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Defluoridation of Water Using Orange Peel Powder As Adsorbent: Kinetics and Equilibrium Studies

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Abstract: Fluoride contamination of ground water is one of the serious problem in world. Larger contributor of fluoride is drinking water. Geological and Anthropogenic, two factors are responsible for contamination of water with fluoride. Geological conditions involve physiological conditions of rock decomposition dissociation and subsequent dissolution along with long residence time which are responsible for F⁻ leaching. Anthropogenic factors involve industrialization, urbanization and improper utilization of water resources. In lower conc. fluoride is an essential nutrient which aids in formation of bones, prevents tooth decay whereas in high conc. it causes fluorosis, brittling of bones, curvature of bones, mental disorders etc. Permissible limit of fluoride in drinking water is 1.5 ppm. Due to harmful effects of fluoride it is urgent to remove fluoride from water. Present study deals with removal of fluoride by using orange peel powder as adsorbent. The effect of various operational parameters was studied by varying the adsorbent dose, contact time, initial fluoride concentration and pH. Equilibrium and Kinetic study of adsorption has also been studied.

Keywords: Adsorption, Langmuir, Fluoride, Kinetics, Spectrophotometer.

1. INTRODUCTION: Water is an important natural resource. It covers around 70% of earth's surface and makes up around 60% of the human body. It is an important resource for both domestic as well as industrial purposes. Water is required for all forms of life and safe drinking water is very important for every living organism. Pure water is not available at all [1]. Water may be contaminated by natural sources and anthropogenic sources [2]. Volcanic eruptions, Earthquakes, Tsunamis, Weathering of rocks etc. are known to alter water naturally while industrialization, disposal of waste in water bodies, oil spills are the man made sources of water pollution. In simple words the contamination of water bodies means water pollution. Water pollution is a major global problem and is the main cause of diseases and deaths [3]. Water Pollution occurs when the substances those alter the water quality in negative way are discharged into it. Two main sources of water pollution can be point and Non- point. Point sources means the pollutants those belong to a single source. e.g. emissions from industries. The point sources of pollution can be effectively controlled. Non- point sources means pollutants emitted from multiple sources. Contaminated water after rains that has travelled through several regions is example of non-point sources [4].

Water gets contaminated via waste from agriculture waste, waste from construction sites and then enter into streams and lakes. Non- point sources of water pollution are spread over large areas. It is quite difficult to control non- point sources. There are various causes of water pollution like industrial waste, sewage waste, mining activities, marine dumping, burning of fossil fuels, chemical fertilizer and pesticides, radioactive waste etc. Industrial waste water comprises inorganic and organic chemicals. These chemicals may be toxic to aquatic life as well as terrestrial life even in very low concentration. Therefore, treatment of such toxic waste is required before their discharge into water bodies.

Fluoride is the major inorganic pollutant of natural origin found in the ground water. Fluoride contamination in ground water is one of serious problems in the world [5,6]. Water is a considerable channel of fluoride intake by living organisms [7]. Depending upon the concentrations of fluoride available in water, it is either beneficial or detrimental [8]. Fluoride ions enter into water bodies naturally by the process of dissolution of rock minerals at a gradual pace. Considerably high amount of fluoride ions escaping into the water by means of various applications such as excessive use of phosphate fertilizers and pesticides, sewage sludge in agricultural practices thus leading to the remarkably high concentrations [9].

Weathering of fluoride containing rocks like topaz, fluorite, fluor spar, cryolite, fluorapatite etc and soils leads to leaching of fluoride ions into ground water [10]. Fluorides in the form of salts with monovalent cations i.e. NaF and KF are water soluble but salts of fluoride with divalent cations such as CaF₂ are insoluble in water.

Effects of Fluoride

Depending on the concentration of fluoride ions in drinking water, the impact of fluoride ions can be beneficial or harmful for human beings. When present within permissible limits (1.5 ppm), fluoride is beneficial in human body for calcification of dental enamel and for the maintenance of healthy bones. Beyond this level it is harmful and not suitable [11]. Fluoride in drinking water has a profound effect on teeth and bones. Upto a small level (1–1.5 mg/L) it strengthens the enamel of teeth. If range of fluoride in drinking water is 1.5–4.0 mg/L then it results in dental fluorosis and higher fluoride concentrations (4–10 mg/L) leads to skeletal fluorosis [12].

High fluoride concentrations produce, reproduction problems and immunological effects [13], interference in metabolism of carbohydrates, proteins, vitamins and minerals [14].

Due to high toxicity of fluoride ions, there is urgent need to treat fluoride contamination to make it safe for human use. The process of removal of fluoride ions is called defluoridation. There are many techniques of defluoridation like ion exchange technique, membrane filtration technique [15] but those are not in much use because of their high cost and inefficiency.

In recent years biosorption has emerged as most suitable technique for the removal of fluoride ions due to convenient operational conditions, low cost, minimum chemical/biological sludge and regeneration properties.

2.EXPERIMENTATION:

2.1 Adsorbent:

Peels of orange fruit were used as such in natural form without any chemical, thermal or surface modification. Peels of orange fruit were collected, washed under tap water and double distilled water to remove soil, dust and other contaminants. Peels were cut into small pieces, dried in air and sunlight for 72 hours to remove moisture and then crushed in grinder to get fine powder. Prepared bioadsorbent peel powder was stored in air tight containers to protect it from moisture.

2.2 Adsorbate:

Groundwater obtained from Giddarbaha have fluoride conc. 5ppm, it is harmful because permissible limit of fluoride is 1.5ppm. It act as adsorbate so act as stock solution. For study of effect of initial fluoride conc. fluoride solution of 100mg/L was prepared by dissolving 0.221g of AR Grade sodium fluoride (Merck) in 1 L of double distilled water. The solution was diluted to obtain working solution.

2.3 Adsorption Experiment:

The Batch experiment studies were performed by shaking fluoride solution of known concentration with bioadsorbents in shaker. Then sample was filtered through Whatmann no.42 filter paper. Filtrate was analysed for determination of fluoride conc. by SPADNS Method using UV-Spectrophotometer at wavelength of 570nm.[16] The results were reported in terms of percentage removal and adsorption capacity. The percentage removal (% Removal) of the Fluoride ions was calculated for each run by following expression:

$$\% \text{ Removal} = \left(\frac{C_i - C_e}{C_i} \right) \times 100$$

where C_i and C_e were the initial and final concentrations of fluoride ions in the solution.

Further adsorption capacity was calculated in terms of the amount of fluoride ions adsorbed per unit mass of biosorbent by using the expression:

$$Q = \left(\frac{C_o - C_e}{m} \right) \times V$$

Where Q (mg/g) is the amount of fluoride adsorbed, C_o (mg/l) is the initial concentration of Fluoride, C_e (mg/l) is the final concentration of fluoride, V is the volume of Fluoride solution (l) and m (g) is the mass of biosorbent used.

3. RESULTS AND DISCUSSION:

Preparation of Standard Curve: Fluoride standard sample in the range of 0.25 mg/l to 2.5 mg/l were prepared from stock solution. The spectrophotometer was set to zero absorbance with reference solution and absorbance readings of standard were obtained.

Table1: Absorbance readings of standards

Conc. In mg/l	Absorbance
0.25	0.418
0.5	0.378
1	0.297
1.5	0.22
2	0.141
2.5	0.079

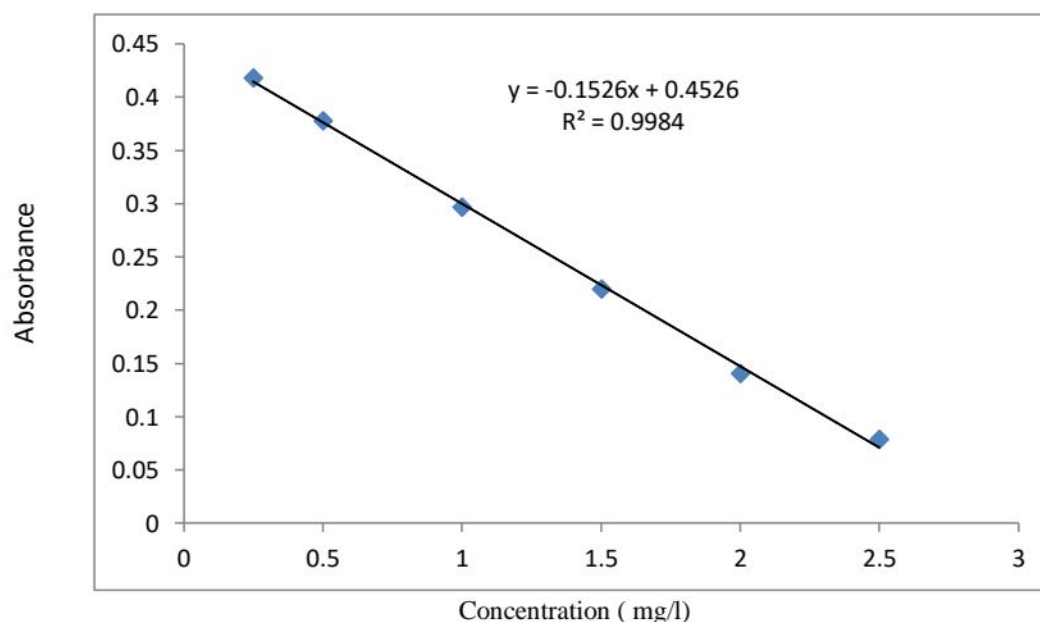


Figure 1: Absorbance w.r.t different conc. of fluoride

After preparing the standard curve effect of various parameters on adsorption were studied. For this stock solution of 5ppm fluoride conc. is shaken for 1 hour with 1 gm peel powder & filtered & filtrate was analyzed for residual conc. of fluoride.

Effect of various process parameters on removal efficiency

- a) **Effect of pH:** pH plays an important role in adsorption process on bioadsorbents. Adsorption of fluoride as a function of pH was measured and results are shown in Figure 2. A range of pH from 2.0 to 10.0 was selected. Maximum adsorption of fluoride was found at pH 6. In the alkaline pH range, there was sharp drop in adsorption, which may be due to the competition of the hydroxyl ions with the fluoride for adsorption.

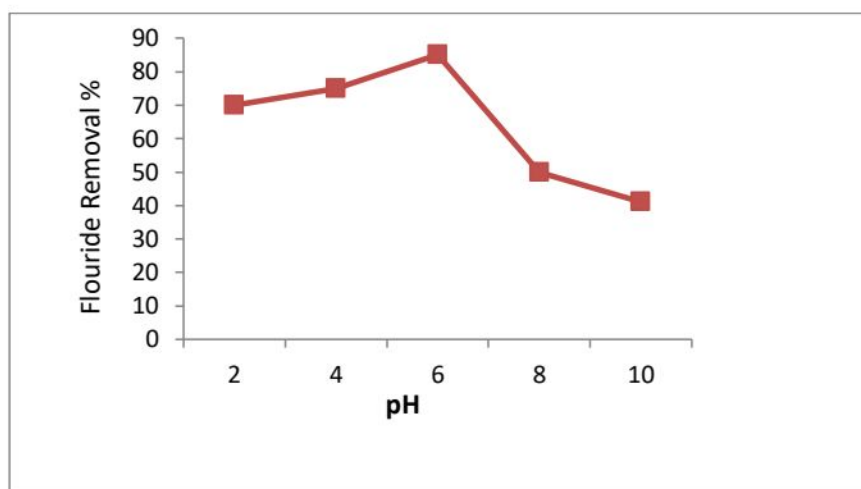


Figure2 : Effect of pH on the percentage removal of fluoride ions

- b) **Effect of contact time:** The effect of contact time was studied by varying the contact time (20-70 min) keeping other parameters constant on removal efficiency of biosorbent..

A graphical representation of percentage removal efficiency with contact time (min) is shown in figure. It was found that adsorption percentage increased from 60% to 74% as the contact time between fluoride ion and biosorbent was increased from 20 min. to 70 min..

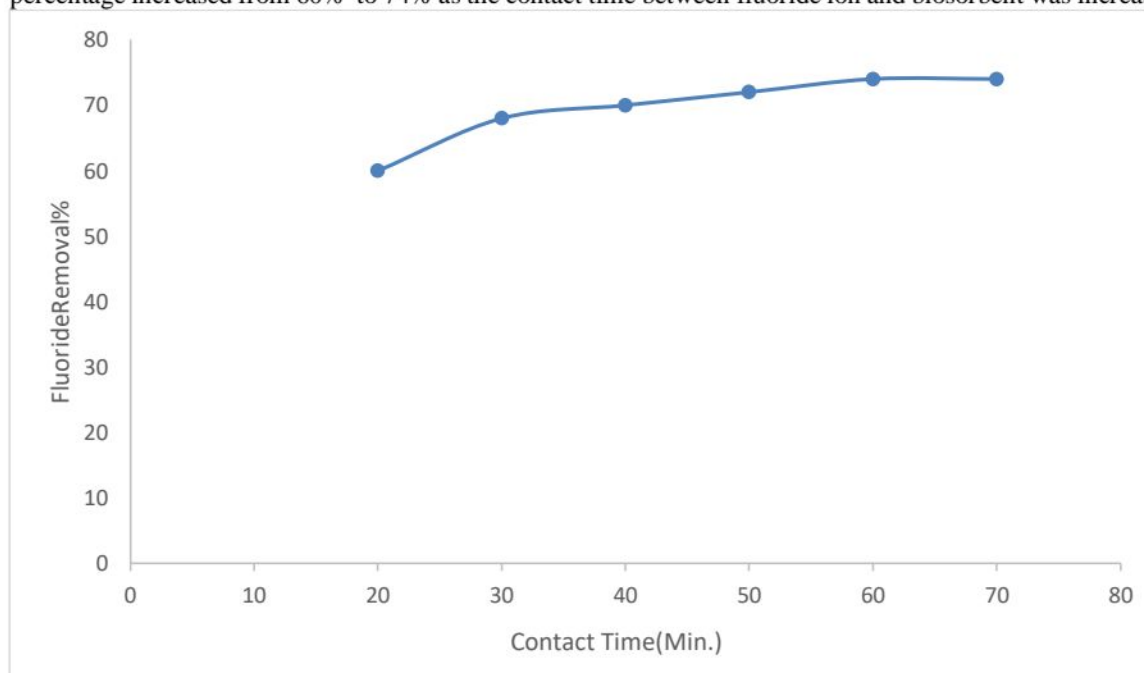


Fig3: Effect of Contact time on removal efficiency of fluoride ions

- c) **Effect of initial fluoride concentration:** Effect of initial fluoride conc. on the percentage removal of fluoride was studied at different initial fluoride conc. ranging from 5 ppm to 9 ppm by keeping all other parameters constant. For this purpose standard solution of sodium fluoride was used. Figure shows that with increase in initial fluoride ion concentration, the percentage removal of fluoride ion decreases. It may be because at higher adsorbate conc. the binding capacity of adsorbent approaches saturation and all the binding sites available for the adsorption of fluoride ions gets filled and then there is decreased removal efficiency.

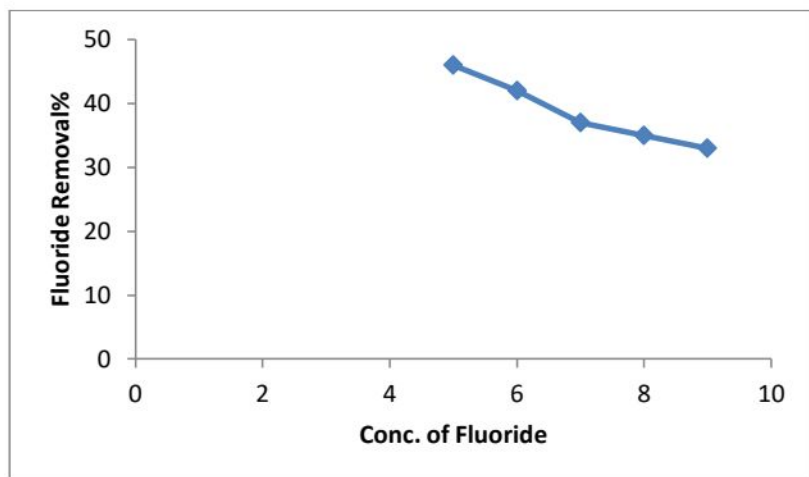


Fig. 4: Effect of initial fluoride concentration on percentage removal of fluoride ions

d) Effect of Adsorbent Dose: The percentage removal of fluoride ions increases with increases in doses from 0.2 g to 1.2 g . It has been observed that after certain dose of bioadsorbent, the maximum adsorption is attained and hence the amount of ions remain constant even with further addition of dose of adsorbent. The increase in fluoride removal %age with increase in adsorbent dose is due to the greater availability of exchangeable sites at higher conc. of adsorbent. Any further addition of adsorbent beyond this did not cause any significant change in the adsorption. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles.

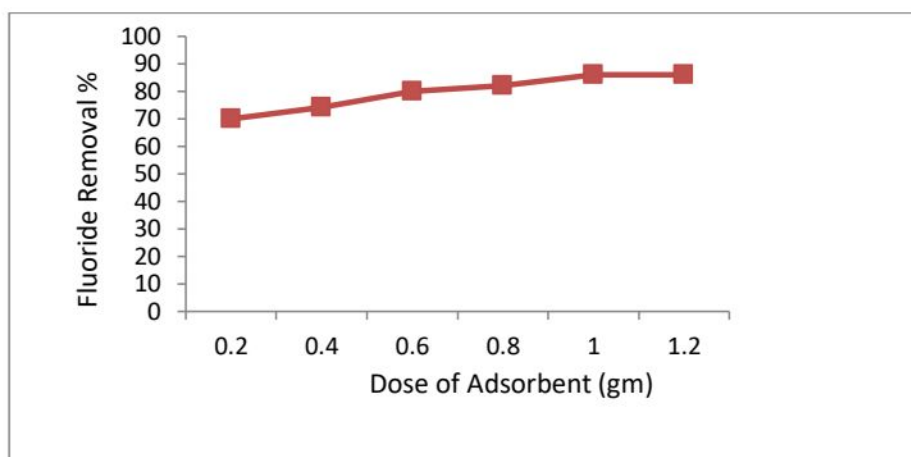


Figure :5 Effect of adsorbent dose on the percentage removal of fluoride ions

Equilibrium Studies

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbatespecies[17]. Adsorption data are usually described by adsorption isotherms, such as Langmuir, Freundlich isotherms shown in table.

Table2: Various parameters required for Langmuir and Freundlich isotherms

C_i	C_e	X	$x/m=q_e$	C_e / q_e	$\log C_e$	$\log q_e$
5	2.7	2.3	2.3	1.1739	0.4313	0.3617
6	3.5	2.5	2.5	1.4	0.544	0.3979
7	4.4	2.6	2.6	1.692	0.6434	0.4149
8	5.2	2.8	2.8	1.857	0.7160	0.4471
9	6.0	3.0	3.0	2.0	0.7781	0.4771

Where C_i = initial conc. of fluoride in solution ; C_e = equilibrium conc. of fluoride in solution
 m = weight of adsorbent taken; q_e = amount of fluoride adsorbed per unit weight of adsorbent

a) Langmuir isotherm :

The Langmuir model is based on the assumption that maximum adsorbent occurs when a saturated monolayer of solute molecules is present on the adsorbent surface. Langmuir model signifies the homogeneous adsorption in which all adsorption sites have equal affinity for the adsorbate. Linearized form of Langmuir isotherm is given as,

$$(C_e/q_e) = (1/Q_0b) + (C_e/Q_0)$$

Langmuir constant Q_0 and b is calculated from intercept and slope of the graph plotted between C_e/q_e Vs. C_e . which is shown below.

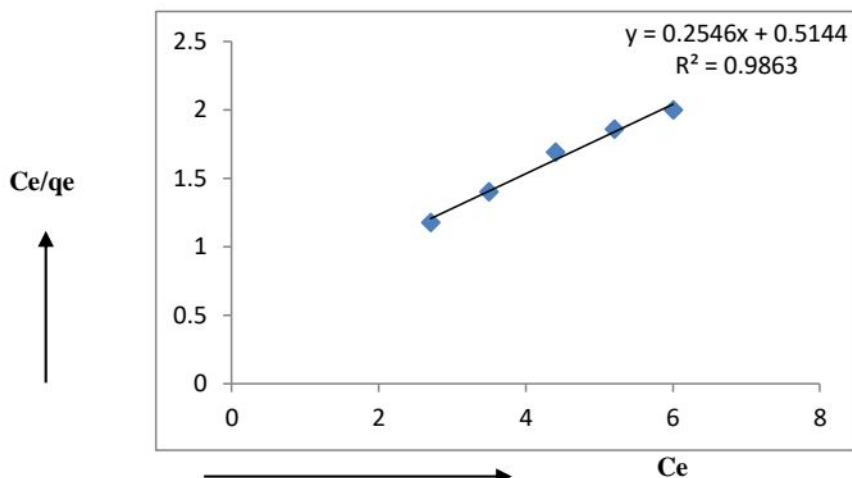


Figure 6: Langmuir adsorption isotherm

From Langmuir isotherm plot

Straight line equation is

$$y = 0.254 x + 0.514$$

$$R^2 = 0.986$$

$$(C_e/q_e) = (1/Q_0b) + (C_e/Q_0)$$

$$(C_e/Q_0) = mx = 0.254 x$$

$$(C_e/Q_0) = 0.254 C_e$$

$$Q_0 = 1 / 0.254 = 3.93$$

$$1/Q_0b = 0.514$$

By substituting value of Q_0 we get

$$b = 0.495$$

b) The Freundlich isotherm

The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a liquid to solid surface and assumes that different sites with several adsorption energies are involved. Freundlich adsorption isotherm is the relationship between the amount of adsorbate adsorbed per unit mass of adsorbent i.e. q_e and conc. of adsorbate at equilibrium i.e. C_e .

The non-linear form of this isotherm is generally expressed as

$$q_e = KC_e^{1/n}$$

where, K is the Freundlich adsorption coefficient representing the adsorption capacity and n represents the intensity of adsorption.

This equation is converted to the linear form by using log on both sides, as

$$\log q_e = \log K + (1/n) \log C_e$$

The constant K and n can be determined from the intercept and the slope of graph, $\log q_e$ Vs $\log C_e$.

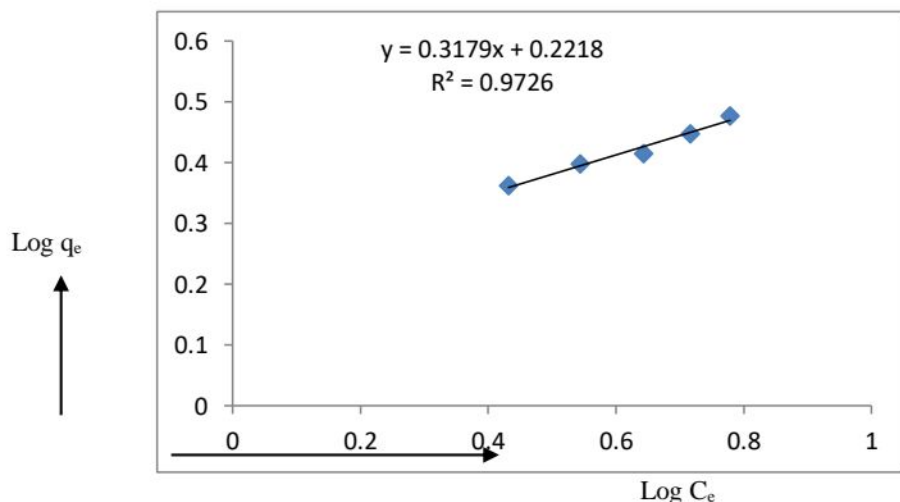


Figure 7: Freundlich adsorption isotherm

From Freundlich isotherm straight line equation is

$$y = 0.317 x + 0.221$$

$$R^2 = 0.972$$

$$\log q_e = \log K + (1/n) \log C_e$$

$$(1/n) \log C_e = 0.317 x$$

$$(1/n) \log C_e = 0.317 \log C_e$$

$$1/n = 0.317$$

$$\log K = 0.221$$

$$K = 1.66$$

The values of adsorption coefficient (K) and correlation coefficient (R²) are summarized below in table.

Table3 : The isotherm model constants and correlation coefficients

Langmuir Isotherm	Q ₀ = 3.93	b = 0.495	R ² = 0.986
Freundlich isotherm	K = 1.66	1/n = 0.317	R ² = 0.972

Since value of R² is higher in case of Langmuir Isotherm , so Langmuir Isotherm is better fit model for orange peel powder.

Kinetic Studies

In order to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, the pseudo-first order and pseudo-second order equations are applied to model the kinetics of fluoride adsorption on to peel powder[18].

The pseudo first order rate equation is given.

$$\log (q_e - q_t) = \log q_e - k_{ad} / 2.303 t$$

Where q_t and q_e are amount adsorbed (mg/g) at time t, and at equilibrium respectively and k_{ad} is the rate constant of the pseudo first order adsorption process (min⁻¹).

Table 4: Data showing the q_e and q_t values for orange peel powder for fluoride ion removal

Time in Minutes	C _i	C _e	x	q=x/m	q _e -q _t	log q _e -q _t	t/q _t
20	5	2	3	3	0.7	-0.1549	6.667
30	5	1.6	3.4	3.4	0.3	-0.5228	8.823
40	5	1.5	3.5	3.5	0.2	-0.6989	11.428
50	5	1.4	3.6	3.6	0.1	-1	13.88
60	5	1.3	3.7	3.7			

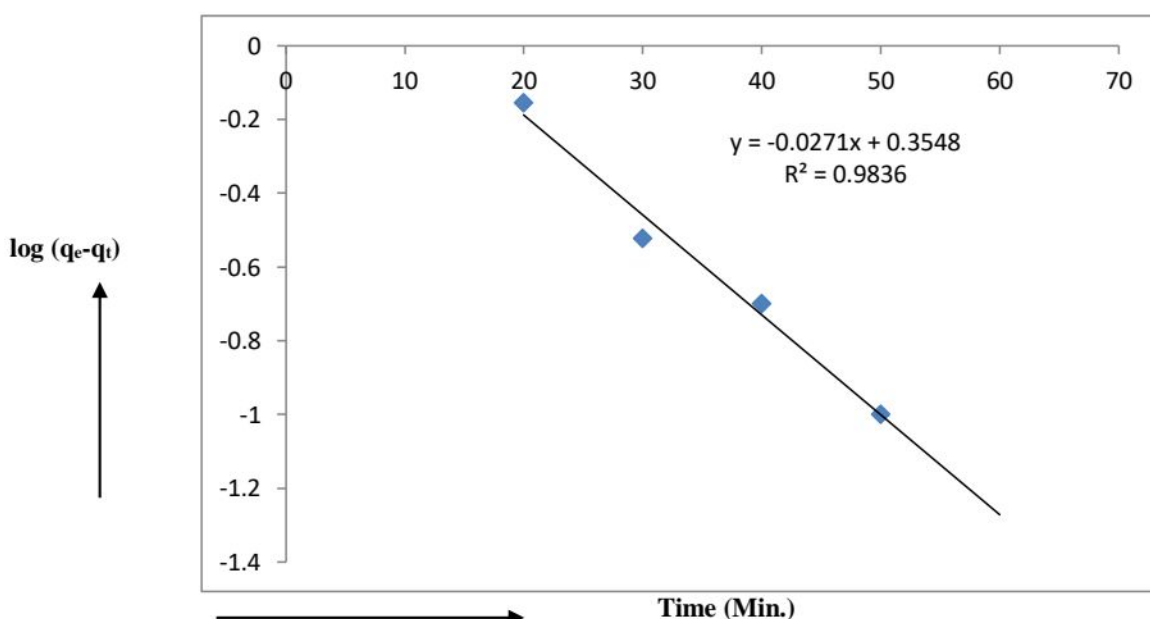


Figure8: Pseudo-first-order reaction for fluoride adsorbed

The Pseudo-second order equation is expressed

$$t/q_t = 1/h + 1/q_e t$$

Where $h = kq_e^2$ ($\text{mg g}^{-1} \text{min}^{-1}$) can be regarded as the initial adsorption rate as $t \rightarrow 0$ and k is the rate constant of pseudo-second order adsorption

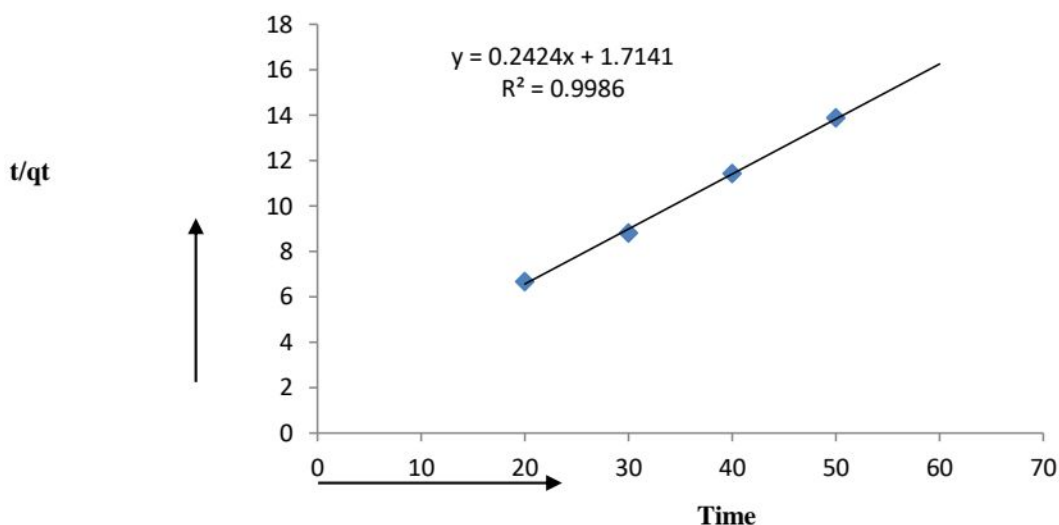


Figure9: Pseudo second order reaction for fluoride adsorbed

Comparison between the Adsorption rate constants and correlation coefficient associated with pseudo-first-order and pseudo-second-order rate equation

a) Pseudo first order rate equation

$$Kt/2.303 = 0.027t$$

Therefore adsorption rate constant

$$K_{ad} = 0.062$$

correlation coefficient

$$R^2 = 0.9836$$

b) Pseudo second order rate equation

$$t/q_e = 0.242t$$

$$q_e = 4.13$$

$$h = kq_e^2$$

$$1/h = 1.714$$

Therefore adsorption rate constant

$$K = 0.034$$

correlation coefficient

$$R^2 = 0.99$$

Since R^2 obtained from pseudo second order rate equation is greater than R^2 obtained from pseudo first order rate equation, so adsorption by orange peel powder fits in pseudo second order reaction.

CONCLUSIONS: Orange peel powder is good adsorbent for fluoride removal. Adsorption is maximum at pH 6 and there is 74% removal of fluoride at contact time 70 min. Equilibrium studies show that it follows Langmuir adsorption. Kinetic study shows that adsorption obeys pseudo-second order equation.

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