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A.S. Parlikar
Assistant Professor in Civil Engineering, SVPM's College of Engineering, Malegaon (Bk), Baramati Dist. Pune, India.

S.S. Mokashi
Assistant Professor in Chemistry, SVPM's College of Engineering, Malegaon (Bk), Baramati Dist. Pune, India.

Correspondence
A.S. Parlikar
Assistant Professor in Civil Engineering, SVPM's College of Engineering, Malegaon (Bk), Baramati Dist. Pune, India.

A Comparative Study of Defluoridation of Water by Tea Waste and Drumstick as Bioadsorbants

A.S. Parlikar, S.S. Mokashi

Abstract
The water available for daily consumption may be contaminated by natural sources or by industrial effluents. One such a contaminant is fluoride. In drinking water fluoride has a number of adverse effects on human health. There are many naturally available alternatives for defluridation of water like tea waste, seed powder of Moringa Oleifera, powder of bark of Pipal tree, Rice husk etc. Here the comparison is done between adsorption efficiency of Tea waste and Moringa Oleifera powder. Using colorimetric method tests were conducted to get optimal values of pH of water in acid & alkali treated powder of both. Optimal contact time for 212µ and 600µ were determined. For higher removal percentage efficiency of fluoride, optimal dosage of adsorbent was also determined.

Keywords: Fluoride, adsorption, Tea Waste, Moringa Oleifera, contact time, adsorbent dose.

1. Introduction

Pure water is scarce and is not easily available to all. Deprived sections of the society consume contaminated water and take ill periodically, often resulting in epidemics. The water may be contaminated by natural sources or by industrial effluents. One such a contaminant is fluoride. Geological formation is the main source of fluoride in the groundwater. The other sources of fluoride occurrence in water are industrial discharge from aluminum industries, phosphate industries, coal plants as well as due to water, food, air, medicament and cosmetics. Removal of fluoride from water is important because of its ill-effects for human. Defluoridation is removal of fluoride from water. Although there are several sources of fluoride intake, it is roughly estimated that about 60% of the total intake is through drinking water. There are various methods adopted for fluoride removal but they are costlier and some are time consuming. Hence, there is an urgent need of developing low cost method of defluoridation.

Fluoride is one such compound that is widely present in groundwater worldwide. Exposure to fluoride in drinking water has a number of adverse effects on human health including crippling skeletal fluorosis that is a significant cause of morbidity in a number of regions of the world. Fluoride is more toxic than lead even in minute dose as it accumulates in brain damaging it, also affects on mind development of children. Ground water is polluted due to industrial effluents and municipal waste in water bodies. In rural and undeveloped countries people living in extreme poverty are presently drinking highly turbid and microbiologically contaminated water. They lack knowledge of proper drinking water treatment and they do not afford costly chemical coagulants. To overcome chemical coagulant problems it is necessary to increase the use of natural coagulants for drinking water treatment. Naturally occurring coagulants are usually presumed safe for human health. Some studies on natural coagulants have been carried out and various natural coagulants were produced or extracted from microorganisms, animals or plants.

The use of Tea ash as well as Moringa Oleifera as an added advantage over the chemical treatment of water because it is biological and has been reported as edible. Hardness removal efficiency of both was found to increase with increasing dosage. Tea ash acts as a natural adsorbent and antimicrobial agent as well.


Fig 1: Tea leaves (Camellia Siensis) **Fig 2:** Drumstick tree (Moringa Oleifera)

Tea ash has been shown to be one of the most effective as a primary coagulant for water treatment and can be compared to that of alum a conventional chemical coagulant. The leaves and powder can be stored but the paste needs to be fresh for purifying the water. The coagulation mechanism of the Moringa Oleifera coagulant protein has been described as adsorption, charge neutralization and inter-particle bridging. Flocculation by inter-particle bridging is mainly characteristic of high molecular weight polyelectrolyte. Among all the plant materials that have been tested over the years, powder processed from the seeds from Moringa Oleifera has been shown to be one of the most effective as a primary coagulant for water treatment.

1.1. Literature review

Nalgonda technique [15] comprises sequential addition of sodium aluminates or lime, bleaching powder and filter alum to the fluoride water followed by flocculation, sedimentation and filtration. Sodium aluminates have settlement of precipitate and bleaching powder ensures disinfection. Mariappan *et al*. [11] studied defluoridation technique using poly aluminum hydroxyl sulphate (PAHS). It was concluded that, flock formation and settling are quick and volume of resulting sludge is less. Murugan *et al*. [13] studied the use of Aloe Vera (Indian aloe) a medicinal plant and concluded that at neutral pH the defluoridation was maximum. Sanjaykumar *et al*. [17] studied defluoridation methods by using indigenous chemicals and minerals. It was concluded that alum could insure effective defluoridation if alum dose, alkalinity of water pH and colloidal concentration are optimized. Also it was observed that fluoride removal was dependent on initial fluoride ion concentration and dose of coagulant. Muthuganesh *et al*. [14] studied fluoride removal techniques by using poly aluminum chloride (PAC) and compared with Nalgonda technique where there is reversible reaction. The results indicated that PAC can be an effective coagulant for fluoride removal with higher removal efficiency of about 65% -75% with less detention time. Also it was observed that fluoride removal was dependent on initial fluoride ion concentration and dose of coagulant. Prabavathi *et al*. [16] studied defluoridation techniques by using lignite rice husk and rice husk powder as adsorbent by varying pH, concentration of fluoride, weight of adsorbent and contact time. A better result was obtained after 2 hrs at pH 6 by using lignite. Jamode *et al.* [8] used pipal (Ficus Religliusa) leaf powder for uptake of fluoride ion from fluoridated water. During the study, it was found that various parameters like pH, contact time, adsorbent dose, size of adsorbent and initial fluoride ion concentration affect the controlling efficiency for adsorption of fluoride. It was also observed that alkali and acid treated pipal leaf powder removes fluoride ions at optimum conditions. Defluoridation up to 90 – 96% can be achieved by this process.

Bhargava *et al.* [3] used fishbone charcoal prepared from fishbone in coastal areas. The fluoride removal was found to be function of pH, contact time, initial fluoride ion concentration and adsorbent (fishbone charcoal) dose. Ganguly *et al.* [5] used boiler bottom ash as an adsorbent material for separating fluoride from water. The removal was found to be pH between 6 and 7. Gopal *et al*. [6] used activated carbon developed from leaves of Agave Sisalana by batch process. Maximum fluoride adsorption was observed in the pH 6.76, optimum dosage of 5gm/lit and optimum contact time was observed to be 40 minutes. Defluoridation up to 86% can be achieved by this process.

2. Effects of Fluoride on Human Health

The effects of fluoride on human health were dependent on the concentration of fluoride in Water.

Table 1: Biological Effects on Human Health

Fluoride conc. (mg/lit)	Source	Effects
0.002	Air	Destructive effect on plants
1.00	Water	Prevention of dental caries
2	Water	Effect dental enamel
3 to 6	Water	Osteoporosis
8	Water	10 % Osteoporosis
20 to 80	Air & Water	Crippling skeletal fluorosis
50	Food & Water	Changes in thyroid
100	Food & Water	Defective development
>125	Food & Water	Changes in Kidney
2500	Acute dose	Death

Permissible Limits for Fluoride Concentration in Drinking Water by various agencies**:**

1. Indian Council of Medical Research (ICMR-1975) - 1 mg/lit
2. Bureau of Indian Standards (BIS)-0.6 to 1.2 mg/lit
3. World health Organization (WHO-1984) for drinking water-1 to 1.5 mg/lit
4. World Health Organization (WHO) European Standards - 0.7 to 1.7 mg/lit related to temperature.

3. Materials and methods

In the present study, it is proposed to use the adsorption method by using natural adsorbent. Adsorption is defined as the change in concentration at the interfacial layer between the two phases of a system due to surface forces. Adsorption is mass transfer operation in that a constituent in the liquid phase is transferred to the solid phase. The adsorbent is the solid, liquid, or gas phase onto which the adsorbate accumulates. Factors affecting adsorption methods are surface area, nature of adsorbate, pH, temperature, presence of mixed solutes and nature of adsorbent.

The Camellia Sinesis (Tea) and Moringa Oleifera are evergreen plants that mainly grow in tropical and subtropical climate around the world and they have been used in drinking water treatment in small scale in Sudan and India for generations. The coagulant in the powder is believed to be one or several proteins that act as a cationic polyelectrolyte. The soluble particles in the water attache to the active agent, that binds them together creating large flocs in water. Camellia sinesis is a native tree of the sub-Himalayan parts of Northwest India, China. Due to the small size of the Tea ash coagulant protein, a bridging effect may not be considered as the likely coagulation mechanism.The use of Camellia Sinesis has an advantage over the chemical treatment of water because it is biological and has been reported as edible. It is believed that the seed is an organic natural polymer. The active ingredients are dimeric proteins. The protein powder is stable and totally soluble in water.

The coagulation mechanism of Moringa Oleifera coagulant protein has been explained in different ways. It has been described as adsorption and charge neutralization and inter-particle bridging. Flocculation by inter-particle bridging is mainly characteristic of high molecular weight polyelectrolytes.

Seed powder of Drumstick **Tea Ash**

3.1 Materials used

For Tea Ash**-** Regular tea ash powder is used as adsorbant.

For Moringa Oliefera**-** Drumstick powder was collected from local trees as adsorbent.

For preparing synthetic fluoride water sample anhydrous sodium fluoride (NaF) and distilled water was used. The nitric acid (1 N HNO_3) was used for acid washing of adsorbent. The sodium hydroxide (0.5N NaOH) was used for alkali washing of adsorbent. The adsorbent powder acid washed or alkali washed was further used. For fluoride detection studies with spectrophotometer, various solutions were prepared. Reference solution was prepared by using conc. hydrochloric acid (HCL) and SPADNS reagent (zirconyl chloride octahydrate).

Synthetic fluoride bearing water sample having initial fluoride ion concentration of 10mg/lit was used. The sample was filtered by using Whatmann's filter paper no. 41 for further uses. In this filtrate, SPADNS and zirconyl acid solution of 5 ml each was used. The sample was checked for fluoride detection in spectrophotometer at wavelength 570nm. Absorbance readings were compared with standard curve and the removal efficiency was found.

3.2 Development of standard curve

The fluoride standard sample in the range of 1 mg/lit to 11 mg/lit was prepared by taking appropriate quantities of standard fluoride solution with distilled water. Then pipette 5 ml each of SPADNS solution and zirconyl acid solution to each standard and mix it well or 10 ml SPADNS and zirconyl acid mix solution. Avoid contamination. The spectrophotometer was set to zero absorbance with reference solution and absorbance readings of standard curve were obtained. Reference solution was used as a blank solution. Spectrophotometer used at 480 nm wavelength; filter number 4, sensitivity medium was taken as per standard procedure. The procedure is same for both the bioadsorbants.

Table 2: Standard curve

Sr. No.	Initial Fluoride ion Concentration (mg/lit)	Absorbance Reading (for Tea Ash)	Absorbance Reading (for Moringa Oliefera)
1	1	0.341	0.250
2	2	0.388	0.345
3	4	0.419	0.480
4	6	0.469	0.670
5	8	0.502	0.865
6	10	0.539	1.035

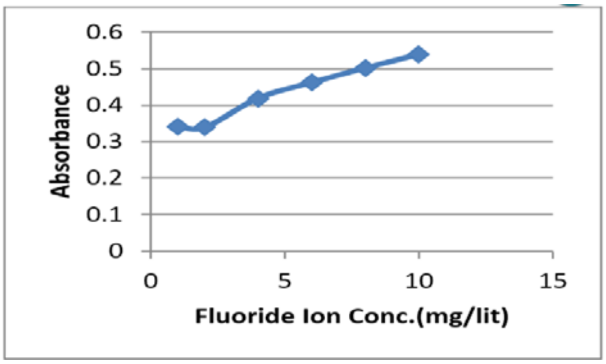

Fig 3: Standard curve - Tea ash

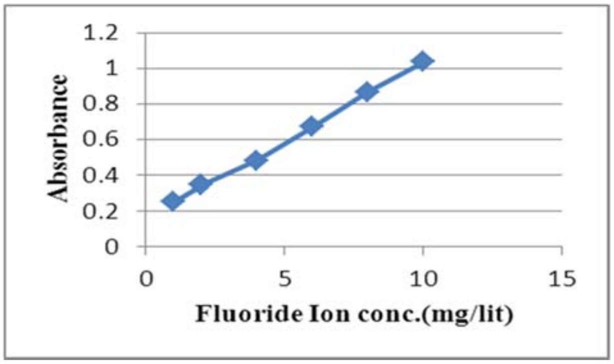

Fig 4: Standard curve - Moringa Oleifera

3.3 Experimental setup

The fluoride removal studies by adsorption were conducted in 250 ml conical flask using 100 ml of synthetic water sample containing different pH and initial concentrations of fluoride ion. In these conical flasks adsorbent with varied dosage was added. Then the contact period was given for different particle sizes. After giving the required contact time, the contents of the flasks were filtered using Whatmann's filter paper number 41. The filtrate was used for fluoride ion estimation using SPADNS method. The above procedure was repeated for different pH, contact times, adsorbent doses, particle sizes and different initial fluoride ion concentrations. The pH was varied from 1 to 10. The contact time was varied from 0.5 hrs to 3.5 hrs for various adsorbent sizes. The adsorbent dosages used were 0.5 gm/lit to 4 gm/lit in multiples of 0.5 gm/lit. The initial fluoride ion concentration was varied from 2 mg/lit to 11 mg/lit for the Camellia Sinesispowder (tea ash powder) as well asfor MoringaOleifera seed powder (drumstick). The parameters were varied to find the maximum fluoride removal efficiency. Synthetic fluoride bearing water sample having initial fluoride ionconcentration of 10 mg/lit was used. Under same experimental conditions percentage removal efficiency of fluoride content for two different bioadsorbants are calculated.

Fig 5: Spectrophotometer

4. Results and discussions

4.1 Optimal pH

For Tea Ash-

The adsorbent having 600 µ size, acid washed as well as alkali washed, was used to determine optimal pH at which the adsorption was maximum. For these experiments initial fluoride ion concentration was 10 mg/lit, with adsorbent dose of 2.5 gm/lit and contact time of 1 hr.In case of acid washed adsorbent the maximum removal efficiency was 72 % at pH 10. Whereas in case of alkali washed adsorbent the maximum removal efficiency was 62.85 % at pH 1. But the extreme pH values will give rise to higher costs for post treatment. It is generally recommended to maintain near neutral pH for the solutions. From figure it is seen that the percentage removal was 67 % and 47.35 % for acid washed and alkali washed adsorbents respectively.

Table 3: Optimum pH (Tea Ash)

Sr. No.	pH	Acid Washed Powder (600µ)		Alkali Washed Powder (600µ)	
		Absorbance	% Removal Efficiency	Absorbance	% Removal Efficiency
1	1	0.340	47	0.242	62.85
2	2	0.325	49	0.255	60.07
3	4	0.250	61	0.267	58.41
4	6	0.211	67	0.388	47.35
5	8	0.199	70	0.350	45.48
6	10	0.185	72	0.376	41.43

In case of acid treated bioadsorbents (both), the results were due to neutralization of the negative charge at treated tea ash bioadsorbent surface by greater hydrogen ion concentration at lower pH values, thus reducing hindrance to diffusion of the negatively charged fluoride ions on to the increased active surface of acid treated bioadsorbents. In case of alkali treated bioadsorbents (both), the maximum removal of fluoride was observed at high pH. It was due to increase of hydroxyl ion concentration in the solution; hence the rate of fluoride ion adsorption was maximum on the active surface, due to cation ion exchange phenomenon of alkali treated tea ash bioadsorbent at high pH value. Therefore, it was decided to use acid washed adsorbent and maintain neutral pH.

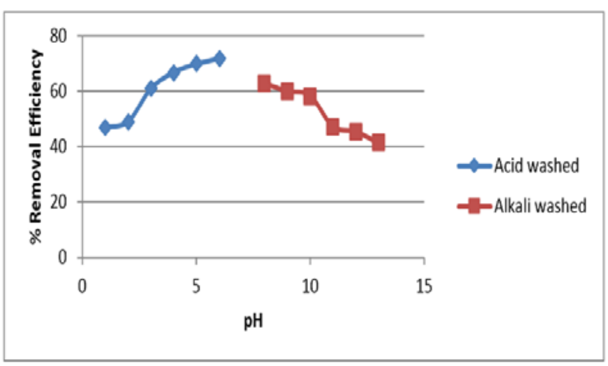

Fig 6: Optimum pH

For Moringa Oleifera-

The experiments were carried out for acid treated and alkali treated Moringa Oleifera seeds powder for determining optimum pH. The procedure was similar for acid and alkali treated powder. The pH was varied from 1 to 10 for acid treated Moringa Oleifera seed powder and 2 to 10 for alkali treated Moringa Oleifera seed powder.

Table 4: Optimum pH (Moringa Oleifera)

Sr. No.	pH	Acid washed powder (600 µ)		Alkali Washed Powder (600 µ)	
		Absorbance	% Removal Efficiency	Absorbance	% Removal Efficiency
1	1	0.680	39	-	-
2	2	0.765	31	0.760	31
3	4	0.815	24	0.730	37
4	6	0.850	20	0.665	41
5	8	0.905	13	0.595	49.5
6	10	0.920	12	0.580	51

The adsorbent having 600 µ size, acid washed as well as alkali washed, was used to determine optimal pH at which the adsorption was maximum. For these experiments initial fluoride ion concentration was 10 mg/lit, with adsorbent dose of 2.5 gm/lit and contact time of 1 hr. In case of acid washed adsorbent the maximum removal efficiency was 39 % at pH 1.Whereas in case of alkali washed adsorbent the maximum removal efficiency was 51 % at pH 10. The extreme pH values will give rise to higher costs for post treatment. Therefore it is not advisable to adopt extreme pH values. It is generally recommended to maintain near neutral pH for the solution. Therefore at pH of 6 to 8, the percentage removal were 13 % and 49.5 % for acid washed and alkali washed adsorbents respectively,which were close to higher adsorption values.

4.2. Optimal Contact Time

The experimental study was carried out to determine optimal contact time using adsorbents with different particle sizes. The pH was 8 and dose was 2.5 gm/lit for the study. It was found that the contact time reduces with decrease in particle size. For the given particle size, after a particular contact time, the removal efficiency remains almost constant. Therefore contact time of 150 min for both particle sizes and both bioadsorbants is preferable for high % removal efficiency. For this 480 nm wavelength, providing a light path of at least 1 cm. is used.

Table 5: Optimal contact time for tea ash

Sr. No.	Contact Time (min.)	600µ		212µ	
		Absorbance	% Removal Efficiency	Absorbance	% Removal Efficiency
1	30	0.392	39	0.372	42
2	60	0.338	47	0.319	50
3	90	0.294	54	0.264	59
4	120	0.243	62	0.224	65
5	150	0.212	67	0.206	68

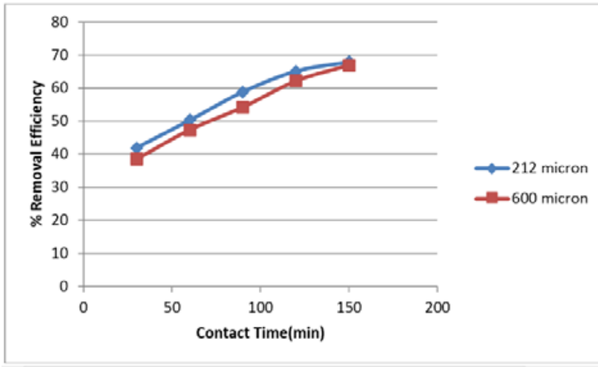

Fig 7: Optimal contact time for tea ash

Table 6: Optimum contact time for Moringa Oleifera

Sr. No.	Contact Time (min)	600 µ		212 µ	
		Absorbance	% Removal Efficiency	Absorbance	% Removal Efficiency
1	30	0.680	39	0.565	53
2	60	0.615	48	0.480	62
3	90	0.545	56	0.520	68
4	120	0.495	61	0.415	70
5	150	0.485	62	0.415	70

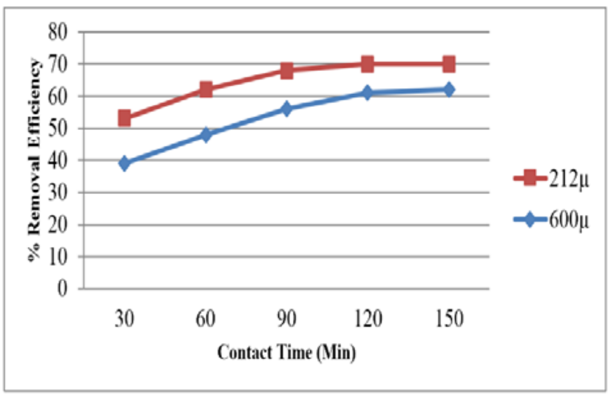

Fig 8: Optimum contact time for Moringa Oleifera

4.3. Optimal Adsorbent Dose

It was seen that the removal of fluoride increases with an increase in the amount of adsorbent. For all the experiments, initial fluoride ion concentration was fixed at 10 mg/lit, pH 8, and optimum contact time 3 hrs and 2 hrs for 600 µ and 212µ respectively. The amount of adsorbent dose was varied from 100mg to 400mg in aqueous solutions. Results show that for 212µ acid treated tea ash bioadsorbent, the maximum removal efficiency of fluoride was 74 % at 400 mg/lit. Similarly, for 600µ alkali treated tea ash bioadsorbent, the maximum removal efficiency of fluoride was 72 % at 400mg/lit.

Table7: Optimum adsorbent dose for Tea Ash

Sr. No.	Adsorbent dose (mg)	600µ		212µ	
		Absorbance	% Removal Efficiency	Absorbance	% Removal Efficiency
1	100	0.367	43	0.343	47
2	200	0.298	54	0.282	56
3	300	0.245	62	0.230	64
4	400	0.179	72	0.167	74

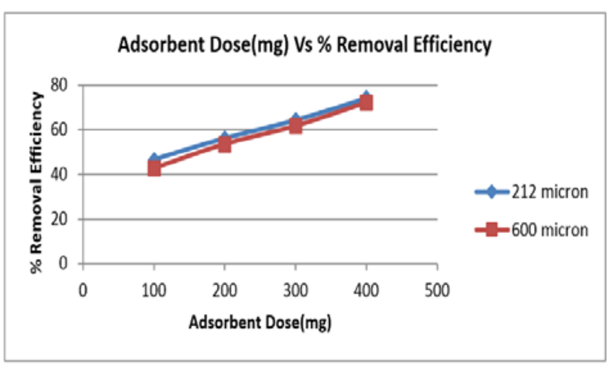

Fig 9: Optimal adsorbent dose- Tea Ash

Results show that for 212µ alkali treated Moringa Oleifera bioadsorbent, the maximum removal efficiency of fluoride was 76 % at 400mg/lit. Similarly, for 600µ alkali treated Moringa Oleifera bioadsorbent, the maximum removal efficiency of fluoride was 68 % at 400 mg/lit.

Table 8: Optimal adsorbent dose for Moringa Oleifera

Sr. No.	Absorbent Dose (mg)	600 µ		212 µ	
		Absorbance	% Removal Efficiency	Absorbance	% Removal Efficiency
1	100	0.620	47	0.615	48
2	200	0.525	58	0.485	62
3	300	0.490	61	0.525	67
4	400	0.520	68	0.365	76

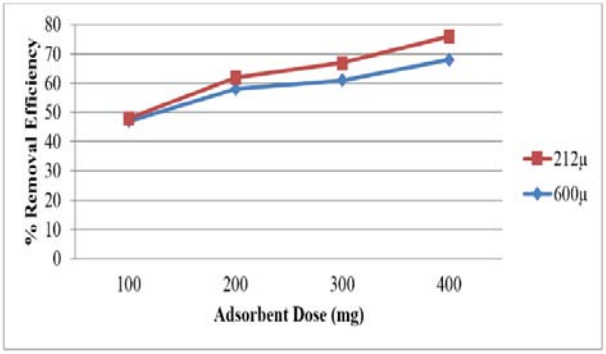

Fig10: Optimal adsorbent dose- Moringa Oleifera

5. Conclusion

Based on the present study following conclusions are drawn.

1. Use of the Tea ash powder as well as Moringa Oleifera as bioadsorbents for removal of fluoride are feasible.
2. The acid treated Tea ash powder was found better than alkali treated Tea ash powder at neutral pH for fluoride ion removal. But alkali treated Moringa Oleifera powder was found better than acid treated Moringa Oleifera powder at neutral pH.
3. The removal of fluoride by adsorption increases as the pH value increases for both bioadsorbents and adsorption is maximum at neutral pH.
4. The removal by adsorption was found to be optimum at adsorbent dose of 400mg/lit. for both bioadsorbents.
5. The optimum contact times were 150mins. for 212 µ and 600 µ respectively for both bioadsorbents.
6. It is observed that rate of adsorption is more for small particle size (212µ) of bioadsorbent due to increase in surface area than large particle size (600µ).

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