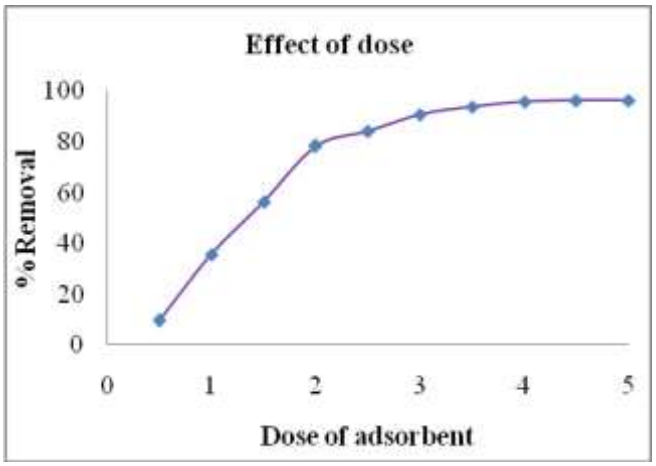

Fig. 2: Dose of Adsorbent Vs. % Removal.

Initial Conc. 15 mg/L; pH 7; agitation 150 rpm; temp.30^{0}C; Volume of sample 100 mL

Effect of pH

In this experimental study it has observed that pH of synthetic solution plays a vital role in the process of removal of fluoride ions. The pH of the solution affects the surface charge of the adsorbent as well as the degree of ionization of the materials present in the solution. The hydrogen ions and hydroxyl ions are adsorbed quite strongly and, therefore, the adsorption of other ions is affected by the pH of the solution. The range of pH solution was selected from 2.0 to 12.0 with the optimized dose 2.0 gm/L at room temperature. This study shows the effect of pH on the uptake capacity of fluoride ions and observed that the rate of percentage removal of fluoride goes on increasing up to pH 6.5 and then after it has been decreased which clearly shows in figure 3. The optimum pH 6.5 is selected throughout the study.

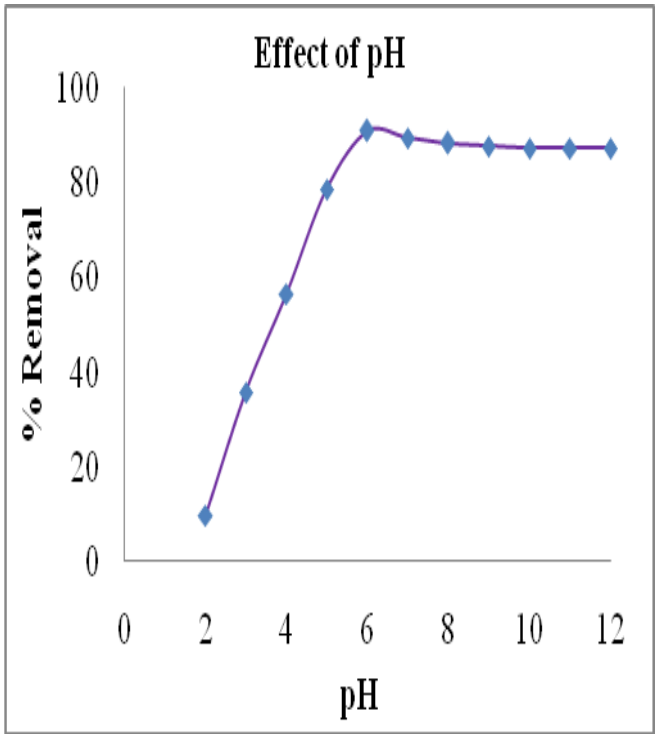

Fig. 3: .pH Vs. % Removal.

Initial Conc. 15 mg/L; pH 7; agitation 150 rpm; temp.30^{0}C; Volume of sample 100 mL

Effect of initial metal ion concentration

In this experimentation different initial concentrations were selected ranges from 5.0 mg/L to 20 mg/L. This study shows the effect of initial concentration on the uptake capacity of fluoride ions. Figure 5.0 clearly shows that when the initial concentration of fluoride was less, then the percentage removal was increased and then decreases as the concentration increases shown in figure 4.

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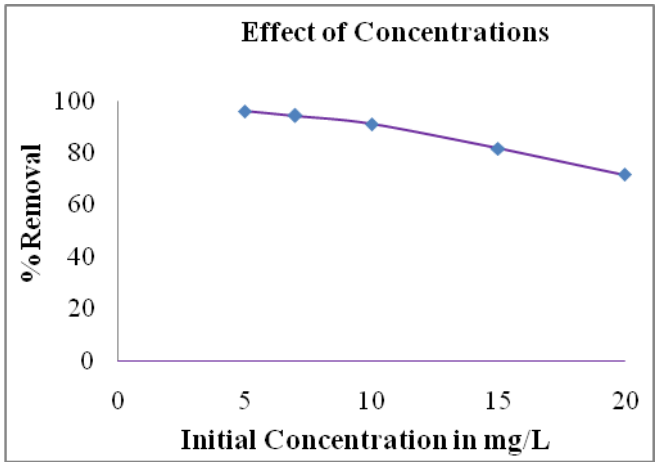

Fig. 4: Initial Concentration Vs. % Removal.

pH 7; rpm 150; temp.30^{0}C; Volume of sample 100 mL

Effect of Particle Size

Particle size is the one of the important parameter in batch adsorption study which directly affects the process of adsorption. The particle sizes of 75 µm to 600 µm were used in this research study analysis. The result shows the particle size increases the % removal of fluoride decreases. It proves that the removal capacity of adsorbent is also depends on the particle size of adsorbent used as shown in fig. 5.

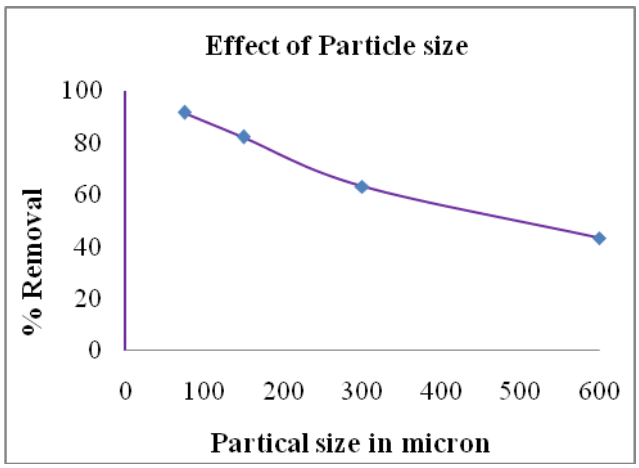

Fig. 5: Particle Size Vs. % Removal.

Initial Conc. 15 mg/L; pH 7; agitation 150 rpm; temp.30^{0}C; Volume of sample 100 mL

Effect of Contact time

In the batch study analysis this is an important parameter observed during the experimentation. The effect of contact time on the removal of fluoride by VBSC was studied at initial concentration 15.0 mg/L at a room temperature with rpm-150 and time selected 1-12 hour.

Figure 6.0 shows the contact time vs. % removal of fluoride which reflects the contact time curves increases the adsorption gradually up to 9 hours and thereafter the adsorption rate almost constant. Aggregation of Fluoride molecules with the increase in contact time makes it almost impossible to diffuse deeper into the adsorbent structure at highest energy sites. This aggregation negates the influence of contact time as the mesopores get filled up and start offering resistance to diffusion of aggregated fluoride molecules in the adsorbents. This is the reason why, an adsorption remains constant during further 9 hours. Hence further experiments were conducted for optimum contact time 6 hours.

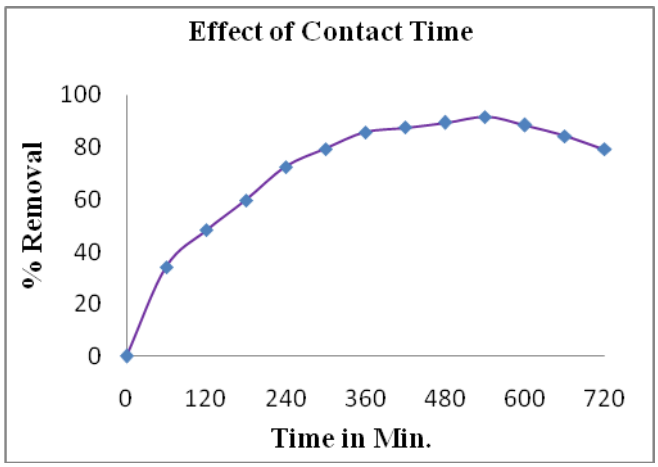

Fig. 6: Contact time Vs. % Removal

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Initial Conc. 15 mg/L; pH 7; agitation 150 rpm; temp.30^{0}C; Volume of sample 100 mL

SEM ANALYSIS

Scanning electrons microscopes (SEM) analysis was performed to understand the morphology of VBSC. From fig.6, it is observed that the openings are enough to remove fluoride from the water whereas fig. 7, shows the openings are blocked after adsorption of fluoride.

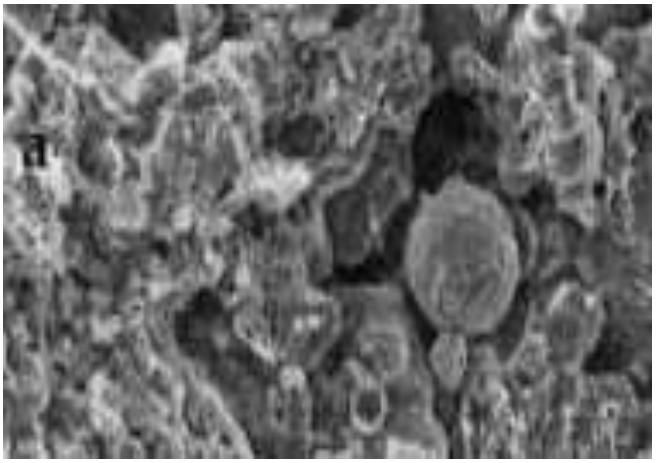

Fig. 7: VBSC, SEM analysis of Loaded adsorbent

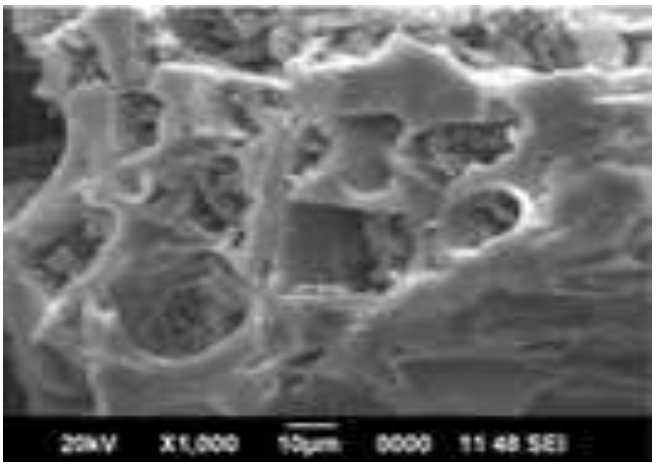

Fig. 8:VBSC, **SEM analysis of Unloaded adsorbent**

XRD ANALYSIS

XRD test of VBSC samples were scanned for 2ø range from 5 to 60°.The X-ray diffraction spectrum pattern. It shows the amorphous nature of the product.

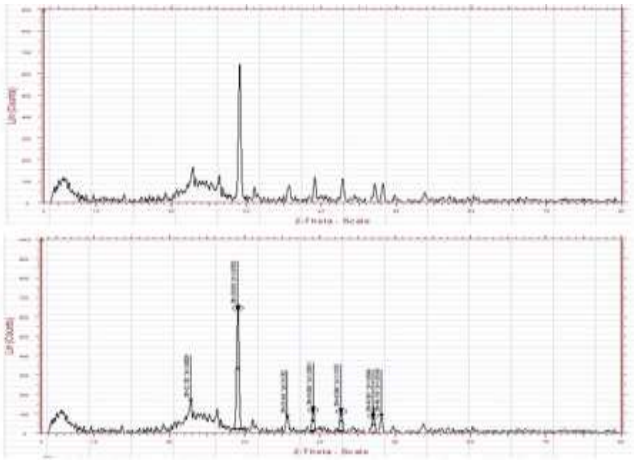

Fig. 9: XRD of VBSC

XRD was used on the treated Velvet Bean Seed Coat (VBSC) to predict changes in the crystal structure. Since years and years prior, X-Ray diffraction (XRD) examination has been perhaps of the most well known strategy in the logical period for deciding the sort of material and the distinguishing proof of identifying crystals. XRD patterns of VBSC before and after fluoride ions were adsorbed. The VBSC before fluoride particle adsorption is portrayed in figure 9 as having symmetric, sharp peaks. This peaks shows the structure is crystalline, and the figure underneath delineates the position and sort of peaks following the adsorption of fluoride particles. It was found that no peaks had framed, it is indistinct to recommend that the structure found amorphous.

ADSORPTION MODEL

A different adsorption isotherm was prepared and the analytical data matched well with Langmuir than Freundlich, which achieved the good adsorption capacity of the adsorbent. The

interaction of the adsorbate and the adsorbent was the focus of the isotherm study. The information was seen in a relationship between the Langmuir and Freundlich adsorption isotherms. The Freundlich isotherm is equilibrium based adsorption based on homogeneous surfaces, where as the Langmuir isotherm is an assumption based on the removal due to monolayer sorption happening on a homogeneous surface of the adsorbent without any collaboration between adsorbed particles. The linear equations for the Langmuir and Freundlich isotherms are provided below and are denoted by the equations (a) & (b, respectively.

$$\frac{1}{qe} = \frac{1}{(qmaxKL)}\frac{1}{Ce} + \frac{1}{qmax}$$ Equation (a)

The greatest quantity of fluoride that may be adsorbed which is shown by qmax in mg/g in the equation above. The equilibrium fluoride concentration is indicated by Ce in mg/L and the Langmuir isotherm constant is indicated by KL in L/mg.

$$log\ q_e = log\ K_f + \frac{1}{n} \log C_e$$ Equation (b)

Ce is the equilibrium fluoride concentration, and qe is the amount adsorbed in mg/g in equation 2; K_F is the observational consistent of Freundlich in mg/g and 1/n is the Freundlich type. Plot shows the isotherms in fig.10 and 11.

Freundlich Isotherm

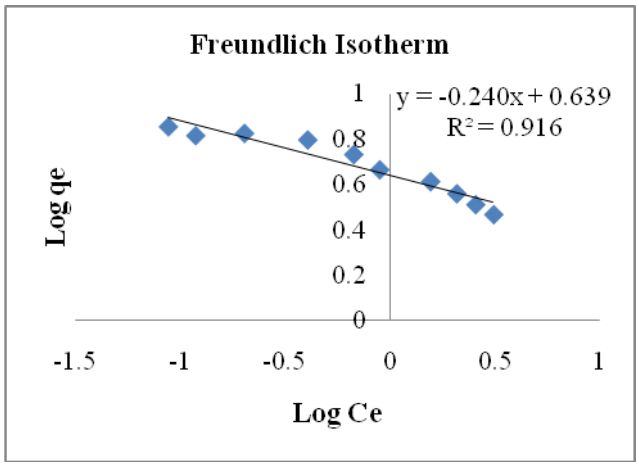

Fig. 10: Freundlich Adsorption Isotherm

Langmuir Isotherm

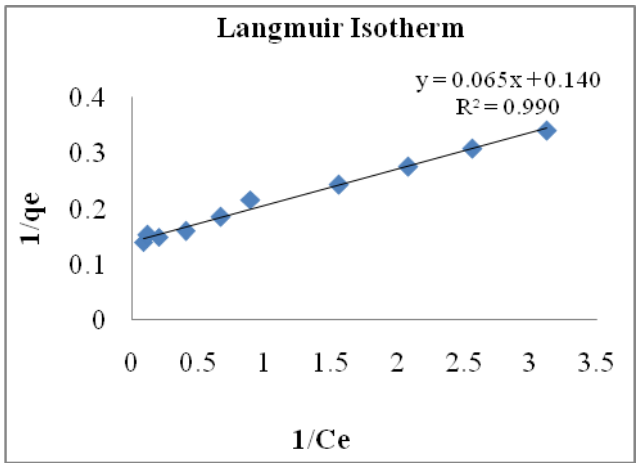

Fig. 11: Langmuir Adsorption Isotherm

CONCLUSIONS

1. The results conclude that the Velvet Bean Seed Coat (VBSC) physically activated carbon has the good fluoride removal capacity.

2. The optimum dose of VBSC was found 2.0 gm/L for an initial fluoride concentration of 15 mg/L.

3. Adsorption capacity was obtained more in the pH range of 5-6.

4. The maximum removal of fluoride was found at lower particle size of adsorbent.

5. The optimal contact time was found 6 hrs.. which has got a required % removal as per the norms.

6. The adsorption equilibrium data follows Langmuir isotherm than Freundlich isotherm.

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