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Removal of Chromium (Cr^{+6}) & Fluoride (F^{-}) From Water by Adsorption on Peepal (*Ficus Religiosa*) Leaves Biomass

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ABSTRACT: Heavy metal pollutants released from industrial effluents to water bodies are highly toxic, non degradable and accumulate in living organism through food chain and cause harmful effects on human beings. Out of various heavy metals released by these industries chromium and fluoride are more toxic, carcinogenic and mutagenic to the living organisms. In the present work adsorption through batch study have been undertaken for the removal of chromium (Cr^{+6}) and fluoride (F^{-}) ions from aqueous solution. Biomass from Peepal (Ficus Religiosa) leaves is used for the adsorption by activation. Effect of various process parameters such as pH, contact time, initial concentration & adsorbent dosage on to the % removal was investigated. Kinetic and equilibrium isotherm modelling is carried out in order to understand the nature of adsorption process. At an initial concentration of 50 mg/L of Cr^{+6} the best removal of 88.34% was achieved and 80.33% for removal of Fluoride F^{-}. Pseudo second order model was best fitted to the experimental data, for Cr^{+6} and F^{-}. Both Langmuir & Freundlich isotherms agreed well the experimental data for Cr^{+6} and F^{-}.

Keywords: Pollutants, bioadsorption, Chromium(VI), fluoride, kinetics, isotherms, Ficus religiosa leaves

I. INTRODUCTION

Environmental pollution is currently one of the most important issues facing human beings. It was increased exponentially in the past few years and reached alarming levels in terms of its effects on living creatures. Toxic heavy metals and inorganic compunds are considered one of the pollutants that have direct effects on flora and fauna. Industrial wastewater containing lead (Pb), fluoride (F), arsenic (As) , copper (Cu), cadmium (Cd) and chromium (Cr), etc. contaminates groundwater resources and thus lead to a serious groundwater pollution problem.

Chromium is one of the contaminants which exist in hexavalent form which is recognized as a carcinogenic and mutagenic agent [1]. Sources of chromium pollution are leather tanning, textile, metal processing, paint and pigments, dyeing and steel fabrication [2]. Permissible limit of Cr (VI) is .05mg/L according to WHO and according to Indian surface standards it is .10 mg/L.

Fluoride, highly reactive in nature, does not occur in elemental state. Fluorides are released into the environment naturally through the weathering and dissolution of minerals, in emissions from volcanoes and in marine aerosols, via coal combustion and process waters and waste from various industrial processes, including steel manufacture, primary aluminium, copper and nickel production, phosphate ore processing, phosphate fertilizer production and use, glass, brick and ceramic manufacturing, and glue and adhesive production. The permissible for fluoride in drinking water is 1.5 mg/L as recommended by WHO [3]. According to BIS (Bureau of Indian Standards), acceptable fluoride concentration is 1.0 mg/l and maximum allowable concentration is 1.5 mg/L in drinking water.

In general Chromium (VI) and fluoride are removed from waste water by various methods such as chemical precipitation,electrochemical reduction, sulphide precipitation, cementation, ion-exchange, reverse osmosis, electro dialysis, solvent extraction, and evaporation, etc. These methods have been found to be limited, since they often involve high capital and operational costs. Among these methods adsorption is the most efficient technique because of its convenience, easy operation and simplicity of design [4]. Adsorption which have proven to be effective for the removal of Cr(VI) and fluoride from aqueous solutions and industrial effluents. AgricuLural by-products have been widely studied for effulent removal from waste water. These include peat, wood, pine bark, banana pith, soybean and cotton seed hulls, rice husk, saw dust, tamarind seeds, compost and leaves [5].

In the present study, activated Ficus religiosa leaves are used as low-cost adsorbent for the removal of Cr(VI) and fluoride from aqueous solutions. Leaves of different trees are very versatile natured chemical species as these contain a variety of organic and inorganic compounds. Ficus religiosa Linn commonly known as ‘Peepal tree’ is a large widely branched tree with leathery, heart-shaped, long-tipped leaves on long slender petioles and purple fruits growing in pairs. The tree is regarded as a sacred tree to both Hindus as well as Buddhists [6]. Cellulose, hemicelluloses, pectin and lignin present in the cell wall are the most important sorption sites. Leaves have chlorophyll, carotene, anthocyanin and tannin which contribute to metal biosorption. The important feature of these compounds is that they contain hydroxyl, carboxylic, carbonyl, amino and nitro groups which are important sites for metal sorption [2]. The influence of pH, contact time, metal ions concentration and adsorbent dose were investigated and experimental data obtained were evaluated and fitted using adsorbent equilibrium isotherms, and kinetic models.

II. MATERIAL & METHODS

Material

All chemicals used were of analytical reagent grade. Hexavalent chromium solution of 1000 mg/L concentration was prepared by dissolving 2.827 g potassium dichromate in one litre distilled water and fluoride solution of 1000 mg L^{-1} was prepared by dissolving .221g of Sodium Fluoride (NaF) in deionised distilled water (DDW). These solutions were further diluted to get solutions of various known concentrations of chromium. For pH adjustments throughout the experiment hydrochloric acid and sodium hydroxide solutions were used. 1M Nitric acid was used for the treatment of leaves.

Adsorbent Preparation

Ficus Religiosa leaves were collected from local environment of Modinagar (India). These leaves were washed, many times with distilled water to remove dust and soluble impurities and were allowed to dry in shadow at room temperature for two days. The dried leaves were converted into fine powder by using mixer grinder. The powder was sieved to obtain particles of size 100 mesh. 50 g leaves powder was activated in 1 litre 0.1 N HCl solutions for 24 h to precipitate out already adsorbed metals on the biomass surface from the environment. It was then filtered and washed with distilled water to remove acid contents. The filter cake was first dried at room temperature and then in an oven at 90°C to constant weight. The biomass was then stored in vacuum desiccators to protect it from moisture**.**

Batch Experiment

Batch experiment was carried out for the adsorption of Cr (VI) and fluoride using Peepal leaf biosorbents in 250 ml batch reactor. The 50 ml synthetic solution of 50 mg/l was taken in a conical flask for the adsorption process. The biosorbents was weighed in a weighing balance and then added in to the batch reactor for the adsorption of Cr (VI) and fluoride and covered with aluminium foil and then kept in incubator shaker at 30°C for given contact time. After the time has elapsed, they were taken out from the shaker and filtered using whatmann filter paper. After filtering 10ml of filtrate was taken in test tube and the residual concentration of Cr (VI) and fluoride in filtrate was analysed using calorimetric method in UV spectrophotometer [7]. The equilibrium uptake or adsorption capacity, *qe* (mg/g) can be calculated using the following equation

$$q = [(Ci - Ce) \times V]/W$$

where V is the volume of the solution (L) and W, the amount of adsorbent (g); Ci and Ce (mg/L), the initial and equilibrium metal concentrations.

The percent removal was calculated as follows:

$$\% \text{ Removal} = [(C_i - C_e) / C_i] \times 100$$

Adsorption isotherm studies were carried out with four different initial concentrations of from 50 mg/L to 80 mg/L at pH 6, contact time 6 h and adsorbent dosage level of 5g/L. The kinetic parameters for the adsorption process were studied on the batch adsorption of 50 mg/L at pH 6. The contact time was varied from 60 min to 360 min and the percent removal was monitored during the study.

III. RESUL & DISCUSSIONS

Effect of pH

For Cr (VI) stability, pH is essential factor which controls the surface properties of adsorbents, functional groups and the ionic state of the metal species. The adsorption abilities of Cr (VI) from aqueous solution on adsorbents are powerfully affected by the pH. Adsorption tests were carried out over the pH range of 4–9 for the adsorbents; while all other parameters were keep constant. The pH of the solution is maintained by using 0.1 N HCl and 0.1 N NaOH. The Cr (VI) uptake was observed to be very high in the range of pH 4-6 as shown in fig.1

Hence, an optimum pH of 5.0 was maintained for further studies.

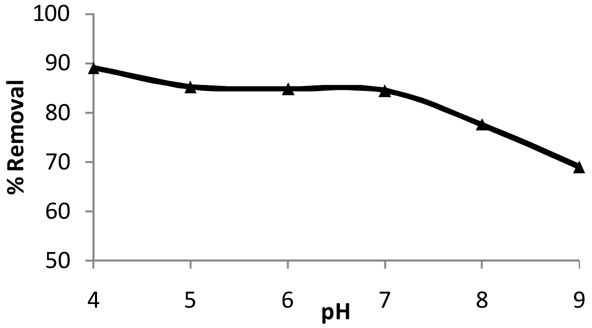

Fig. 1. Effect of initial pH on adsorption of Cr (VI) at 50 mg/L for 6 hours at 303 K and 5g/l adsorbent dose by Peepal leaves.

Fluoride uptake increases with increase in pH up to 6, there being 80% removal and then decreases to 18% removal at pH 10 as shown in fig.2. The decrease of fluoride uptake at pH greater than 7.0 is perhaps due to the electrostatic repulsion of F- ion to the negative charge of surface and opposition for active sites by excessive amount of OH- ions. The specific adsorption of anion on metal ox hydroxide surface sites occurs by following ligand-exchange reaction:

$MOH + F^- \leftrightarrow SF^- + H_2O$

$MOH_2^+ + F^- \leftrightarrow MF^- + H2O$

Where, M stands for Fe, Al, and Si.

Hence, an optimum pH of 6.0 was maintained for further studies.

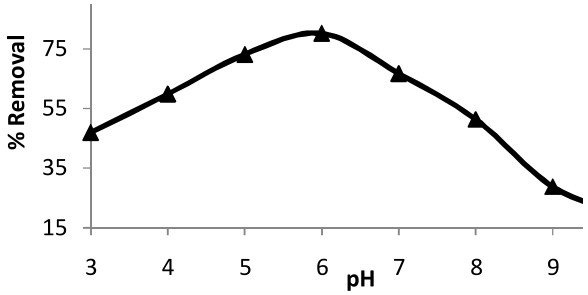

Fig. 2. Effect of initial pH on adsorption of fluoride at 50mg/L for 6hours at 303 K and 5g/l adsorbent dose by Peepal leaves.

Effect of Adsorbent Dosage

Adsorbent dosage is an important parameter since it determines the ability of an adsorbent for removal of Cr (VI) and fluoride at a given initial concentration and the separation cost. The effect of absorbent dosage was investigated by varying the dosage of adsorbent in the range 2 to 12 g/litre. The results are mentioned figure 3 and 4 for Cr (VI) and fluoride respectively.

Figure 3 show that an increase in adsorbent dose increases the percentage removal of Cr (VI) as more surface area is available for adsorption. At lower dose, the adsorbent surface becomes saturated as the Cr (VI) concentration is high. It is found that the optimum adsorbent dose for adsorbent was obtained 8g/L which showed 88 % removal. After optimum dose the removal was unaffected with increases in dose because on increasing the dose further, equilibrium is approached between solution of Cr (VI) and surface. Hence, adsorbent dosage was optimized to be 8 gm/L for Cr (VI).

In the present study, percentage fluoride removal increases with increase in the adsorbent dose and for maximum removal of 80 % of fluoride as shown in figure 4. The minimum adsorbent dose required was found to be 6gm/L. But no noteworthy change was observed beyond this dose. Hence, sorbent dosage was optimized to be 6 gm/L.

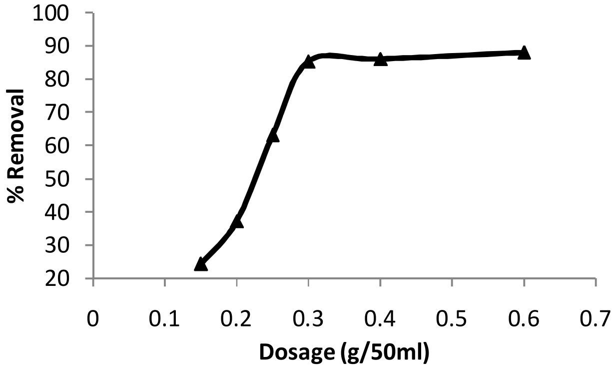

Fig. 3. Effect of adsorbent dose on adsorption of Cr (VI) at 50mg/L for 6hours at 303 K and pH 6 by Peepal leaves.

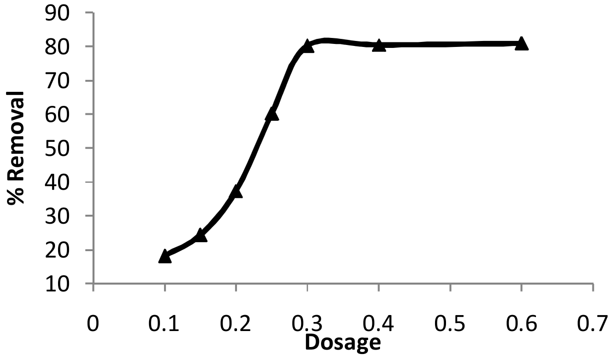

Fig. 4. Effect of adsorbent dose on adsorption of fluoride at 50mg/L for 6hours at 303 K and pH 6 by Peepal leaves.

Effect of Contact Time

Figure 5 shows the result of effect of changing the contact time on the amount of adsorption of Cr (VI) on the adsorbent, at initial concentration of Cr (VI) at 50 mg/l, pH 5.0 and temperature 303 K and 8 g/l of acid treated Peepal leaves.

Result obtained after the experiments show that the rate of adsorption of Cr (VI) metal is very high at the starting stage and then gradually declines very slowly till the equilibration point is reached. At the start, large numbers of empty sites are accessible and Cr (VI) is bound quickly on adsorbent surface at a quick adsorption rate. As the contact time increases, the availability of such sites become limited and ultimately an equilibrium is established between the Cr(IV) on the solid surface and that in the solution. As there is no significant increase in percentage of Cr (VI) removal after 360 min, it is concluded that an equilibration time of 360 min is sufficient.

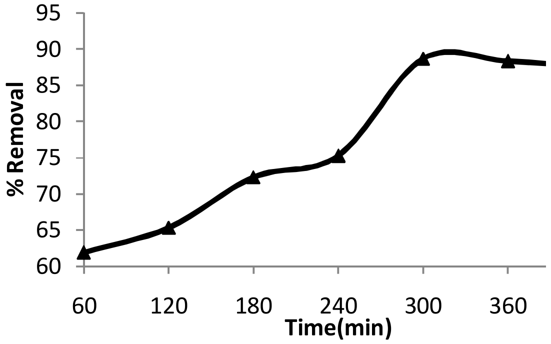

Fig. 5. Effect of contact time on adsorption of Cr (VI) at 50mg/L with 8 gm/L adsorbent at 303 K and pH 6 by Peepal leaves.

Figure 6 shows the effect of contact time on percentage removal of fluoride. It is found that the removal of fluoride ion increases with increase in contact time. The rate of increment in percentage removal of fluoride is appreciably fast in the initial stage, i.e. from 120 to 300 min.

At initial stage percentage removal increases very fast but after some time it slowly approaches a constant value (80% removal), representing accomplishment of equilibrium.

As there is no significant increase in percentage of fluoride removal after 360 min, it is concluded that an equilibration time of 360 min is sufficient**.**

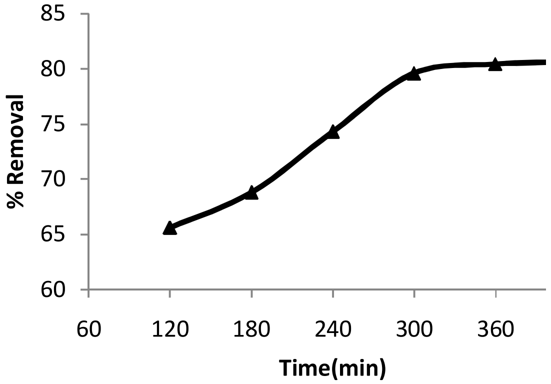

Fig. 6. Effect of contact time on adsorption of fluoride at 50mg/L for 6hours at 303 K and pH 6 by Peepal leaves.

Effect of Initial Concentration

The effect of initial concentration Cr (VI) and fluoride on adsorbents was investigated at different concentrated solutions in the concentration range of 50 mg/l to 80mg/l. The results are presented in figure 7 and 8..

From the results so obtained, it is clear that the maximum removal of Cr(VI) takes place at lower ion concentration at optimum pH and adsorbent dose. Increasing Cr (VI) concentration decreased the per cent removal at optimum pH 5.0as shown in figure 7. With the growth in initial concentration of Cr (VI), the % removal changes from 88.3 % to 86.8% though there is a gradual rise in adsorption uptake capacity.

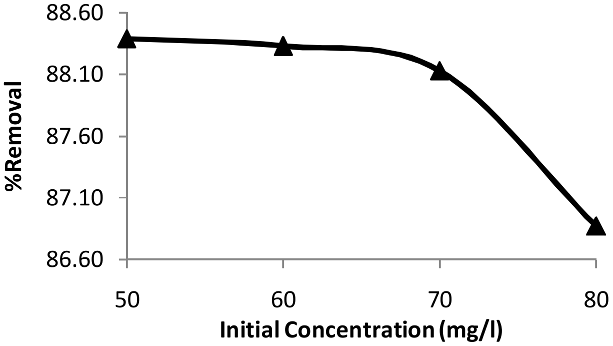

Fig. 7. Effect of initial Cr (VI) concentration for 6hours at 303 K, pH 6 and 5g/l adsorbent dose on adsorption by Peepal leaves.

The figure 8 shows effect of initial fluoride concentration on percentage removal by Peepal leaf. Percentage removal decreases gradually from 80% to 79.06% as the fluoride concentration is increased from 50 to 80 mg/l. As the fluoride concentration increases, the percentage removal decreases as less sorption sites are available for adsorption of fluoride on Peepal leaf and the already adsorbed fluoride ions also hinder the adsorption of new fluoride ions on the leaf surface.

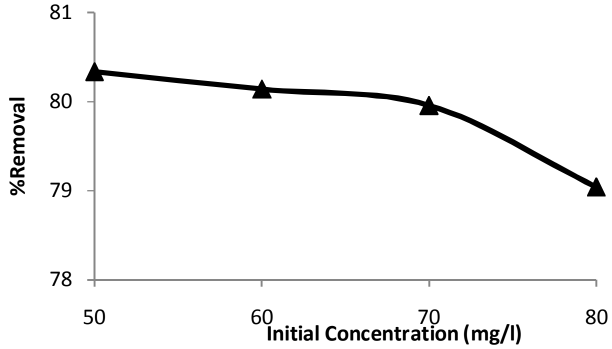

Fig. 8. Effect of initial fluoride concentration for 6hours at 303 K, pH 6 and 5g/l adsorbent dose on adsorption by Peepal leaves.

KINETIC MODELLING

For Chromium (VI)

By comparing the pseudo first order equation with the regression equation obtained from the experimental data as shown in figure .9, the values of parameters of pseudo first order equation is calculated is given in table I. The adsorption capacity according to pseudo first order model for Cr (VI) was 3.146 mg/g. The regression coefficient (R^2) calculated for the adsorption of Cr (VI) was 0.8495, therefore the experimental data agreement with pseudo first order model is moderate.

It was found that for first order plot, calculated *qe* does not agree with experimental value. This suggests that adsorption process does not follow first order kinetics.

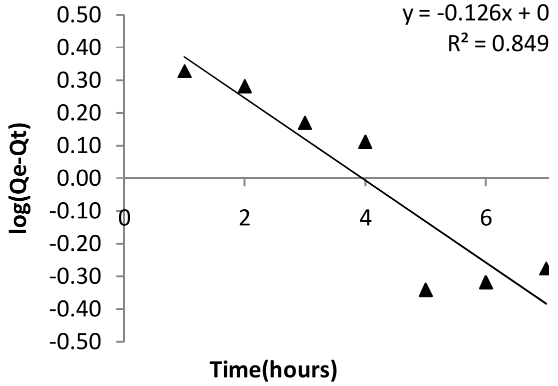

Fig. 9. Plot for first order kinetics model for Cr (VI) adsorption.

Table 1: First order adsorption rate constants and experimental *qe* and calculated values for Cr (VI) adsorption.

q_e(exp)(mg/g)	**First order kinetics**		
	k_1 (1/min)	**Q*e*(cal) (mg/g)**	**R^2**
6.00	0.29	3.14	.84

By comparing the pseudo second order equation with the regression equation obtained from the experimental data as shown in figure 10, the values of parameters of pseudo second order equation were calculated and are given in table II. The adsorption capacity according to pseudo second order model for Cr (VI) was 6.23 mg/g. The regression coefficient (R^2) calculated for the adsorption of Cr (VI) was 0.9854, therefore the experimental data agreed well with pseudo second order model as compared to the agreement with pseudo-first order kinetics model.

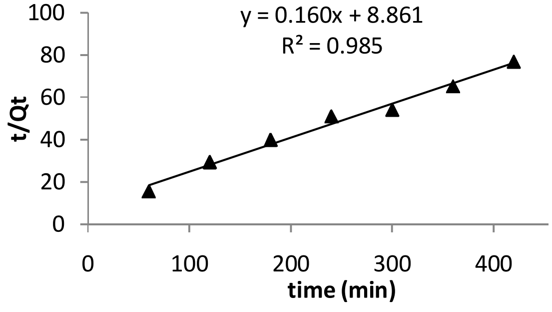

Fig. 10. Plot for second order kinetics model for Cr (VI) adsorption.

For the second order plot, calculated *qe* matches with experimental *qe* and correlation coefficient, R^2 value for second order kinetic plot is closer to unity. These resuLs indicate that adsorption system belongs to second order kinetic model.

Table 2: Second order adsorption rate constants and experimental *qe* and calculated values for Cr (VI) adsorption.

Second order kinetics		
k_2 (gm/mg/min)	**Q*e* (cal) (mg/g)**	**R^2**
0.002	3.14	.84

For Fluoride

By comparing the pseudo first order equation with the regression equation obtained from the experimental data as shown in figure 11, the values of parameters of pseudo first order equation is calculated is given in table III. The adsorption capacity according to pseudo first order model for F^- was 2.3577 mg/g. The regression coefficient (R^2) calculated for the adsorption of F^- was 0.9357, therefore the experimental data agreed well with pseudo first order model.

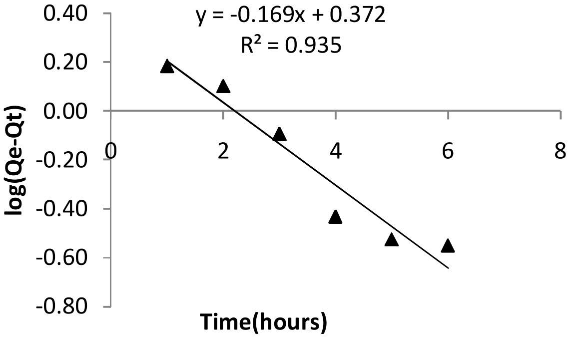

Fig. 11. Plot for first order kinetics model for fluoride adsorption.

Table 3: First order adsorption rate constants and experimental *qe* and calculated values for Fluoride adsorption.

***qe* (exp) (mg/g)**	**First order kinetics**		
	k_1 (1/min)	***qe* (cal) (mg/g)**	**R^2**
7.00	0.38	2.35	.84

The values of parameters of pseudo second order equation is calculated is given in table IV. The adsorption capacity according to pseudo second order model for F⁻ was 6.22665 mg/g. The regression coefficient (R^2) calculated for the adsorption of F⁻ was 0.9854, therefore the experimental data was also agreed well with pseudo second order model.

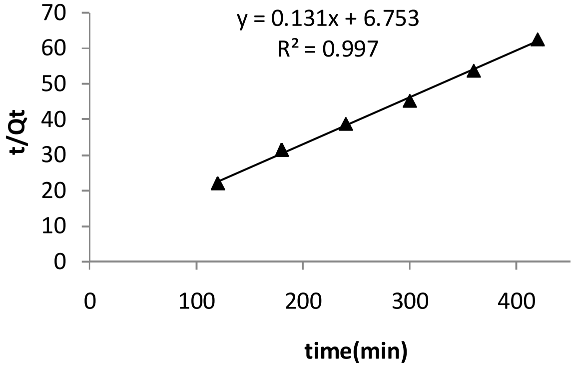

Fig. 12. Plot for second order kinetics model for fluoride adsorption.

Table 4: Second order adsorption rate constants and experimental *qe* and calculated values for Fluoride adsorption.

Second order kinetics		
***k*₂ (gm/mg/min)**	***qe* (cal) (mg/g)**	**R^2**
0.002	**7.60**	.98

The values of kinetics parameters are shown in table III & IV. It was found that for first order plot, calculated *qe* does not agree with experimental. This suggests that adsorption process does not follow first order kinetics. Whereas for second order plot, calculated *qe* matches with experimental *qe* and correlation coefficient, R^2 value for second order kinetic plot is closer to unity. These resuLs indicate that adsorption system belongs to second order kinetic model.

ADSORPTION ISOTHERMS

For Cr (VI)

Langmuir Adsorption Isotherm for Cr (VI)

Langmuir isotherm plot has been generated and depicted in figure 13. By comparing the Langmuir adsorption isotherm equation with the regression equation obtained from the experimental 13, the values of parameters of Langmuir adsorption isotherm equation were calculated and are mentioned in table V. The maximum adsorption capacity according to Langmuir adsorption isotherm model for Cr (VI) was 34.427mg/g. The regression coefficient (R^2) calculated for the adsorption of Cr (VI) was 0.9851, therefore the experimental data agreed well with Langmuir adsorption isotherm model

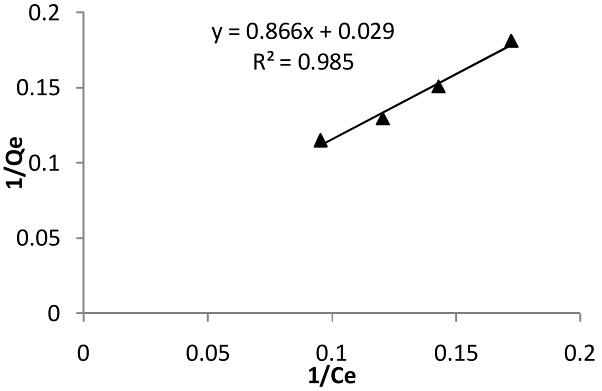

Fig. 13. Langmuir plot for Cr (VI) adsorption.

Table 5: Langmuir isotherm data for Cr (VI) adsorption

Langmuir Isotherm		
Parameters		
q_{max}(mg/g)	**K_L**	**R^2**
34.42	.03	.98

Freundlich Adsorption Isotherm for Cr (VI)

Freundlich isotherm plot has been generated and depicted in figure 14. By comparing the Freundlich adsorption isotherm equation with the regression equation obtained from the experimental data as shown in figure 14, the parameters for the Freundlich isotherm were calculated. The values of parameters are given in table VI. The value of constant n according to Freundlich adsorption isotherm for Cr (VI) was 1.304 that it is in range set by Freundlich model which is between 1 and 10 showing favourable adsorption of Cr (VI) on the Peepal leaves prepared in this work. The regression coefficient (R^2) calculated for the adsorption of Cr (VI) was 0.977, therefore the experimental data was also agreed well with Freundlich adsorption isotherm model.

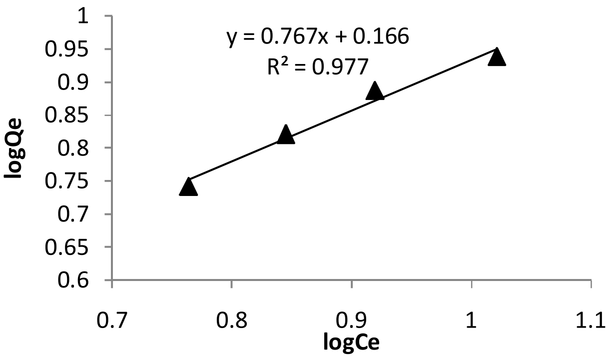

Fig. 14. Freundlich plot for Cr (VI) adsorption.

Table 6: Freundlich isotherm data for Cr (VI) adsorption.

Freundlich Isotherm		
Parameters		
K_F ((mg/g)(L/mg)1/n)	n	R^2
1.46	1.30	.97

From Table 6 it can be seen that the value of n = 1.304, that it is in range set by Freundlich model which is between 1 and 10 showing favourable adsorption of Cr (VI) on the Peepal leaves prepared in this work. In view of correlation coefficient, R^2 values, for Freundlich and Langmuir it is closer to 1. Thus we can say Cr (VI) adsorption on Peepal leaves at 303 K follows both Freundlich and Langmuir adsorption isotherm.

For Fluoride

Langmuir Adsorption Isotherm for F^-

By comparing the Langmuir adsorption isotherm equation with the regression equation obtained from the experimental data as shown in figure 15. The values of parameters of Langmuir adsorption isotherm equation is calculated is given in table VII. The maximum adsorption capacity according to Langmuir adsorption isotherm model for F^- was 64.516 mg/g. The regression coefficient (R^2) calculated for the adsorption of F^- was 0.9969 therefore the experimental data was agreed well with Langmuir adsorption isotherm model

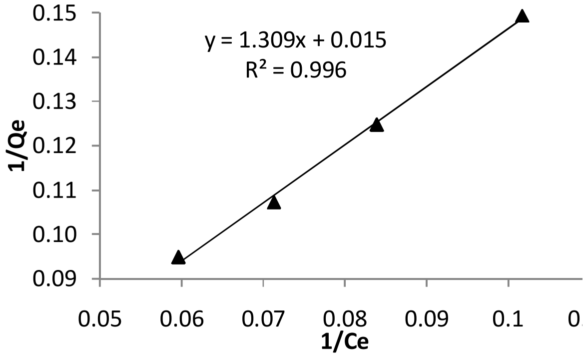

Fig. 15. Langmuir plot for fluoride adsorption.

Table 7: Langmuir isotherm data for fluoride adsorption.

Langmuir Isotherm		
Parameters		
Q_{max}(mg/g)	K_L	R^2
64.51	0.011	.99

Freundlich Adsorption Isotherm for F^-

By comparing the Freundlich adsorption isotherm equation with the regression equation obtained from the experimental data as shown in figure 16, the values of parameters of Freundlich adsorption isotherm equation is calculated is given in table VIII. The value of constant n according to Freundlich adsorption isotherm for F^- was 1.166 that it is in range set by Freundlich model which is between 1 and 10 showing favourable adsorption of F^- on the Peepal leaves prepared in this work. The regression coefficient (R^2) calculated for the adsorption of F^- was 0.9947, therefore the experimental data was also agreed well with Freundlich adsorption isotherm model.

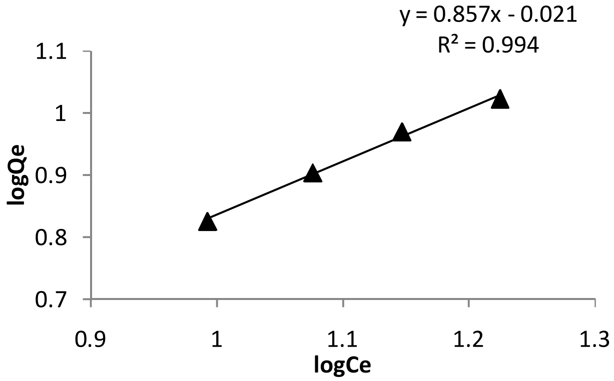

Fig. 16. Freundlich plot for fluoride adsorption.

Table 8: Freundlich isotherm data for fluoride adsorption.

Freundlich Isotherm		
Parameters		
K_f ((mg/g)(L/mg)1/n)	n	R^2
0.95	1.16	.99

From the table VII & VIII it can be seen that the value of n = 1.166, that it is in range set by Freundlich model which is between 1 and 10 showing favourable adsorption of fluoride on the Peepal leaves prepared in this work. In view of correlation coefficient, R^2 values, for Freundlich and Langmuir it is closer to 1. Thus we can say fluoride adsorption on Peepal leaves at 303 K follows both Freundlich and Langmuir adsorption isotherm.

IV CONCLUSION

In the present study, following conclusions obtained are:

1. The biomass obtained from Peepal Leaves (Ficus Religiosa) has proved to be a potential biosorbent for both the species. The maximum removal obtained is 88.39% and 80.34% for the removal of Cr (VI) and fluoride respectively.
2. The maximum adsorption capacity for the adsorption of Cr (VI) and fluoride onto the

surface of Peepal leaf was 8.68 mg/g and 10.53 mg/g respectively.

3. The adsorption of Cr (VI) and fluoride was both through physical adsorption and chemisorption. Therefore the adsorption of Cr (VI) and fluoride is maximum for this biosorbent.
4. For both Cr (VI) and F^- pseudo second order model was best fitted to the experimental data.
5. For both Cr (VI) and F^- both adsorption isotherm models i.e. Langmuir & Freundlich well described the experimental data. Therefore, the adsorption of Cr (VI) and F^- onto the surface of biomass of Peepal leaf is both uniform & multilayer in nature.

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