MARBLE POWDER: AN ADSORBENT FOR REMOVAL OF FLUORIDE FROM AQUEOUS SOLUTION

Buddharatna Godboley and Prashant Nagarnaik
Civil Engineering Department, G.H. Raisoni College of Engineering Nagpur, India

ABSTRACT
Water defluoridation experiments were carried out on solid waste i.e Marble Powder (MP). The 10 ppm fluoride concentration solution and 4.5 gm of MP were employed in experiments to determine defluoridation capacities, effects of pH and effects of temperature, effect of initial concentration, and effect of contact time on defluoridation. The highest defluoridation capacity of 90% was obtained with the dose of 4.5g/L. The adsorption follows a Pseudo second order kinetics, Intra-particle diffusion model, Elovich equation, Modified Freundlich equation. Equilibrium study is done and it follows Langmuir, Freundlich, and Temkin isotherm. The value of thermodynamic parameter ΔH indicated an exothermic adsorption process and the negative value of ΔG show the feasibility and spontaneity of material-anion interaction.

Key words: Defluoridation, fluoride, Marble Powder (MP).

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1. INTRODUCTION

Water is very essential natural resource for growth of life on earth which has considered to be plenty available. Ground water is one of the major & important sources of drinking water. In developing country like India more than 90% population is dependent on the ground water. Due to modernization and industrialization these ground water sources were polluted. F- is one of the very common element present over the earth crust. This element is most electronegative of all other elements. The high level of fluoride in drinking water imparts the human health hazards, so it is our prime duty to de-fluoridation the ground water. Many researches & scientists have done lots of work for defluoridation such as Precipitation, membrane processes, ion-exchange, and adsorption processes are most studied. Adsorption is one the most trusted methods for de-fluoridation. Many materials or adsorbents were developed and can be used with high adsorption capacity. In this present study we have try to use a solid waste material as an adsorbent De-fluoridation of ground water can be done for drinking purpose. It has been found that fluoride has a great affinity with silica, alumina, and % calcium.
2. MATERIALS AND METHODS

2.1. Adsorbent Collection and Preparation

MP was collected from the neighboring market having high calcium content in pulverized form. It is washed with de-ionized water and followed by drying in an oven at 110°C for 24 hrs. The dried powder were sieved well with 75μm mesh size particles. The prepared material was preserved and again it is washed with de-ionized water followed by oven drying for 24hrs as shown in Figure 1. The prepared material is sent for the chemical composition test and the outcomes are graphically shown in Figure 3.

![Figure 1 Raw material and Fine particles after passing from 75μ size sieve](image1)

![Figure 2 SEM analysis for MP](image2)

2.2. Instruments and Apparatus

The morphology of MP was study using SEM analyzer. Infrared spectroscopy of the MP was recorded on a Labindia double beam Spectrometer. Determination of pH for the solution is done by using digital pH meter. Orbital shaking incubator is used to control the temperature and orbital shaking for the adsorption experiments. SPANDS methods can be used for determination of fluoride concentration in aqueous solution. Fig.4 shows the adsorbent is amorphous in nature; this is done by X-Ray diffraction method.

![Figure 3 Chemical composition](image3)

![Figure 4 XRD analysis on MP showing amorphous nature](image4)
2.3. Preparation of Adsorbate Solution
Small amount of 0.22g sodium fluoride is measured and is dissolved in 1L doubled distilled water to prepare stock solution of fluoride. Serial dilution of 100 mg/L fluoride stock solution was done to prepare the required concentration of fluoride solution.

2.4. Adsorption Experiment and Analysis
Large no of experiment were done for the study of effect of pH, effect of adsorbent dose, kinetics study, kinematics study, selection of an isotherm, and assessment of thermodynamic parameters. The variation of pH was like 2, 4, 6,8,10 &12, adsorbent dose variation was like 0.5-5.5 g in 100 ml and particle size is less than 75μm, contact time (15 min to 1440 min), initial fluoride concentration (0,2,4,6,8,10,14 and 16 mg/L) and temperature (293,303, and 313K) were assessed during the study in a 250 ml conical flasks and 100 ml of fluoride solution of 10mg/l concentrated is added. The solution was kept in orbital shaking incubator at 150 rpm for 24 hr at 303 ± 1K and then the solids particles were separated through normal filtration process. With the help of double beam spectrophotometer the concentration of fluoride solution can be determine. For each experiment value we have conducted experiments for thrice and average values was reported. The amount of fluoride adsorbed per unit adsorbent can be calculated by using mass balance concept.

3. RESULTS AND DISCUSSION

3.1. Effect of Adsorbent Dose
Experimental study was carried to understand and check the effect of dose adsorbent by varying doses between 0.5 to 5.5 g/L. The pH was maintain at 7, whereas initial fluoride concentration was fixed at 10 mg/L and time of contact were kept as 24 hrs. Figure 5 shows the effect of adsorbent dose on the adsorption of fluoride. The data shows that as dose an increase there will be rapidly increase in % removal. As the surface area increase, the removal efficiency also increases with immediate increase in adsorbent dose, and hence extra active sites were available for the adsorption of solution. It is cleared that MP gives 90 % removal of fluoride ions at the dose at room temperature of 30°C. Further no significant changes found and hence 4.5g/l dose is selected for further studies.

![Figure 5 Effect of adsorbent dose on fluoride removal](image1)

![Figure 6 Effect of pH on fluoride removal](image2)

3.2. Effect of pH
The effect of pH of the fluoride solution is one of the important factors in the process of adsorption. Therefore the range of pH between 2 to 14 was observed. The pH was maintained at by adding 0.5N HCl for acidic zone and 0.1N NaOH for alkali zone in 1000 ml of prepared solution of 10mg/L of fluoride
solution for 24 hrs contact time with a dose of 225 mg/100 ml of MP. Fig. 6 shows the influence of pH on % removal of fluoride. As pH increases an increase in % removal is found but after the optimum pH at 8.6 the curve decreases with increase in pH. The decline in adsorption at higher pH values may be probable due to plenty of OH\(^{-}\) ions because increased hindrance to diffusion of fluoride ions. From fig. it was noted that the highest fluoride removal is achieved at range of pH 9.2 to 10.4. Thus, pH 9.2 was taken into concern for further studies.

### 3.3. Effect of Stirring Rate

Experiments work were carried out to check the effect of stirring rate by changing speeds from 20 to 200 RPM, at optimum pH of 9.2 with adsorbent dose of 4.5 g/L and 24 hrs of contact time. A curve is plotted between stirring rate vs. % removal as shown in Figure 7. From figure we can conclude removal is function of stirring rate. As stirring rate increases there will be an increase in %removal for a given time. The adsorption is archived at 90.70% at 140 rpm. Further there is no significant change with increase in stirring rate, so 140 rpm is considered for further study.

![Figure 7](image1.png) 
**Figure 7** Effect of stirring rate on fluoride removal

### 3.4. Effect of Contact Time

Experiments were conducted to check the effect of contact time on removal of fluoride, by varying it from 15 to 1440 minutes. Considering adsorbent dose of 4.5g/L, pH of 9.2 and rate of stirring 140 rpm by keeping temperature 293, 303 and 313K experimental data is collected. A curve is plotted between time vs % removal as shown in Figure 8. It is clear that initially adsorption takes place very rapidly then afterwards slowed down gradually until it attained equilibrium. Beyond which there is no significance to increase in the rate of adsorption. For temperature 293K, the removal percentage of fluoride is very fast and within 480 minute about 90.47% removal is found and there was no considerable change in the rate of removal which denoting accomplishment of equilibrium. However the removal efficiency increases trend usually from 480 to 360 min in case of 303K & 313K. Further increase in contact time does not change % removal, because there is a deposition of fluoride ions on the vacant adsorption sites on adsorbent material. Therefore equilibrium time of 360 minute is selected for the study at room temperature.

![Figure 8](image2.png) 
**Figure 8** Effect of contact time on fluoride removal

### 3.5. Effect of Initial Concentration and Temperature of Fluoride

Experimental were carried out to check the effect of initial concentration fluoride by varying initial concentration from 2,4,6,8,10,12,14 and 16 mg/L at different temperatures (293, 303 and 313K ) at adsorbent dose of 4.5g/L, stirring rate of 140 rpm pH of 9.2, and contact time of 360 minutes. Experimental data is collected and a curve is plotted between initial concentration vs % removal as shown in Figure 9 and Figure 10. As initial concentration increases there is decline in the removal percentage of fluoride ion. Also as temperature increases there is an increased mobility of the adsorbate and a decrease in
the retard force action on the diffusing adsorbate. Moreover as temperature increases there will be increase in active sites of the adsorbents.

3.6. Adsorption Isotherms

Study on equilibrium was carried out pH at 9.2 for adsorption onto the MP and temperatures of 293, 303, & 313K, as shown in Fig. 11 to 12. Results clears that the MP has a good affinity for fluoride. The equilibrium study includes isotherm model equations, viz. Langmuir (Figure 11), Freundlich (Figure 12), and Temkin (Figure 13). The value of slope & intercept provides the related parameters. Table 1 shows the linear plots of equilibrium models. The figure and table shows that Langmuir well fitted curve $R^2 = 0.926, 0.981 & 0.989$ for 293K, 303K & 313K respectively. The average monolayer adsorption capacity ($q_m$) obtained for MP is is 0.691, 1.198, 1.410 mg/g for 293, 303, 313K respectively. The Freundlich isotherm model is based on multilayer adsorption, and data represent that it is fairly fitted ($R^2 = 0.899, 0.970 & 0.989$ for 293K, 303K & 313K respectively). From the linear plot Freundlich adsorption constants ($K_F$) were obtained 0.745, 1.156, & 1.294 for 293K, 303K & 313K respectively. The Freundlich coefficient ($n$), having values ranging from 2.920 to 6.649. A very simple form of adsorption model is developed by taking consideration of the chemisorptions for an adsorbate onto the adsorbent ($R^2 = 0.945, 0.978, 0.986$ for 293, 303 & 313K respectively). A well fitted curve shows that the adsorption process is might be going on onto the adsorbent due to chemisorptions with physical forces. Therefore, the order of isotherm equations obeyed by the present data is Langmuir > Temkin > Freundlich isotherm.

A relationship between $R_L$ and $C_0$ was obtained and shown in Figure 14. It shows the necessary features of the Langmuir isotherm. $R_L$ values for MP at different temperatures are represented in Table 2. for the present study , the values of $R_L$ for fluoride concentration are found to be in the range of 0.014–0.4, which suggests the good adsorption of fluoride onto the adsorbent, under the experimental conditions.
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Figure 11 Langmuir isotherms

Figure 12 Plot of the Freundlich isotherm

Figure 13 Adsorbent response to Temkin isotherm

Figure 14 Separation factor RL values verses initial fluoride concentration for various temperatures derived by Langmuir constants.

Table 1 Isotherm parameters obtained using the linear method for the adsorption of fluoride onto MP

<table>
<thead>
<tr>
<th>Models</th>
<th>Parameters</th>
<th>293K</th>
<th>303K</th>
<th>313K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir Isotherm</td>
<td>R²</td>
<td>0.926</td>
<td>0.981</td>
<td>0.989</td>
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<td></td>
<td>q_m (mg/g)</td>
<td>0.691</td>
<td>1.198</td>
<td>1.410</td>
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<td></td>
<td>K_l (L/mg)</td>
<td>1.501</td>
<td>2.688</td>
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<tr>
<td>Freundlich Isotherm</td>
<td>K_f (L/mg)</td>
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<td>1.156</td>
<td>1.294</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>2.920</td>
<td>4.200</td>
<td>6.649</td>
</tr>
<tr>
<td></td>
<td>l/n</td>
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<td>0.238</td>
<td>0.150</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.866</td>
<td>0.913</td>
<td>0.879</td>
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<tr>
<td>Temkin Isotherm</td>
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<td>5947.271</td>
<td>6313.639</td>
<td>10421.634</td>
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<tr>
<td></td>
<td>K_l (L/mg)</td>
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<td>129.173</td>
<td>1180.967</td>
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<tr>
<td></td>
<td>B</td>
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<td>0.399</td>
<td>0.250</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.945</td>
<td>0.978</td>
<td>0.986</td>
</tr>
</tbody>
</table>
3.7. Thermodynamic Parameters

The temperature effect is a biggest factor for controlling the sorption process and therefore the sorption of MP was monitored at three different temperatures 293, 303, and 313K. Thermodynamics parameters were calculated and presented in Table 3 and graphical representation shown in Figure 15. If values of $\Delta G^\circ$ are negative then it indicates that sorption reaction is spontaneity. If the value of $\Delta H^\circ$ comes negative then it indicates the exothermic nature of the sorption process (Srivistav et.al, 2006). Suppose the value of $\Delta S^\circ$ comes positive then it shows the increasing randomness at the solid/liquid interface during sorption of fluoride. The study shows as temperature increases, adsorption capacity also increase. This is most probably due to control of the adsorption process by diffusion phenomenon. Therefore, reaction is exothermic in nature of the diffusion controlled adsorption process.

![Figure 15 Vant-off Plot for Thermodynamics](image)

<table>
<thead>
<tr>
<th>Table 2</th>
<th>$R_L$ values at different temperatures, which were calculated using Langmuir constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_0$ (mg/L)</td>
<td>293</td>
</tr>
<tr>
<td>1</td>
<td>0.323</td>
</tr>
<tr>
<td>2</td>
<td>0.193</td>
</tr>
<tr>
<td>4</td>
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</tr>
<tr>
<td>6</td>
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</tr>
<tr>
<td>10</td>
<td>0.046</td>
</tr>
<tr>
<td>12</td>
<td>0.038</td>
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</table>

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Thermodynamic parameters of fluoride sorption on MP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta G$ (kJ/mol)</td>
<td>$\Delta H$ (kJ/mol)</td>
</tr>
<tr>
<td>293K</td>
<td>303K</td>
</tr>
<tr>
<td>-0.9901</td>
<td>-2.491</td>
</tr>
</tbody>
</table>

3.8. Adsorption Kinetics

Several kinetics models have been applied to express the mechanism of solute sorption onto a sorbent. In this present study pseudo first & second order, inter-particle diffusion model, Elovich and Modified Freundlich has been used to study the adsorption process of fluoride on MP. The time dependent adsorption data shown in Figure 16-19 have been analysed using the linear form of kinetics equations. Considering initial concentration of 10mg/L, kinetics study on adsorption had been studied at 293k, 303k & 313k and pH 9.2 for the kinetic study pseudo second-order reaction rate model, Elovich equation model and intra-particle diffusion fit well.
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The pseudo second-order model is plotted between times vs. log \((q_e-q_t)\) as shown in Figure 20 shows. The model describe the kinetics of sorption with high value of \(R^2\), ranges between 0.981 - 0.992. The adsorption mechanism was predominant and that the overall rate of the fluoride adsorption process appeared to be controlled by chemical process (Gupta, 1998; Ajmal et al., 2003). The sorption process may possibly be ion-exchange in nature where the fluoride molecules attach with the various negatively charged inorganic functional groups present on the surface of the MP.

The Elovich equation model is plot between \(\ln(t)\) vs \(q_t\) as shown in figure 19. This model describes chemisorptions on highly heterogeneous adsorbents, which give a good account of adsorption of fluoride with \(R^2\) value ranges 0.968- 0.943.

Intra-particle diffusion model is linearly plot between \(q_t\) versus \(t^{0.5}\) with regression coefficient \(R^2\) of 0.834-0.817, but the line did not pass through the origin, indicating that this model did not fit the adsorption process (McKay and Poots, 1980).

Modified Freundlich Model is plot of \(\ln(q_t)\) vs \(\ln(t)\). The value of parameters like \(k\) and \(m\) are used empirically to evaluate the effect of surface loading and ionic strength on the adsorption process which is determined by the intercept and slope (Onoal, 2006). The data shows that there is no significant trend is followed by the model in the case of Modified Freundlich Equation. In Table 3 it has been seen that the order of model is obeyed by the present data is Pseudo Second Order Model > Elovich Model > Modified Freundlich Model > Intra-particle Diffusion Model > Pseudo First Order Model.

![Figure 16 Pseudo first order model for adsorption](image1)

![Figure 17 Pseudo second order model for adsorption](image2)

![Figure 18 Intra particle diffusion model for adsorption](image3)

![Figure 19 Elovich model for adsorption of fluoride](image4)
4. CONCLUSION

From the batch study it is clear that MP had comparatively good potential for the removal of fluoride from aqueous solution. The equilibrium study indicates that Langmuir isotherm model is most fitted curve, as compare to Freundlich and Temkin isotherms. Maximum monolayer sorption capacity was 1.198 mg g\(^{-1}\) at 303 K which indicating monolayer sorption on a homogenous surface. The \(R_L\) values showed that MP was favourable for the adsorption of fluoride. It was very clear that the adsorption kinetics of fluoride to MP obeyed pseudo-second-order, Elovich model and Modified Freundlich equation adsorption kinetics. The adsorption kinetics process is chemisorptions this is because pseudo-second-order kinetic model indicating shows the best fitting curve. Thermodynamic parameters showed that adsorption of fluoride on MP were exothermic and spontaneous in nature.
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