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Defluoridation of Water using Mosambi Peel Powder as Adsorbent: Kinetics and Equilibrium Studies

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Abstract:
Fluoride contamination in ground water is one of the serious problem in world. Larger contributor of fluoride is Drinking water. In higher doses fluoride casues fluorosis. So removal of fluoride from water is necessary. Present study deals with removal of fluoride by using mosambi peel as adsorbent. Effect of various parameters like effect of contact time, effect of initial fluoride concentration, effect of adsorbent dose, effect of pH on rate of adsorption has been studied. Equilibrium and kinetic study of adsorption has also been studied. Equilibrium study proves that freundlich isotherm fits for this adsorption and kinetic study shows that adsorption follows Pseudo second order reaction.

Keywords: Adsorbent, kinetics, fluoride, mosambi peel, equilibrium.

I. INTRODUCTION:

Water is required for all forms of life. Safe Drinking water is very important for every human being. Pure water is not available at all. It is observed that most of the diseases in world are due to poor quality of drinking water. Pollution of water occurs when substances that will alter the water in negative way are discharged in it. Water pollutants can be organic or may be Inorganic. Organic water pollutants include Detergents, Disinfection by products, Food processing waste, insecticides and pesticides, petroleum hydrocarbons etc. Inorganic water pollutants include Ammonia from food processing waste, chemical waste as industrial by products, fertilizer containing nitrate and phosphate, heavy metals from motor vehicles. Even in very low concentration, these chemicals may be toxic to aquatic life as well as terrestrial life. Therefore, treatment of these toxic material is required before its discharge. Fluoride is the major inorganic pollutant of natural origin found in ground water. Fluoride contamination in ground water is one of serious problem in world [1]. Larger contributer of fluoride is Drinking water [2]. Fluoride is a naturally occuring compound derived from fluorine, 13th most abundant element on earth. It is found in rocks, soil and fresh water. Fluoride comes in water due to weathering of fluoride containing rocks and soils and leaching from the soil into ground water. Fluoride enters into ground water due to dissolution from minerals/rocks like topaz, fluorite, fluorspar, cryolite, fluorapatite etc. [3]. Fluoride is physiologically more active ion. Salts of fluorides with monovalent cation i.e. NaF & KF are water soluble. But if fluoride make salts with divalent cation such as CaF_2 are insoluble in water. For Human metabolism fluoride is significant element [4]. Fluoride is more toxic than lead and less toxic than arsenic. It is accumulative toxin. It has been observed that in flowing surface fresh water, fluoride concentrations are usually lower than in ground water because of shorter contact time between water and rock. The natural concentration of fluoride also depends on the geological, chemical and physical properties of the aquifer, the porosity and acidity of the soil and rocks [5]. The fluoride conc. in water due to industrial waste is very higher as compared to the leaching of fluoride containing minerals [6]. Fluoride has gained importance due to its dual influences on human beings. In lower conc., fluoride is an essential nutrient which aids in information of bones, prevents tooth decay whereas in high conc. it causes fluorosis, brittling of bones, curvature of bones, mental disorders etc. So fluoride is often called a two edge sword. i.e. In small doses, it prevents tooth decay, while in high doses, it causes fluorosis.

Health Impacts of fluoride :
Permissible limit of fluoride in drinking water is 1.5 ppm. Beyond this it is harmful and not suitable [7]. Fluoride in drinking water has a profound effect on teeth and bones. Up to a small level (1–1.5 mg/L) this strengthens the enamel of teeth. If range of fluoride is 1.5–4 mg/l it will results in dental fluorosis. In dental fluorosis there are many changes in enamel [8] causing degrees of intrinsic tooth discoloration and, damage the physical structure of teeth. In the mild fluorosis there are mottled patches on half of surface of teeth and in moderate fluorosis all of the surfaces of the teeth are mottled and teeth may be ground down and brown stains appear on teeth. In severe fluorosis there is widespreading of brown stains and pitting in teeth. High risk of fluorosis is from 6 years old age because after that permanent teeth would have undergone complete development and therefore their susceptibility to fluorosis is greatly reduced [9] and if fluoride concentration is (4–10 mg/L), it progresses to skeletal fluorosis [10]. In this case the bone is hardened and thus less elastic, resulting in an increased frequency of fractures. other symptoms include thickening of the bone structure and accumulation of bone tissue, which both contribute to impaired joint mobility [11].

Fluoride is a neurotoxin. Fluoride causes reduced intelligence, impaired memory and reduced IQ level. The human placenta does not prevent the passage of fluoride from a pregnant mother's blood steam to the foetus. so foetus can be harmed by fluoride ingested pregnancy and also affect foetal brain development [12].

II. EXPERIMENTATION:

1. Adsorbent : Peels of Mosambi were collected from local area. Washed them with distilled water and laid flat on clean table to dry. Dry peels were grounded with grinder. After grounded, the peel powders were sieved and stored in plastic bags for further use.

2. Adsorbate : A fluoride stock solution of 100 mg/L was prepared by dissolving 0.221g of AR Grade sodium fluoride (Merck) in 1 L of double distilled water at room temp. The solution was diluted as required to obtain working solution. Fresh solution were used for each study.

3. Adsorption experiment : Test solution of 5 mg/l was prepared by dilution from fresh stock solution. All experiment were done out in Batch mode. In the Batch adsorption process, fluoride solution of known concentration were agitated with peel powder in a mechanical shaker till equilibrium was achieved. This study included the influence of various parameters like adsorbent dose, pH, Contact time and initial fluoride concentration. Sulphuric acid (0.1 N) and Sodium Hydroxide (0.1 N) were used for adjusting the pH values either to acidic or alkaline conditions. At the end of experiment, sample was filtered through Whatman no. 42 filter paper. Filtrate was analyzed for determining the fluoride concentration through SPADNS photometric method using UV-Spectrophotometer at the wavelength of 570 nm [13].

III. RESULTS AND DISCUSSION:

i. Effect of contact time : The effect of contact time on fluoride biosorption on mosambi peel powder is shown in table.

Table.1. Effect of contact time on adsorption of fluoride

Contact time in Minutes	Initial Conc. in mg/l	Final Conc. in mg/l	Reduction	% F removal
20	5	2.4	2.6	52
30	5	1.9	3.1	62
40	5	1.1	3.9	78
50	5	0.8	4.2	84
60	5	0.7	4.3	86

Graph between %age of F^- adsorption vs contact time (min) is shown as below. It was found that adsorption quantity of fluoride ion on mosambi peel increases as the contact time increased.

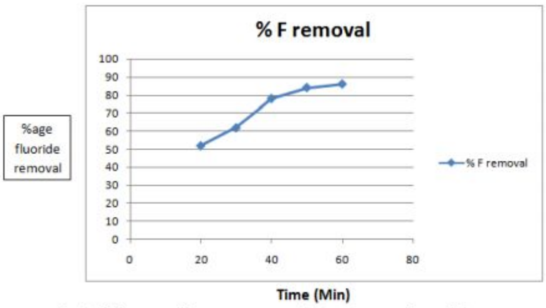

Figure.1. Effect of contact time on the %age removal of fluoride

ii) Effect of initial fluoride concentration : Biosorption experiments with mosambi peel were conducted for solution containing 8 mg/l to 12 mg/l fluoride ion, by keeping all other parameters constant.

Table.2. Effect of fluoride concentration on the %age removal of fluoride

Initial Conc. in mg/l	Final Conc. in mg/l	Reduction	% F removal
8	4.8	3.2	40
9	5.6	3.4	38
10	6.2	3.7	37
11	7.0	4.0	36
12	7.8	4.2	35

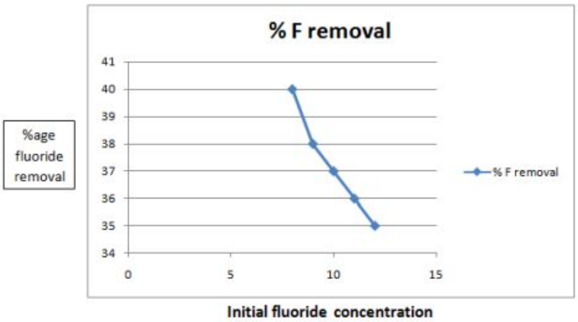

Figure.2. Effect of initial fluoride concentration on adsorption

iii) Effect of adsorbent dose : The percentage removal of fluoride ion increases with increases in mosambi peel doses from 0.2 g to 1.2 g. 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 exchangable sites at higher conc. of adsorbent.

Table.3. Effect of adsorbent dose on adsorption

Adsorbent dose in gm	Initial Conc. in mg/l	Final Conc. in mg/l	Reduction	% F removal
0.2	5	1.1	3.9	78
0.4	5	0.9	4.1	82
0.6	5	0.65	4.35	87
0.8	5	0.55	4.45	89
1	5	0.3	4.7	94
1.2	5	0.4	4.6	92

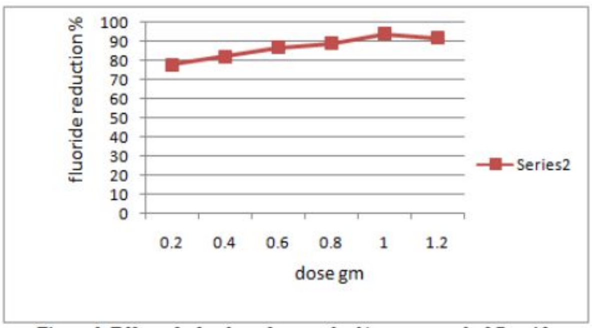

Figure.3. Effect of adsorbent dose on the %age removal of fluoride

iv) Effect of pH : Adsorption of fluoride as a function of pH was measured and results are shown in Table. 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.

Table .4. Effect of pH on adsorption

pH	Initial Conc. in mg/l	Final Conc. in mg/l	Reduction	% F removal
2	5	2.79	2.21	44.13
4	5	2	3	60
6	5	1.25	3.75	75
8	5	2.25	2.75	55
10	5	2.3	2.7	54

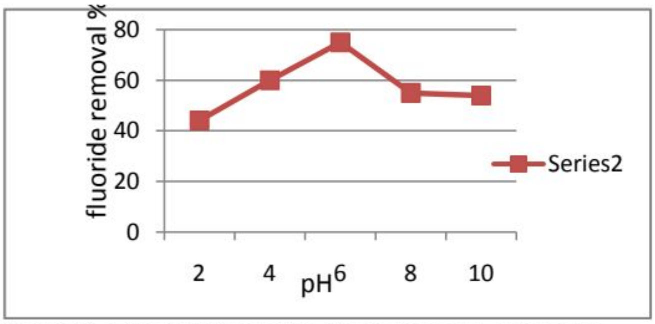

Figure.4. Effect of pH on the %age removal of fluoride

Equilibrium Studies for Mosambi Peel Powder:

Table .5. Data 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
8	4.8	3.2	3.2	1.5	0.681	0.505
9	5.6	3.4	3.4	1.65	0.748	0.5314
10	6.3	3.7	3.7	1.70	0.799	0.5682
11	7.0	4.0	4.0	1.75	0.845	0.602
12	7.8	4.2	4.2	1.86	0.892	0.6232

Where C_i = initial conc. of fluoride in solution
Ce = equilibrium conc. of fluoride in solution
m = weight of adsorbent taken i.e. 1 gm
qe = amount of fluoride adsorbed per unit weight of adsorbent

a) Langmuir isotherm :

The Langmuir model [14] 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. It is generally given in the form, linearized form of Langmuir isotherm is given as,

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

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

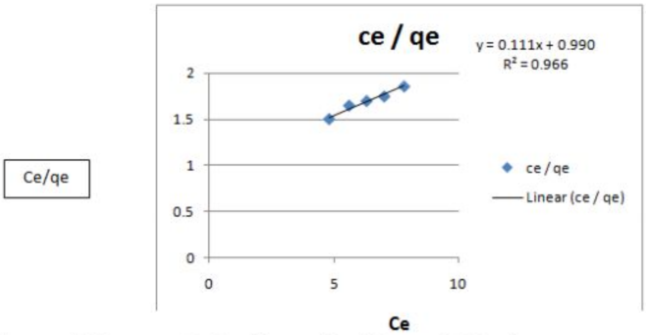

Figure.5. Langmuir Isotherm for Mosambi Peel

From Langmuir isotherm plot

Straight line equation is = 0.1113x + 0.9907

$R^2 = 0.9662$

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

$(C_e/Q_o) = mx = 0.111$ x

$(C_e/Q_o) = 0.111\ C_e$

$Q_0 = 9.009$

$1/Q_0 b = 0.990$

By substituting value of Q_0 we get

b = 0.112

b) The Freundlich isotherm

The Freundlich isotherm model [15] 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.

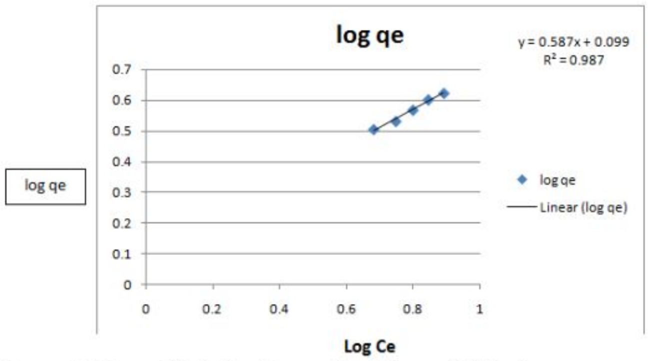

Figure.6. Freundlich Isotherm for Mosambi Peel

From Freundlich isotherm straight line equation is

Y = 0.587x + 0.099

1/n = 0.587

log K = 0.099

K = 1.26

ISOTHERM MODEL CONSTANTS AND CORRELATION COEFFICIENTS FOR ADSORPTION OF FLUORIDE BY MOSAMBI PEEL POWDER

a) Langmuir Isotherm:

$Q_0 = 9.009$

$b = 0.112$

$R^2 = 0.9662$

b) Freundlich isotherm:

$K = 1.26$

$1/n = 0.587$

$R^2 = 0.9871$

Comparitins both isotherms it is clear that orange peel adsorbent fitted Freundlich isotherm better than Langmuir isotherm because of high correlation coefficient.

Kinetic Study

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 orange peel powder. The pseudo first order rate equation is given by [16].

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

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.6. Data showing the q_e & q_t values for Mosambi peel powder

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	2.4	2.6	2.6	1.2	0.079	7.69
30	5	2.1	2.9	2.9	0.9	-0.0457	10.34
40	5	1.8	3.2	3.2	0.6	-0.2218	12.5
50	5	1.6	3.4	3.4	0.4	-0.3979	14.71
60	5	1.2	3.8	3.8			

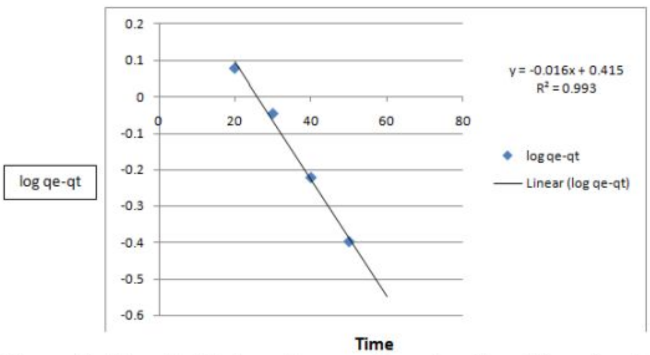

Figure.7. Pseudo first order reaction for fluoride adsorbed onto mosambi peel powder

The Pseudo-second order equation is expressed [17]

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

Where $h = kq_e^2$ (mg g^{-1} min^{-1}) can be regarded as the initial adsorption rate as $t\rightarrow0$ and k is the rate constant of pseudo-second order adsorption

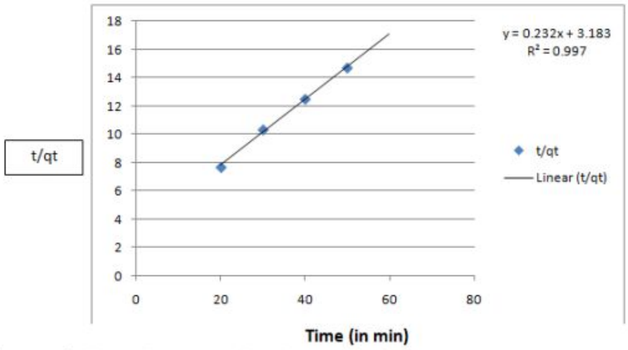

Figure.8. Pseudo second order reaction

Since R^2 of pseudo second order reaction is more than pseudo first order reaction so data fits better into pseudo second order reaction.

IV. CONCLUSION:

Mosambi peel powder is found to be efficient adsorbent for removal of fluoride from water. Maximum fluoride removal was at 60 minute of contact time and pH = 6. Freundlich isotherm fits better than Langmuir isotherm for this adsorption and kinetic study tells us that reaction is pseudo second order.

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