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Removal Of Fluoride From Water And Waste Water By Using Low Cost Adsorbents

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Abstract: India is among 23 nations where in a large population suffers from dental and skeletal flourosis due to high fluoride concentration in ground water. The prominent states, which are severely affected, are Andhrapradesh, Rajasthan, Gujarat, Uttar Pradesh and Tamil Nadu. Fluoride beyond desirable amounts (0.6 to 1.5 mg/l) in ground water is a major problem in many parts of the world. Taking the severity of the problem into consideration, the present study is carried out to study on effective and cheap adsorbents for the removal of fluoride from the water. Batch adsorption studies are carried out. Batch adsorption studies demonstrate that the adsorbents have the significant capacity to adsorb the Fluoride from water. The experiments were carried out in laboratory on certain low cost adsorbents like concrete, ragi seed powder, Red soil, horse gram seed powder, orange peel powder, chalk powder, pineapple peel powder and multhani matti.
Key words: Fluoride, Adsorption, Multani matti, Chalk powder, pine apple peel, Batch adsorption.

Introduction:

There are three kinds of water available namely rain water, ground water and surface water. Rain water is clean and it is suitable for cooking and drinking. But storage of rain water requires large storage reservoirs which are expensive to build and to maintain. Rain fall is also uneven ground water sources are bore wells and wells. Surface water sources are tanks, dams, canals and rivers. In Andhrapradesh, nalgonda is a district which has a population of 3,483,648. Clean drinking water, water supply for irrigation is a major and most important problem in nalgonda. Nearly 500 villages are affected by high fluorine content in water. One million people are affected by fluorosis in nalgonda district. Due to scarcity of waters, the people depend on well water and bore well waters. The range of fluoride content is ranging between 0.4 to 20 ppm in different villages of nalgonda district. Fluorosis is a disease caused by excessive ingestion of fluoride through water and food. Previous attempts to solve the fluorosis problem in Nalgonda by using the alum precipitation technique have been of little success. Instead the Sai Oral Health Foundation assisted by the Government of Andhra Pradesh, has adopted a strategy of providing low fluoride water in affected villages through the use of bone char based domestic defluoridators and rainwater harvesting systems.

Treatment of water and wastewater containing fluoride ions requires a suitable and effective method. Membrane filtration [1], precipitation [2], nanofiltration [3], ion-exchange [4], electrocoagulation flotation [5], and

adsorption [6] have been used for fluoride removal. Among these methods, adsorption is the most effective and widely used method because it is universal, has a low maintenance cost, and is applicable for the removal of fluoride even at low concentrations. In recent years, considerable attention has been focused on the study of fluoride removal using natural, synthetic, and biomass materials such as activated alumina [7], fly ash [8], alum sludge [9], chitosan beads [10, 11], red mud [12], zeolite [13], calcite [14], hydrated cement [15], attapulgite [16], and acid-treated spent bleaching earth [17]. As the many regions in the Andhrapradesh are affected by fluoride the present study is carried out to develop a cheap and effective method for the removal of fluoride in water.

Materials and Methods:

In this paper an attempt has been made to suggest certain low cost materials as effective adsorbents of fluoride. The adsorbents primarily screened were horse gram powder, ragi powder, multhani matti, red mud, concrete, pine apple peel powder, chalk powder and orange peel powder. Initially, all the adsorbents are screened by adding 1gm of each adsorbent to 100 mL of solution of Fluoride.

Adsorption methods are adopted for removal of fluoride and these methods are suitable when fluoride is present in low concentrations. For this purpose, an aqueous solution of 100 mL of fluoride of various concentrations is taken in 100 mL Stoppard bottles and 1 gm of adsorbent is added to the solutions. Batch adsorption experiments are carried out at room temperature, a contact time of 24 hrs is maintained. The initial and final concentrations of aqueous solutions solution of fluoride and industrial waste water were determined by spectrophotometer and percentage removal of fluoride was determined.

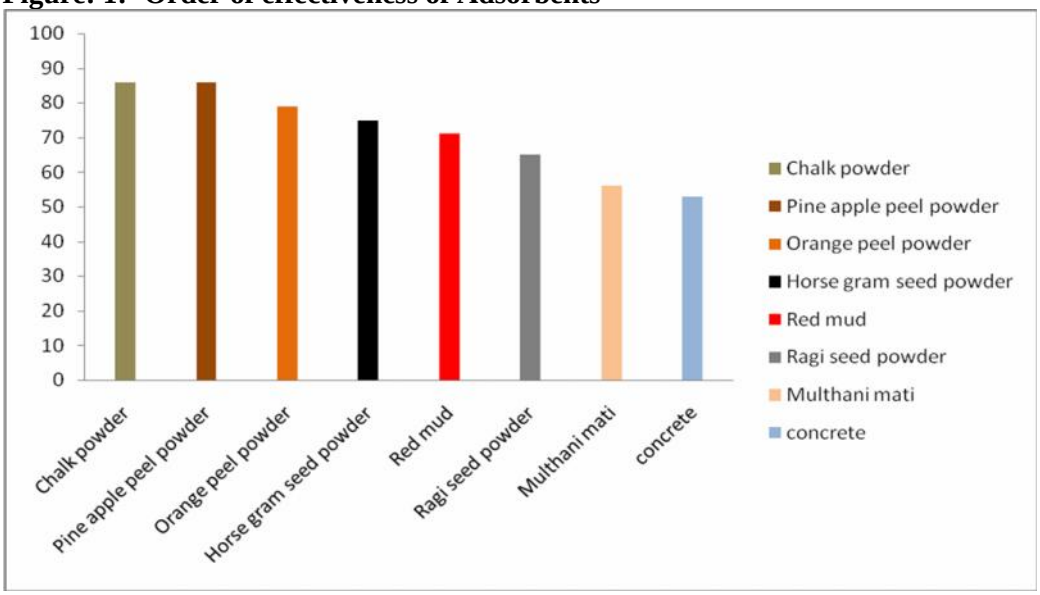
Table 1: Adsorbents and sampling sites

Adsorbent	**Sampling site**
Horse gram powder	Fields
Ragi powder	Fields
Multhani matti	Super market
Chalk powder	Class room
Red soil	Construction site in Hyderabad city
concrete	Construction site in Hyderabad city
Pine apple peel powder	field
Orange peel powder	field

Table 2: Percentage removal of Fluoride with different adsorbents

S.No	Adsorbents	Initial concentration of fluoride in mg/l	Final concentration of fluoride in mg/l	Amount adsorbed in mg/l	% removal
01	Chalk powder	12	1.6	10.4	86
02	Pine apple peel powder	12	1.6	10.4	86
03	Orange peel powder	12	2.5	9.5	79
04	Horse gram seed powder	12	3	9	75
05	Red mud	12	3.4	8.6	71
06	Ragi seed powder	12	4.2	7.8	65
07	Multhani mati	12	5.2	6.8	56
08	concrete	12	5.6	6.4	53

Figure: 1:- Order of effectiveness of Adsorbents



Chalk powder, pine apple peel powder > orange peel powder > Horse gram seed powder, > red mud > ragi seed powder > multhani mati > concrete.

Results And Discussion:

The adsorbents selected for the present study are Chalk powder, Ragi seed powder, horse gram seed powder, pine apple peel powder, orange peel powder, red soil, multhani matti and Concrete and the sampling sites are tabulated in Table 1. From Table 2 it is observed that the order of adsorption is Chalk powder, pine apple peel powder, orange peel powder, Horse gram seed powder, red soil, ragi seed powder, multhani mati and concrete. The adsorption capacity is more at lower concentrations compared to higher concentration. In the present study, it is observed that physical adsorption is taking place. Multhani matti is known as montmorillonite and it contains grains of fine sand particle. They contain complex multi centre crystalline structures of oxides and hydroxide of magnesium, aluminum, zinc and silicon and it is known as Fullerene mud and rich in lime.

Chalk powder is the waste material collected from classrooms. Chalk is the form of Calcium carbonate with minor amount of silt and clay. As Calcium carbonate decomposes only at 900^0C, the adsorption taking place in the present study is physical adsorption. Chalk powder due to certain porosity adsorbs fluoride from aqueous solution.

Horse gram seeds are collected from fields. It is a bio adsorbent and it consists of higher trypsin inhibitor and heamagglutinin activities and polyphenols. These components are responsible for adsorption observed in the present study .hence it is an effective adsorbent for removal of fluoride.

Ragi seeds are the low cost material collected from fields .it act as a bioadsorbent and it consist of proteins, fat, and fiber. These components are responsible for fluoride adsorptiom from aqueous solution.

Red soil is the waste material collected from construction sites and it is used as the adsorbent. It has a high porosity and it is present at Hyderabad city which has iron oxides, and chemical reactents of fluoride which may forms other useful products.

Concrete material is a mixture of silica, stones and cement in the ratio of 1:2:4. As the material consists of all these substances, it is selected as adsorbent. Concrete powder which is a mixture of Portland cement, sand stones in the required strength has adsorption capacity and has shown less adsorption capacity when compared to other adsorbents.

Orange peel chemical composition as well as some trace elements, ascorbic acid, carotenoids dietary fiber, total polyphenols and their antiradical efficiency, using the 2,2-diphenyl-1-picrylhidracyl (DPPH) were assessed in the dried peels of orange (Citrus sinensis), due to certain porosity of orange peel powder adsorbs fluoride from aqueous solution.

Among the all above bio and waste material adsorbents concrete is selected for further studies to check the effect of contact time, concentration, adsorbent dosage and temperature on adsorptive removal of fluoride. Present studies shows that concrete has the capacity to remove fluoride at lower concentration only. The adsorption capacity

is low when compare to other adsorbents. In recent days due to rapid industrialization and urbanization the construction of buildings are taking place, for that they are using concrete as an ingredient to construct a building. After usage builders are dumping the waste concrete into dump yards of Hyderabad city. Taking this factor into consideration concrete selected as adsorbent for removal of fluoride from water and waste water.

Effect of Contact time:

Concentration of Fluoride: 10 mg/ lit.
Volume of fluoride solution: 1 lit.
The optimum contact time for the removal of fluoride is in between 20-30 minutes depending upon the concentration of fluoride. It is observed from figure-1 that the adsorption capacity of fluoride is increases with increase in contact time. The graph showing a smooth curve the initial steep rise in the curve is due existence of free valencies on the surface of horse gram seed powder. After the establishment of equilibrium the lines in the figure become parallel to the time axis, this can be explained on the basis of reaching saturation point. The percentage removal of fluoride with contact time follows a smooth curve which indicates the mono layer coverage.

Effect of Initial Concentration:

When the initial concentration of fluoride was changed (1-4 mg/lit) with a constant concrete amount of one gram, the amount adsorbed per unit mass showed decrease with rise in the concentration of fluoride. At low initial fluoride concentration, the ratio of the fluoride ions to the number of available adsorption site are high and these sites are decreses with increase in fluoride concentration. As a result the amount adsorbed per unit mass is decreases with increase in fluoride concentration.

Figure- 2: Variation of contact time

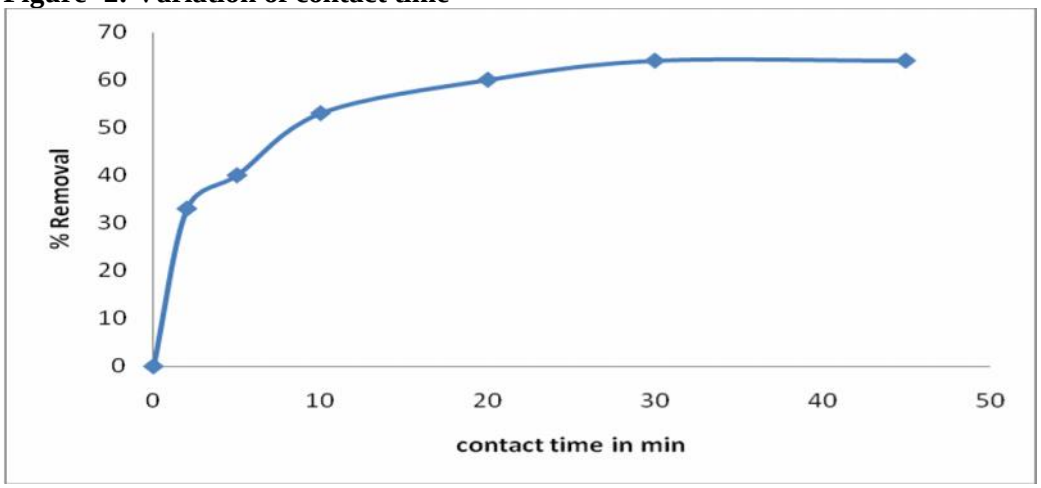
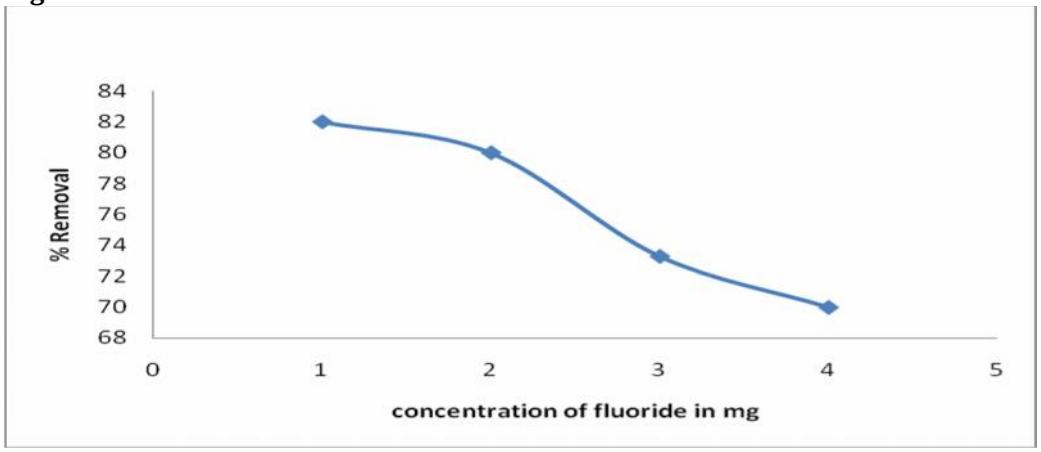


Figure-3: Variation of Initial fluoride concentration:



Effect of Adsorbent Dosage:
The amount of concrete adsorbent was varied from 0.2 gms to 1.4 gms with a constant initial fluoride concentration of 10 mg/L and agitation time of 60 minutes at room temperature. The amount of fluoride adsorbed per unit mass of the adsorbent is increase with increase in amount of adsorbent and became constant at 0.6 gms of adsorbent.

Effect of Temperature on adsorption of Fluoride:

Freundlich Isotherm:

The linear form of Freundlich equation is represented as follows (18)

Log x/m = log k_f + 1/n log C_e

Where x is the amount of fluoride adsorbed in mg. m is the weight of adsorbent in grams. C_e is the residual concentration of fluoride at equilibrium in mg.

K_f and 1/n are Freundlich constants related to the adsorption capacity and adsorption intensity respectively and are evaluated by least square fitting of the data by plotting log x/m vs log C_e with a slope of 1/n and intercept of log K_f. from the figure and statistical analysis it was observed that the experimental data is fit for Freundlich Adsorption isotherm studies compare to Langmuir adsorption isotherm.

Figure-4: Variation of Adsorbent doage on fluoride adsorption

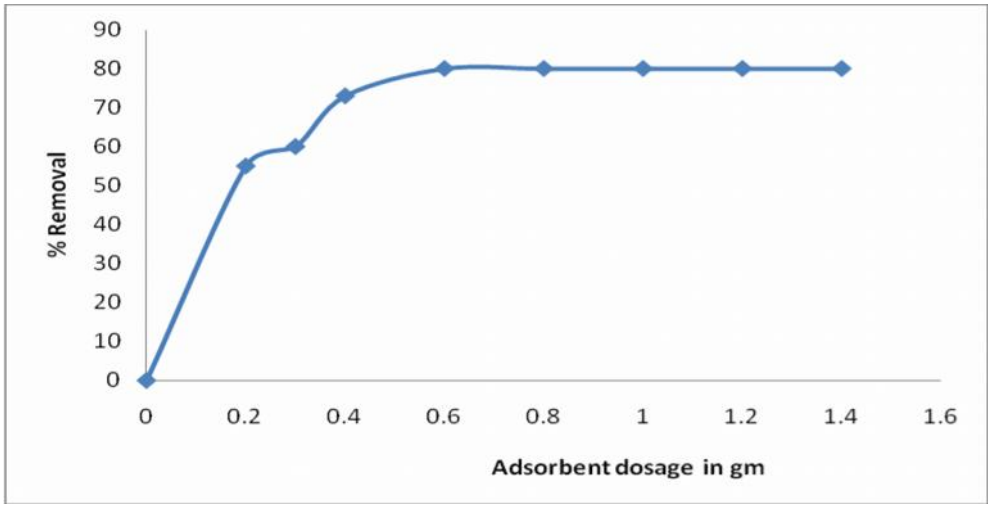
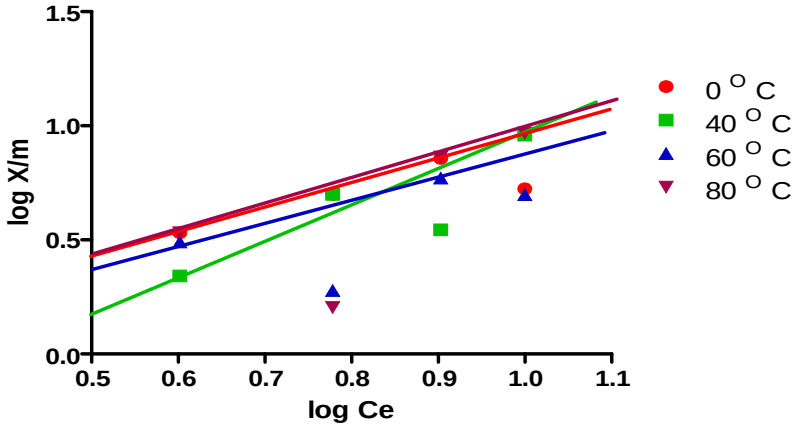


Figure-5: Relationship between log x/m and log Ce (Freundlich Isotherm)



Langmuir isotherm:

Langmuir isotherm model which is probably the best known and most widely accepted and applied adsorption isotherm. The study of the Langmuir isotherm is essential in assessing the adsorption efficiency of the adsorbent. This study is also useful in optimizing the operating conditions for effective adsorption. In this respect, the Langmuir isotherm is important, though the restriction and the limitations of this model have been well recognized,

The Langmuir and the rearranged Langmuir equations are as fallows

$1/qe = 1/Q_o b.\ 1/Ce + 1/Q_o$

$Ce/Qe = Ce/Q_o + 1/Q_o b$

Where qe = the amount of fluoride removed at equilibrium

Ce = the equilibrium concentration of fluoride

Q_o = the Langmuir constant, related to the adsorption capacity

b = the Langmuir constant, related to the energy of adsorption.

From the figure-6 it was observed that the adsorption capacity is increases with increase in temperature. From the statistical analysis it was found that the experimental data is not fit for Langmuir adsorption isotherms.

Kinetic Models:

The adsorption data were tested with pseudo first order kinetic model. The results shown in figure-7. The lagergren pseudo first order mechanism shows poor linear plots. The same data were tested with pseudo second order kinetic mechanism, and results are shown in figure-. The plots have better linearity and the adsorption of fluoride by using concrete is follows pseudo second order kinetic model. The result of sorption of fluoride by using concrete has been represented in the form of Elovich equation in Figure-8, at various initial concentration of fluoride. From the plot a linear relationship between the amount of fluoride adsorbed, q_t and In (t) was established. These plots showed different distinct linear regions within individual sets of data and follows pseudo second order kinetics.

Figure-6: Relationship between Ce/Qe and C_e

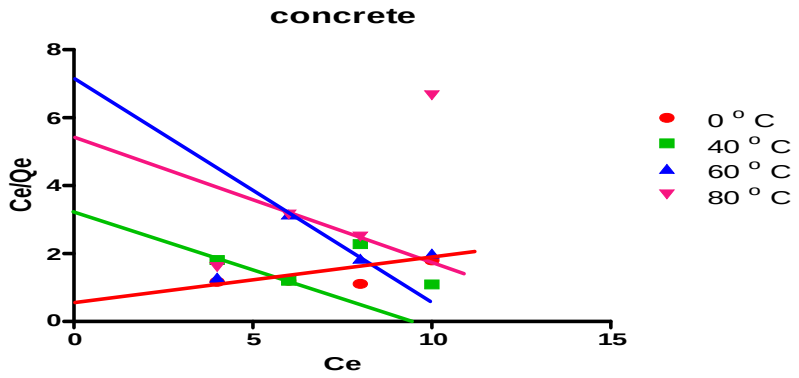


Figure-7: Pseudo First order kinetic model:

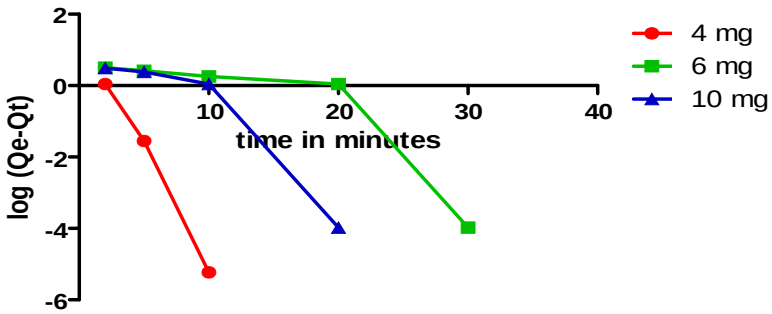


Figure-8: Elovich model

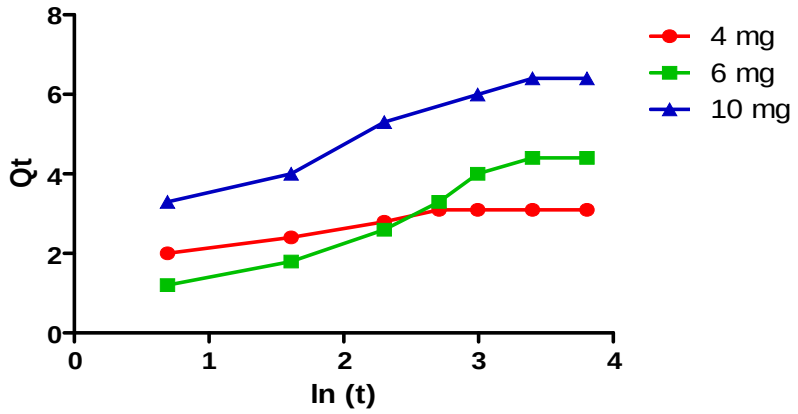


Figure-9: Pseudo Second Order Model:

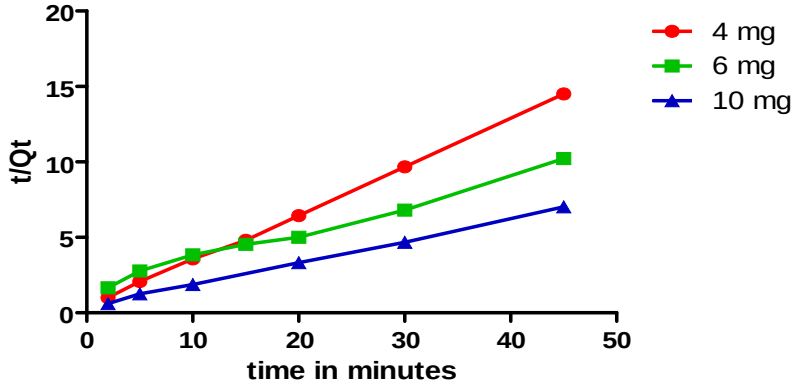


Table-3: Adsorption isotherm constant and statistical comparison values of adsorption isotherm models for Fluoride adsorption by Concrete.

Isotherm models	Isotherm parameters	Adsorption at different temperature.			
		0°C	40°C	60°C	80°C
Langmuir Adsorption isotherm	R^2	0.520	0.062	0.018	0.712
	RSS	0.149	0.868	1.794	4.160
Freundlich Adsorption isotherm	R^2	0.617	0.696	0.366	0.449
	RSS	0.020	0.061	0.093	0.198

Table-4: Adsorption Kinetic constant and statistical comparison values of adsorption kinetic models for Fluoride adsorption by Concrete.

Kinetic Model	Kinetic parameters	Adsorption at different concentration		
		4 mg	6 mg	10 mg
Pseudo first order kinetic model	R^2	0.993	0.732	0.886
	RSS	0.097	3.958	1.573
Elovich Model	R^2	0.999	0.987	0.998
	RSS	0.128	0.623	0.035
Pseudo Second order kinetic model	R^2	0.993	0.959	0.965
	RSS	0.123	0.401	0.293

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