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Adsorption Studies of Fluoride on Multani Matti and Red Soil

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Abstract

The present study deals with the adsorption of fluoride by multani matti and red soil. These two materials are fuller earths which are used to remove stains and non washable materials. Taking that factor into consideration, batch adsorption studies are carried for removal of fluoride from water. It is found that percentage removal increased with contact time and adsorbent dosage. The optimum contact time for multani matti and red soil is within 15 minutes. The percentage removal of fluoride decreased with increased in concentration. Langmuir and freundlich adsorption isotherms are followed. Pseudo second order kinetics and Elovich models explained the phenomena of adsorption.

Keywords: Adsorption, multani matti, red soil, kinetic models, thermodynamic models.

Introduction

Some ground water has fluoride naturally due to the prescence of minerals like fluorspar, cryolite and flouropatite. The recommended range of fluoride in drinking water is 1.5 mg/l. in Andhrapradesh there is 15 defluoridation plants based on nalgonda process which use alum. But this technique is not having success rate. Taking that factor into concederation, a study has been carried out in view of developing a defluoridation technique which uses multani matti and red soil. Batch adsorption studies are carried out in the study and it was found that both adsorbents could remove 50-70% of fluoride in the concentration range of 1-4 mg/l[1-6].

Material and Methods

Selection of adsorbents: Red soils are composed of crystalling and metamorphic rocks. Mostly the areas of telangana especially nalgonda region has this type of red soil. The red colour of the soil is due to presence of iron oxide. The weathering of granites and hill rocks in Hyderabad produces red soil. By studing the physico chemical properties and free availability of soil, red soil is selected as a adsorbent[7].

Multani matti ($ZnCO_3 2Zn(OH)_2 H_2O$) is used as adsorbent to remove the air pollutants (SO_2 and NO_2) on Taj mahal. It is known as mont morillanite and contains grains of fine sand particles. They contain complex multi centre crystalline structure of oxides and hydroxides of magnesium, aluminum, zinc and slicon. It is also known as fullerene and it is rich in lime[5-8].

Red soils are collected from Hyderabad and it is crushed, washed several times until the loosely bound particles are removed. They are dried in a microwave oven at 100^0C for about one hour. Multani matti is bought from the super market and it is dried in a microwave oven at 100 ^{o}C for about one hour. The adsorption studies carried out with respect to contact time, concentration, dosage, pH, and temperature.

Kinetic models: In order to investigate the mechanism of adsorption several kinetic models were tested including the pseudo first order kinetic model, the Elovich model and the pseudo second order kinetic model for batch adsorption process.

Lagergren (Pseudo First Order Equation) Model: The pseudo first order kinetic equation expressed as[9]

$$\log (q_e - q_t) = \log q_e - K_L/2.303 \times t$$

Where, q_e = the amount of fluoride at equilibrium, q_t = the amount of Fluoride adsorbed at time t, K_L = the rate constant for pseudo first order adsorption per minute.

The values of log ($q_e - q_t$) were linearly correlated with t, the plot of log ($q_e - q_t$) versus t should give a linear relationship from which K_L and q_e can be determined from the slope and intercept of the plot.

Elovich Model: The Elovich or Roginsky-Zeldovich equation is generally expressed as follows[10]

$$dq_t/dt = \alpha \exp(-\beta q_t)$$

Where, q_t = the amount of fluoride adsorbed at time t, α = the initial Fluoride sorption rate, per min, β = the desorption constant, during the experiment.

Pseudo Second Order Model: To describe the fluoride adsorption, the modified pseudo second order kinetic equation is expressed as[11]

$$dq_t/dt = k_2 (qe - qt)^2$$

Where, q_e = the amount of fluoride adsorbed at equilibrium, q_t= the amount of fluoride adsorbed at time t, k_2 = the rate constant for pseudo first order adsorption per minute.

Results and Discussion

Effect of Contact Time: The uptake of fluoride from industrial waste water by multani matti and red soil the adsorption rapidly increased in the first 20 minutes after 20 minutes adsorption slowly approached equilibrium. The adsorption rate and percentage removal of fluoride is high in case of red soil than multani matti. Batch adsorption studies are carried out to check the effect of contact time on percentage removal of fluoride by using red soil and multani matti[12-19].

Effect of concentration of fluoride: When the initial concentration of fluoride was changed (1, 2, 3, 4 mg/L), with a constant adsorbent amount (red soil and multani matti) of 1 gm, the amount of adsorbed fluoride is decreased with increase in the concentration of fluoride. The results are shown in figure–2.

Effect of Adsorbent Dosage: The amount of clay adsorbents (multani matti and red soil) was varied from 0.2 to 1.0 gm with a constant initial fluoride concentration of 2 mg/L and equilibrium time is 60 minutes at room temperature. The amount of fluoride adsorbed per unit mass (q_e) of the adsorbent at equilibrium increased with increase in the amount of clay adsorbent. The similar reports have been reported by Stephen Inbaraj and Sulochana, N. basic lead adsorption on low cost carbonaceous sorbent kinetic and equilibrium studies, and Sumanjit and Prasad.N. Adsorption of leads on rice husk Ash.

Effect of pH on Adsorption of Fluoride: The pH of the aqueous solution is an important controlling parameter in the adsorption process. In present work, adsorption of fluoride on the clay (red soil and multani matti) adsorbents was studied over the pH range of 3.0 to 8.0 for a constant clay amount of 1 gm, and 100 ml of fluride solution concentration of 2 mg/L at room temperature. As the acidity of the medium decreased, the amount of adsorbed (q_e) showed a positive variation and rapidly increased at pH 6.5 in case of multani matti, and pH 5 in case of red soil[20-22].

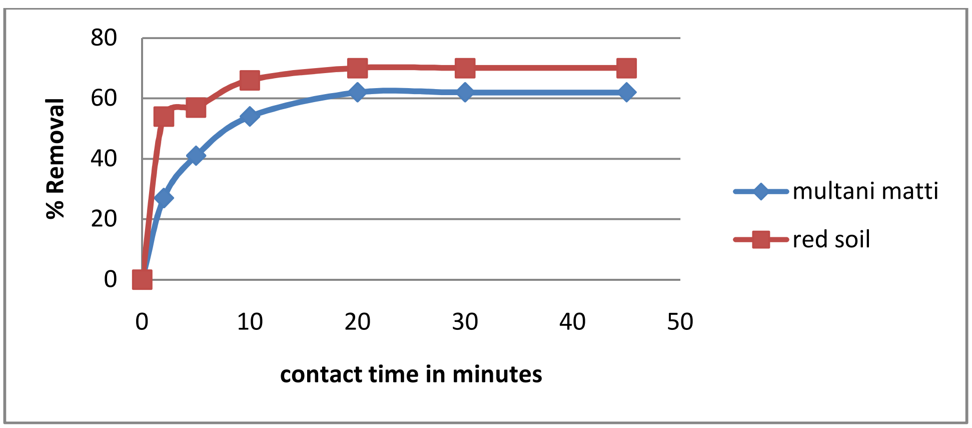

Figure-1
Variation of contact time between adsorbate and adsorbents

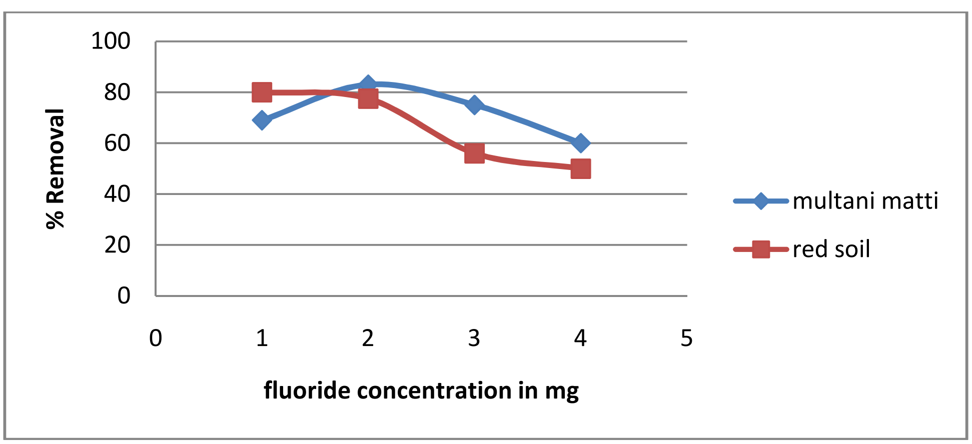

Figure-2
Variation of initial concentration

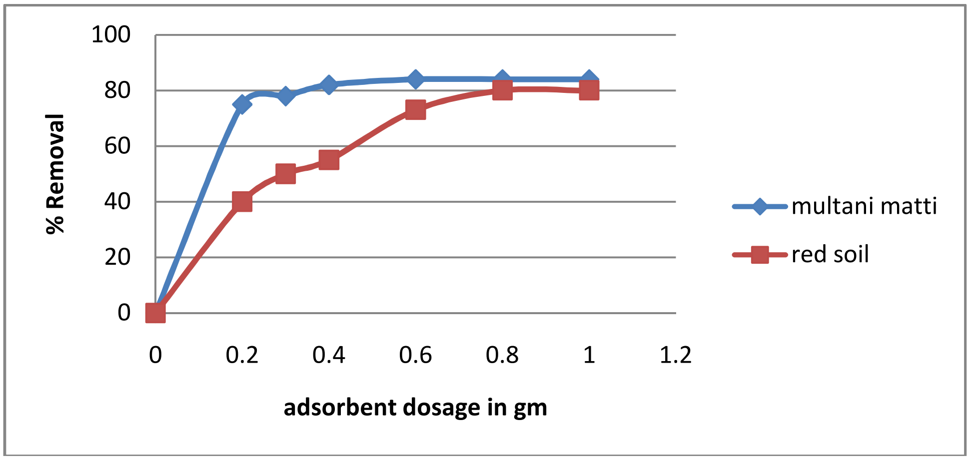

Figure-3
Variation of adsorbent dosage

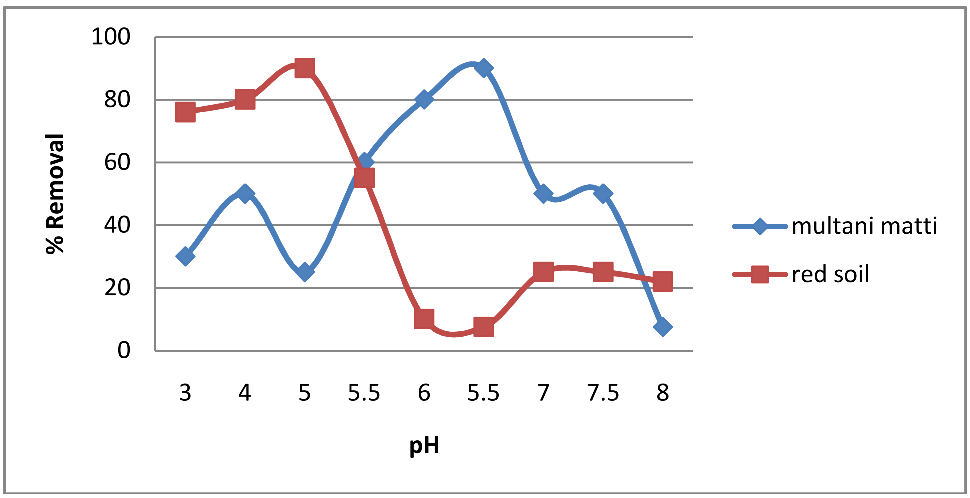

Figure-4
Effect of pH on adsorption of fluoride

Effect of temperature on adsorption of fluoride:

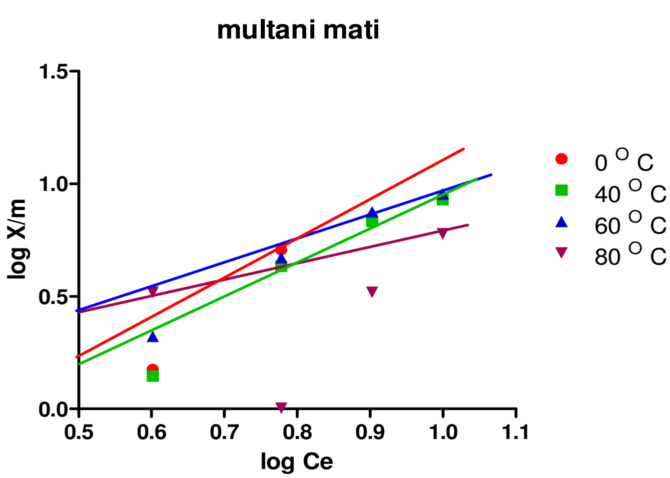

Figure-5(a)

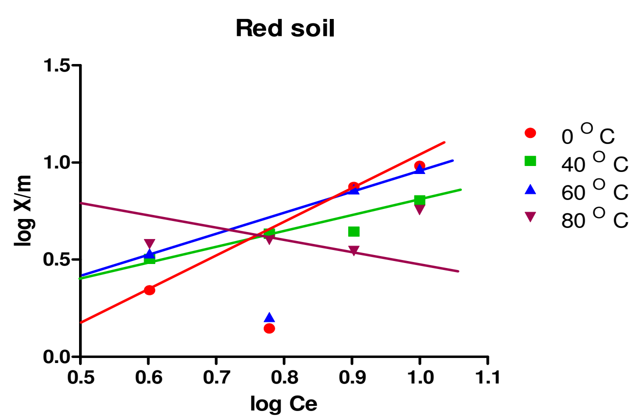

Figure-5(b)
Relationship between log Ce and log x/m (Freundlich isotherm)

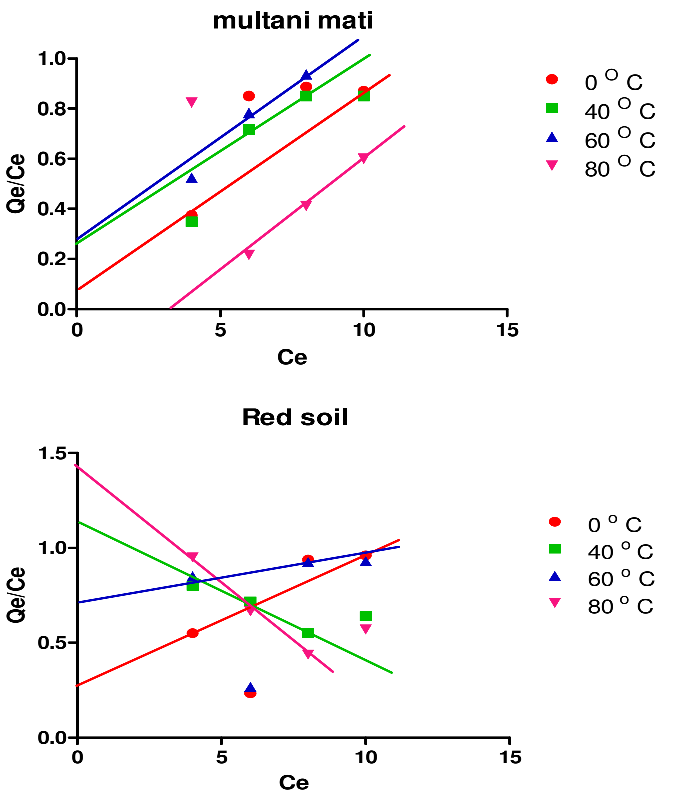

Figure-6
Relationship between Qe/Ce and Ce

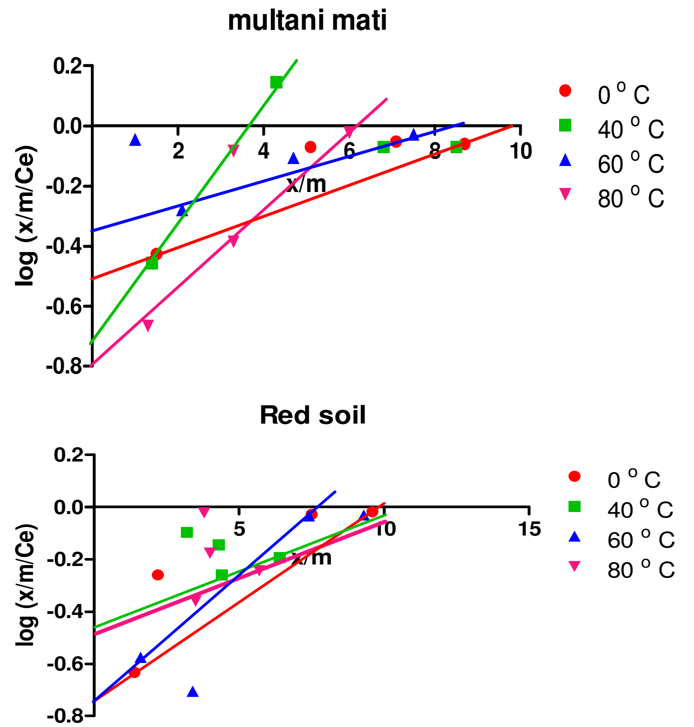

Figure-8
Relationship between log (x/m/Ce) and x/m

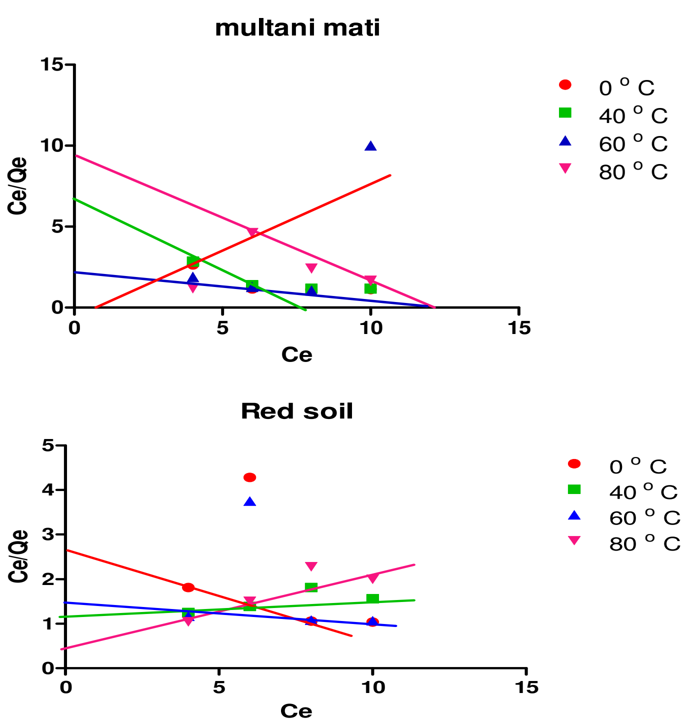

Figure-7
Relationship between Ce/Qe and Ce (Langmuir isotherm)

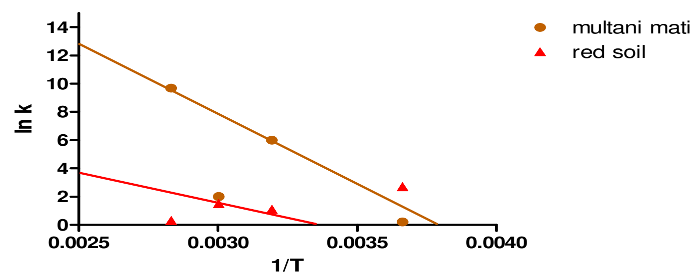

Figure-9
Relationship between ln k and 1/T

The adsorption isotherms are plotted between log x/m and lod Ce (freundlich isotherm) and Ce/qe Vs Ce (Langmuir isotherm) and log (x/m/Ce) Vs x/m for multani matti and red soil. The effect of adsorption temperature on uptake of fluoride by the red soil and multani matti was carried out in the temperature range 0^0C to 80^0C. An increase in the temperature resulted in an increase in the amount of fluoride adsorbed per unit mass of clay adsorbents. The figure- V represents the relationship between log x/m and log C. this figure represents Freundlich adsorption isotherms and shows linear relationship at all temperature in case of multani matti and the lines gets deviated from linearity at (60 to 80^0C) high temperature in case of red soil. The figure–7, represents Langmuir adsorption isotherms at 0 to 80^0C. from the figure it was found that in both condition (red soil and multani matti) the lower temperature is not favourable for adsorption of fluoride. This indicates that the adsorption capacity is increases with increasing in temperature. The thermodynamic parameters, ΔH, ΔS and ΔG, for the adsorption process are computed from the plots of In k Vs 1/T. The adsorption enthalpy, ΔH, is indicates that the adsorption interaction is exothermic. The positive value of ΔS shows that that increased randomness at solid interface during the adsorption of fluoride by multani matti and red soil.

$\Delta G = - RT\log K_c$

$\ln K_c = \Delta S/R - \Delta H/RT$

The negative value of ΔG indicates the feasibility of process and indicates the spontaneous nature of adsorption [23-29]

Kinetic models: Figure-10 represents a plot of the Lagergren equation for the result of adsorption of fluoride from industrial waste water by using multani matti and red soil. The plot does not showing the linear relationship between log (qe-qt) and time in minutes. It represents that lines gets deviated from linearity. From this figure it was found that Lagergren Pseudo first order equation is not suitable for adsorption of fluoride by using multani matti and red soil.

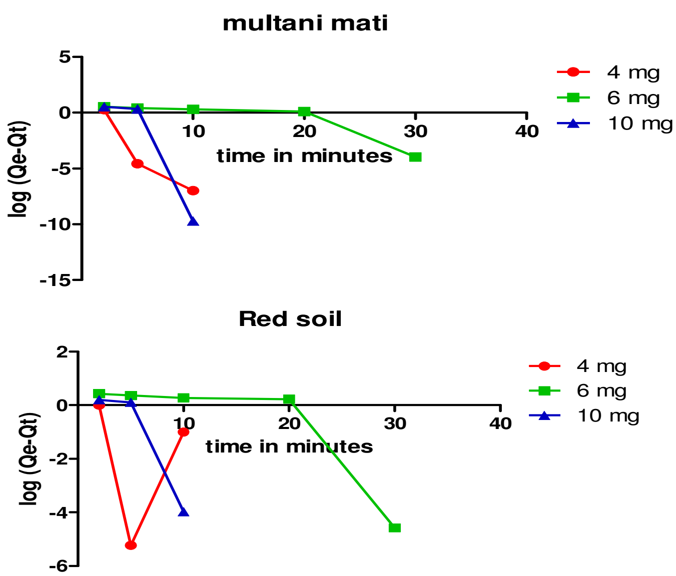

Figure-10
Lagergren (Pseudo First Order Equation) Model

The result of the sorption of fluoride by using multani matti and red soil has been represented in the form of Elovich equation in figure- 11, at various initial fluoride concentration (4 mg, 6 mg, 10 mg). From the plot a linear relationship between the amount of fluoride adsorbed, qt and In (t) was established. These plots showed different distinct linear regions within individual sets of data.

The same data are shown as pseudo second order equations in figure -12. These plots show the fits had good correlation when the pseudo second order euation was employed. Thus, increasing the fluoride concentration from 4 mg to 10 mg the fluoride sorbed at any contact time increases. This is obvious for higher concentration values, as a more efficient utilization of the sorptive capacities of the sorbent would be expected due to greater sorption driving force.

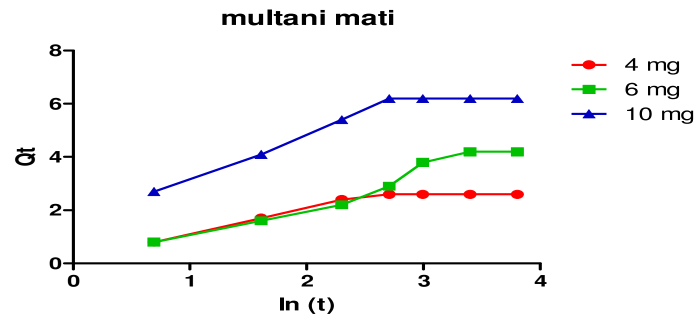

Figure-11(a)

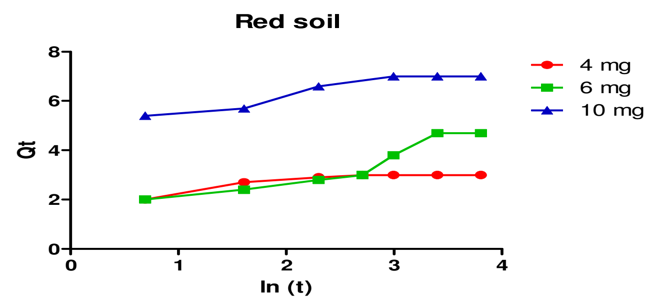

Figure-11(b)
Elovich Model

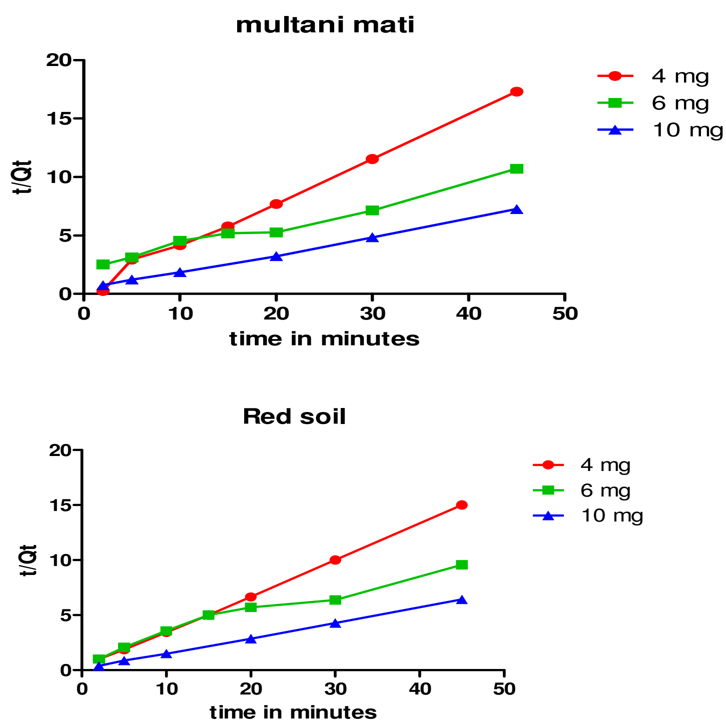

Figure-12
Pseudo Second Order Model

Conclusion

In the present study the adsorbent (red soil) selected are naturally available materials. The cost of producing the material is reducer. It is abundantly available in different parts of Andhrapradesh. The results obtained in this study to develop a column study or for designing a plant for defluoridation. The red soil and multani matti does not cause any increase in pH, or any increase of Iron and aluminum concentration in effluent and drinking water.

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