

# Evaluation of Kinetics of Leaching of Lignins and Tannins in Batch Adsorption of Cr (VI) by *Emblica officinalis* Leaf Powder (EOLP)

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**Abstract:** The present paper is aimed to assess the contents of lignin and tannin leached in the batch adsorption test filtrate and to evaluate the kinetics of leaching of lignin and tannins. For the purpose, raw *Emblica officinalis* leaf powder (EOLP) has been used as adsorbent for removal of Cr (VI) from aqueous solution in batch mode of operation. Test results indicate that EOLP imparts lignin and tannin in batch test filtrate. Both lignin and tannin contents are related to pH, chemical oxygen demand (COD), initial Cr(VI) concentration ( $C_0$ ) residual Cr(VI) concentration in batch test filtrate (C), amount of adsorbent ( $W_{ad}$ ) and the time of contact (t). Dimensionless parameters are developed and the lignin and tannin contents are well correlated with dimensionless parameters. From the studies conducted on rate of leaching of both soluble lignin and tannins, the kinetics of leaching of soluble lignin and tannin follow a pseudo second order type rate kinetics. Linear regression models are developed based on pseudo second order kinetics for determination of lignin and tannin contents in batch test filtrate. However, these findings need further verification in future investigations.

**Keywords:** *Emblica officinalis* leaf powder (EOLP), batch test filtrate, chromium (VI), leaching, kinetics.

## INTRODUCTION

Leaves of different trees are very versatile natured chemical species as these contain a variety of organic and inorganic compounds. Cellulose, hemicelluloses, pectins 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 [1-2]. Agro- based adsorbent materials impart lignin and tannin in the treated effluent. However, there is lack of studies on determination and evaluation of rate of leaching of lignin and tannin during batch adsorption experiments.

Use of agro-based biomass and plant materials as adsorptive agents for removal of heavy metals from aqueous solutions is well documented in literature [1, 3, 4]. Also, the plant materials such as sawdust and plant leaves/leaf powder impart colour after adsorption in the treated effluent, which is objectionable for discharge into water bodies untreated. The residual colour so developed after adsorption needs to be investigated further.

Literature demonstrates that leaves of trees impart lignin and tannin in significant amount when put in aqueous solution [5-9]. Tannins have chemical formula as  $C_{76}H_{52}O_{46}$  and are readily soluble in acetone and glycerin. Tannins has ability to form soluble or insoluble

tannin-protein complexes. Hydrolysable tannins are usually present in low amount in plant [10]. It has been mentioned that the lignin and tannin contents in cow pea seed coats in the ranges 4.8-8.46% and 0.9-23.9% respectively [5]. The concentration of lignin in autumn shed leaves is reported in the range of 19-36 % and the extracted condensed tannin content was observed 21% in spring season and 30 % in summer season [6]. The apparent lignin content in kraft pulp ranges between 12-39% [11]. Lignin is usually insoluble in all solvents and can be degraded by physical or chemical treatments. At low pH (< 3) lignin get dissolved in the solution. Empty fruit bunches fibre contain about 17.2% lignin (v/v). Acid soluble and insoluble lignin makes up about 50% of leaf material [12]. The lignin content in leaf fibres ranges between 6-11% by weight [9].

Literature further reveals that tannin content in different parts of raw *Emblica officinalis* are as follows: Fruits (28%), Stems (8 - 9%), leaves (2.1 - 22% and twigs (21%) [13]. The information available on the website [13] on the tannin content in *Emblica officinalis* leaves shows that *Emblica officinalis* leaves contain about 22% or even more tannins by weight. However no information is available on soluble lignin content in *Emblica officinalis* leaf powder. Also, the determination of soluble lignin and tannin contents in the batch adsorption test filtrate is not available in literature. The batch test filtrates contain colour and COD both. Due to these reasons, the experimental observations are needed for the determination of lignin, tannin, colour, COD and pH in the batch test filtrate.

Keeping above facts in view, it was planned to determine the lignin and tannin contents with progress

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of batch adsorption till equilibrium is fully established between Cr(VI) and raw EOLP.

The aim of the present paper is to determine the lignin and tannin contents leached from EOLP in Cr(VI) batch adsorption test filtrate and also to evaluate the kinetics of leaching of lignin and tannins. Batch adsorption tests were performed at two different initial Cr(VI) concentrations of 49.54 mg/L and 198.69 mg/L with optimum EOLP dose of 2.5 g/L and 6 g/L respectively. The soluble lignin content in batch test filtrate was determined by modified Klason lignin spectrophotometric methods respectively [14]. The tannins content was determined by titrimetric method suggested by [15]. A dimensionless approach has been used to model the lignin and tannin contents. A multiplier functions of dimensionless variables is developed to formulate the kinetics of leaching. Linear kinetic models based on pseudo second order leaching kinetics are derived, which may prove useful in determination of lignin and tannin contents of batch test filtrate.

## MATERIALS AND METHODS

Batch adsorption experiments were performed with initial Cr(VI) concentrations of 49.54 and 198.69 mg/L. The sample pH was maintained at its optimum value of 3. The sample volume was taken as 100 mL. The aliquot was contacted with optimum doses of raw *Embllica officinalis* leaf powder i.e., 2.5 and 6.0 g/L respectively for two Cr(VI) concentrations under study. The samples were withdrawn at different time intervals

i.e. 2.5, 5, 10, 20, 30, 45, 60, 120, 180, 240 minutes and then filtered with Whatman-42 filter paper. The samples were then analyzed for lignin, tannin, residual Cr(VI) concentration, COD, color and pH as per the methods and procedures described below briefly.

The interest was to determine the lignin content in the batch treated effluent i.e. soluble lignin content only. Therefore, the samples were analyzed for soluble lignin content by spectrophotometric method as the soluble lignin content was the cause of colour in the filtrate of batch treated effluent and was determined by modified Klason lignin method [14]. For determination of soluble lignin content, 5 mL of filtrate obtained from the batch test at different time intervals for each Cr(VI) concentrations was contacted with 5 mL of 3 % H<sub>2</sub>SO<sub>4</sub>. The absorbance of the solution was then measured using U-V spectrophotometer at a wavelength of 205 nm. The concentration of soluble lignin content, (C<sub>SL</sub>), g/L in the samples was calculated using the following equation as reported by [14].

$$C_{SL} = \left( \frac{Abs}{110} \right) \times \left( \frac{V_f}{V_i} \right) \quad (1)$$

Where, Abs is the absorbance at a wavelength of 205 nm; V<sub>f</sub> is the final volume of the solution (mL); V<sub>i</sub> is the initial volume of the solution (mL) [5].

The soluble lignin content percent was then calculated using the following equation:

**Table 1: Experimental Results and Computed Lignin and Tannin Contents in Treated Samples after Cr(VI) Adsorption on Raw *Embllicaofficinalis* Leaf Powder (C<sub>0</sub>=49.54 mg/L)**

Time (min.)	Abs (%)	C <sub>SL</sub> (g/L)	W <sub>ad</sub> (g)	W <sub>L</sub> (%)	V (L)	V' (mL)	V <sub>0</sub> (mL)	W <sub>T</sub> (%)	C (mg/L)	COD (mg/L)	Color (mg/L)	pH <sub>i</sub>	pH <sub>e</sub>
2.5	0.633	0.0115	0.25	0.46	0.1	0.54	0.4	0.92	24.04	14.98	2	3	4.3
5	0.688	0.0125	0.25	0.5	0.1	0.59	0.4	1.24	20.76	20.52	3	3	4.32
10	0.880	0.0160	0.25	0.64	0.1	0.61	0.4	1.4	14.86	28.62	5	3	4.36
20	1.183	0.0215	0.25	0.86	0.1	0.86	0.4	3.06	10.12	32.46	6	3	4.38
30	1.650	0.0300	0.25	1.2	0.1	1.15	0.4	4.96	7.13	36.88	7	3	4.41
45	2.118	0.0385	0.25	1.54	0.1	1.24	0.4	5.6	5.06	40.56	9	3	4.42
60	2.915	0.0530	0.25	2.12	0.1	1.28	0.4	5.86	4.88	42.76	10	3	4.47
120	3.300	0.0600	0.25	2.4	0.1	1.35	0.4	6.3	4.88	45.44	12	3	4.52
180	3.355	0.0610	0.25	2.44	0.1	1.35	0.4	6.32	4.88	45.8	12	3	4.5
240	3.383	0.0615	0.25	2.46	0.1	1.36	0.4	6.38	4.88	45.9	12	3	4.5

Abs= Absorbance value (%); C<sub>SL</sub>= Soluble lignin concentration (mg/L); W<sub>ad</sub>=mass of adsorbent (g); W<sub>L</sub>=Soluble lignin content (%) w/w; V= total volume of filtrate (L); V' =Volume of titrant 0.1 N KMnO<sub>4</sub> used for sample; V<sub>0</sub>=volume of titrant 0.1 N KMnO<sub>4</sub> used for blank; W<sub>T</sub>=Tannin content % (w/w); C= residual Cr(VI)concentration in the filtered sample (mg/L); COD= chemical oxygendemand in filtered sample (mg/L); Color= color concentration in filtered sample (mg/L); pH<sub>i</sub>= initial pH of Cr(VI) solution and pH<sub>e</sub>= pH of the filtered sample after adsorption.

**Table 2: Experimental Results and Computed Lignin and Tannins Content in Treated Samples after Adsorption on Raw *Emblicoefficialis* Leaf Powder ( $C_0=198.69$  mg/L)**

Time (min.)	Abs (%)	$C_{SL}$ (g/L)	$W_{ad}$ (g)	$W_L$ (%)	V (L)	$V'$ (mL)	$V_0$ (mL)	$W_T$ (%)	C (mg/L)	COD (mg/L)	Color (mg/L)	pH <sub>i</sub>	pH <sub>e</sub>
2.5	4.224	0.0768	0.6	1.28	0.1	1.3	0.4	2.46	110.61	32.64	12	3	5.24
5	5.082	0.0924	0.6	1.54	0.1	1.9	0.4	4.02	88.43	40.04	14	3	5.26
10	6.534	0.1188	0.6	1.98	0.1	2.6	0.4	5.98	66.08	48.54	16	3	5.29
20	8.844	0.1608	0.6	2.68	0.1	3.2	0.4	7.82	44.18	54.44	18	3	5.3
30	12.672	0.2304	0.6	3.84	0.1	4.2	0.4	10.4	35.63	59.7	18	3	5.34
45	15.642	0.2844	0.6	4.74	0.1	5.2	0.4	13.2	23.84	62.42	20	3	5.36
60	18.612	0.3384	0.6	5.64	0.1	5.6	0.4	14.3	16.76	68.72	20	3	5.38
120	19.206	0.3492	0.6	5.82	0.1	6.1	0.4	15.8	16.78	69.86	20	3	5.4
180	20.394	0.3708	0.6	6.18	0.1	6.1	0.4	15.88	16.76	70.22	20	3	5.42
240	20.460	0.3720	0.6	6.2	0.1	6.2	0.4	15.96	16.76	70.56	20	3	5.42

Abs= Absorbance value (%);  $C_{SL}$ = Soluble lignin concentration (mg/L);  $W_{ad}$ =mass of adsorbent (g);  $W_L$ =Soluble lignin content (%) w/w; V= total volume of filtrate (L);  $V'$  =Volume of titrant 0.1 N  $KMnO_4$  used for sample;  $V_0$ =volume of titrant 0.1 N  $KMnO_4$  used for blank;  $W_T$ =Tannin content % (w/w); C= residual Cr(VI) concentration in the filtered sample (mg/L); COD= chemical oxygendemand in filtered sample (mg/L); Color= color concentration in filtered sample (mg/L); pH<sub>i</sub>= initial pH of Cr(VI) solution and pH<sub>e</sub>= pH of the filtered sample after adsorption.

$$W_L = \frac{C_{SL} \times V}{1000 \times W_{ad}} \times 100 \quad (2)$$

Where,  $W_L$  is the soluble lignin content (%);  $C_{SL}$  is the concentration of soluble lignin in the filtrate (g/L); V is the total volume of the filtrate (mL). The experimental results and the calculated values of ' $W_L$ ' are shown in Tables 1 and 2 for initial Cr(VI) concentrations of 49.54 mg/L and 198.69 mg/L respectively.

Tannin content in the filtrate was determined by the International Pharmacopoeia and AOAC titrimetric method as suggested by [15]. In this method, first the standard solution of Indigo carmine was prepared by dissolving 6 g of Indigo carmine in 500 mL of demineralised water by heating. Solution was then cooled and 50 mL of concentrated  $H_2SO_4$  was then added to it. The solution was then diluted to 1 litre using demineralised water and filtered. A 25 mL of the filtrate was taken into one litre flask. 25 mL of indigo carmine standard solution and 750 mL of demineralised water was added to it. The sample was then titrated with 0.1 N  $KMnO_4$  solutions until the blue colour changed to green colour. Few drops of  $KMnO_4$  were further added till green colour turns to golden yellow. Blank test was performed on the solution mixture containing 25 mL of Indigo carmine solution and 750 mL of demineralised water by titrating it with 0.1 N  $KMnO_4$  solutions.

The tannin content (%) was calculated using the following equation as suggested by [15],

$$W_T(\%) = \frac{(V' - V_0) \times 0.004157 \times 100 \times 100}{W_{ad} \times 25} \quad (3)$$

Where,  $V'$  is the volume of 0.1 N aqueous solution of  $KMnO_4$  for the titration of the sample, mL;  $V_0$  = volume of 0.1 N aqueous solution of  $KMnO_4$  for titration of blank sample, mL; 0.004157 = tannins equivalent in 1 mL of 0.1 N aqueous solution of  $KMnO_4$ ;  $W_{ad}$ = mass of EOLP (g) and 100 = volume of volumetric flask, mL.

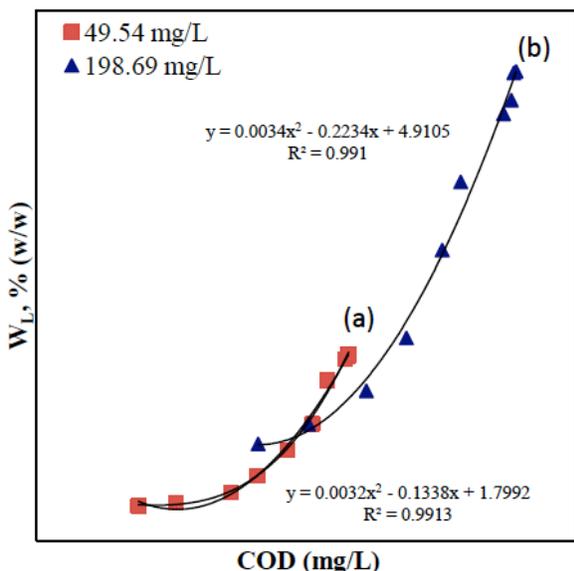
Residual Cr(VI) concentration was determined as per standard methods [16]. Colour concentration was determined by visual comparison with standard colour comparators. COD concentration was determined by reflux method. pH of the treated samples obtained after batch experiments at different time intervals were measured using digital pH meter. The experimental results and calculated tannin contents are presented in Tables 1 and 2 for Cr(VI) concentrations of 49.54 and 198.69 mg/L respectively.

## RESULTS AND DISCUSSIONS

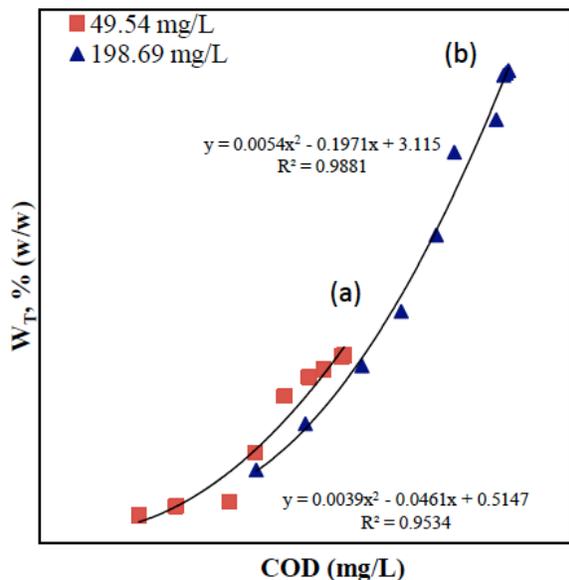
### Variations of Lignin and Tannin Contents with Variables

Variations of soluble lignin ( $W_L$ ) and tannin ( $W_T$ ) contents with COD of batch test filtrate are plotted in Figures 1 and 2 respectively for initial Cr(VI) concentrations of 49.54 and 198.69 mg/L. The trend of the curves drawn indicate the increase in both lignin and tannin contents with increase in COD during 240

minutes of experimental run. The nature of curves further demonstrate that with passage of time the soluble COD content and corresponding soluble lignin and tannin contents increases more rapidly during initial 60-75 minutes and then slows down gradually till 240 minutes of experimental run. Experiments were discontinued after 240 minutes at optimum contact time.



**Figure 1:** Variation of Lignin content with COD in batch test filtrate [ $C_0 = 49.54$  and  $198.69$  mg/L;  $M = 2.5$  and  $6.0$  g/L respectively].

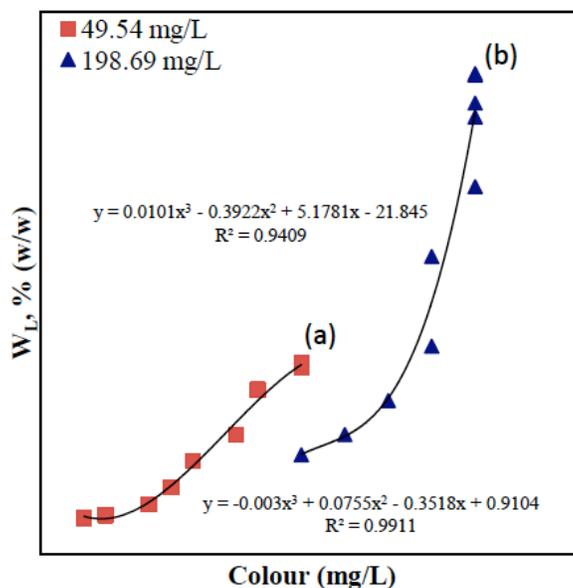


**Figure 2:** Variation of Tannin content with COD in batch test filtrate [ $C_0 = 49.54$  and  $198.69$  mg/L;  $M = 2.5$  and  $6.0$  g/L respectively].

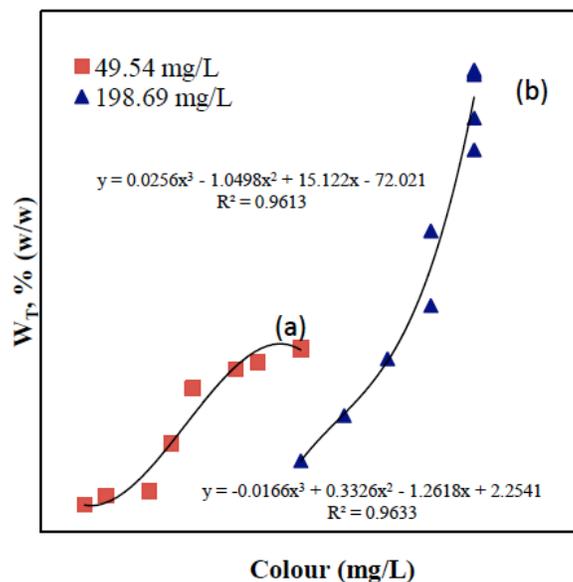
The trend curves drawn in Figures 1 and 2 are best fitted by polynomials of degree 2 with  $R^2$  values 0.95 or

higher. Variations of both soluble lignin and tannin contents (%) with COD indicate a good correlation with the COD of the filtrate. This observation is important and has been used in the further analysis of soluble lignin and tannin contents.

Variation of soluble lignin and tannin contents (%) with colour of the batch test filtrate are plotted in Figures 3 and 4 respectively for two different initial Cr(VI) concentrations. The trend of variation of both



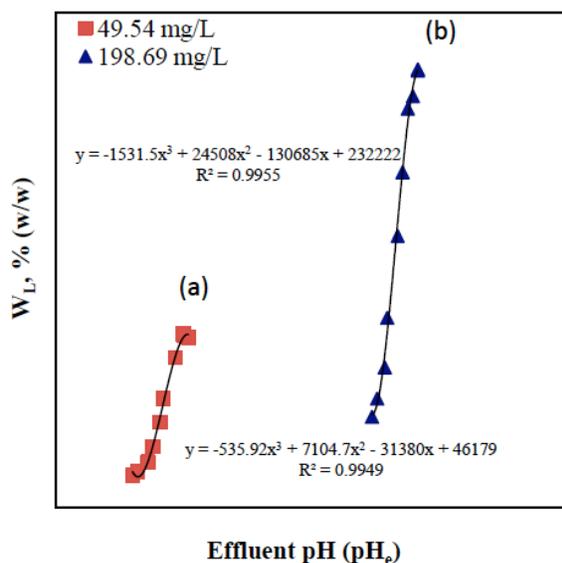
**Figure 3:** Variation of Lignin content with Colour in batch test filtrate [ $C_0 = 49.54$  and  $198.69$  mg/L;  $M = 2.5$  and  $6.0$  g/L respectively].



**Figure 4:** Variation of Tannin content with Colour in batch test filtrate [ $C_0 = 49.54$  and  $198.69$  mg/L;  $M = 2.5$  and  $6.0$  g/L respectively].

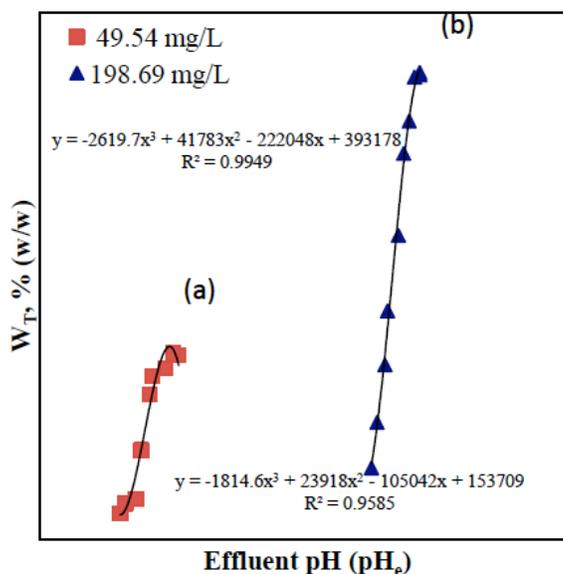
lignin and tannin contents in these figures are observed more or less similar to that of COD and the data are fitted well with polynomials of degree 3 with  $R^2$  values higher than 0.94. The experimental results indicate that the colour developed in the filtrate may be due to the presence of lignin and tannins in the filtrate. This fact is well supported by [17]. A part of the colour in the filtrate may also be due to the residual Cr(VI) concentration in the filtrate. A low pH of Cr(VI) solution (pH 3) may also be a good reason for leaching of colour as well as lignin and tannins under acidic conditions.

Physically, it was observed that the colour intensity was successively increased in the filtrate drawn after 240 minutes of experimental run especially with higher initial Cr(VI) concentration. Also, the FTIR spectra (not shown here) indicate the presence of  $-OH$  group on the surface of EOLP. Therefore, the pH of the filtrate after batch adsorption has been observed higher than the influent pH as evident from Tables 1 and 2. Due to this reason, lignin and tannin contents in the filtrate may thought to be a function of filtrate  $pH_i$ . Variation of soluble lignin and tannin contents (%) with effluent pH are shown in Figures 5 and 6 for two different initial Cr(VI) concentrations. Both soluble lignin and tannin contents are fitted well by polynomial function of degree 3 with  $R^2$ -value higher than 0.96. From these figures, it is evident that the effluent pH varied in a narrow range of 4 to 5.5 but was higher than the pH of influent Cr(VI) solution (pH 3). Thus, it is concluded that both lignin and tannin contents in the filtrate are also a function of effluent pH ( $pH_e$ ). Variation of soluble lignin

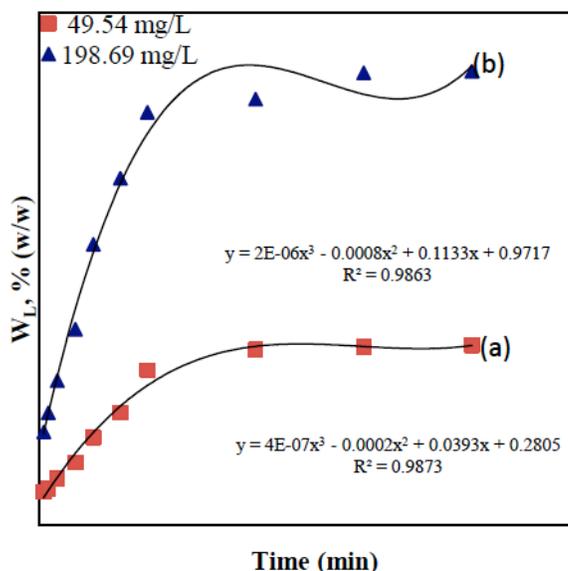


**Figure 5:** Variation of Lignin content with pH in batch test filtrate [ $C_0 = 49.54$  and  $198.69$  mg/L;  $M = 2.5$  and  $6.0$  g/L respectively].

and tannin contents (%) with time are shown in Figures 7 and 8 for two different initial Cr(VI) concentrations. In these figures, the data are fitted well with polynomial of degree 3 with  $R^2$  value of 0.97 and higher.

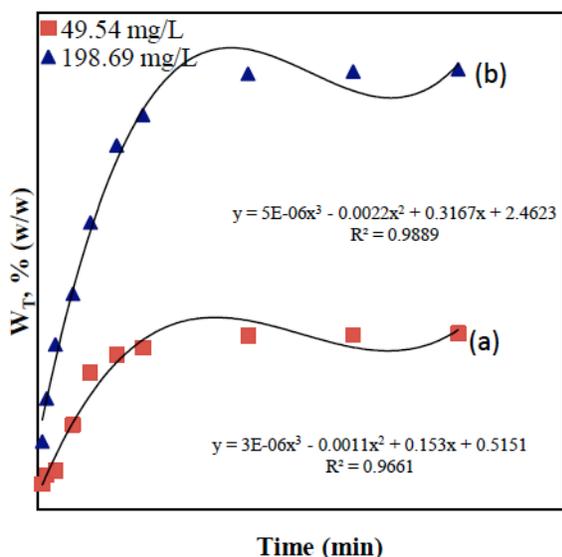


**Figure 6:** Variation of Tannin content with pH in batch test filtrate [ $C_0 = 49.54$  and  $198.69$  mg/L;  $M = 2.5$  and  $6.0$  g/L respectively].



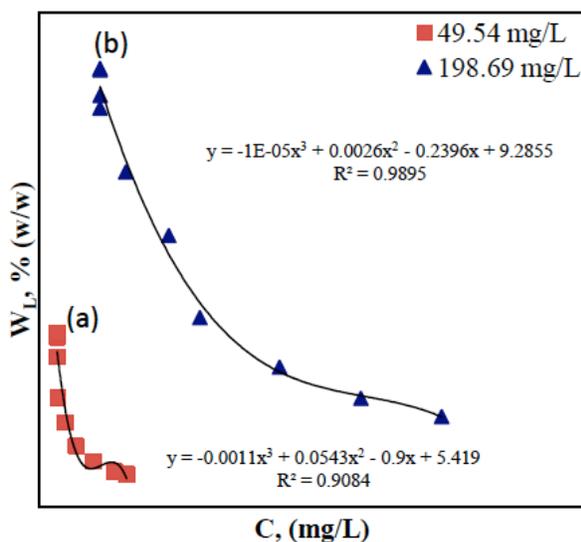
**Figure 7:** Variation of  $W_L$  with time in batch test filtrate [ $C_0 = 49.54$  and  $198.69$  mg/L;  $M = 2.5$  and  $6.0$  g/L respectively].

In order to explore the dependency of soluble lignin and tannin contents (%) on residual Cr(VI) concentration ( $C$ ), the curves were drawn in Figures 9 and 10 respectively for two different initial Cr(VI) concentrations. The experimental data are fitted well with polynomial of degree 3 with  $R^2$ -values 0.91 or higher. An interesting observation recorded from these



**Figure 8:** Variation of  $W_T$  with time in batch test filtrate [ $C_0 = 49.54$  and  $198.69$  mg/L;  $M = 2.5$  and  $6.0$  g/L respectively].

figures is that with higher residual Cr(VI) concentrations both the soluble lignin and tannin contents are low. As the adsorption proceeds the residual Cr(VI) concentration decreases and correspondingly there is rise in both soluble lignin and tannin contents. Therefore, lignin and tannin contents appear to be correlated with residual Cr(VI) concentration in batch test filtrate.

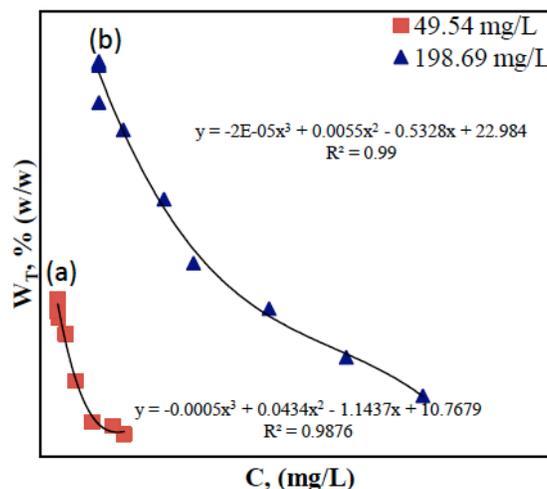


**Figure 9:** Variation of  $W_L$  with  $C$ , mg/L in batch test filtrate [ $C_0 = 49.54$  and  $198.69$  mg/L;  $M = 2.5$  and  $6.0$  g/L respectively].

### Dimensionless Approach to Model Lignin and Tannin Contents

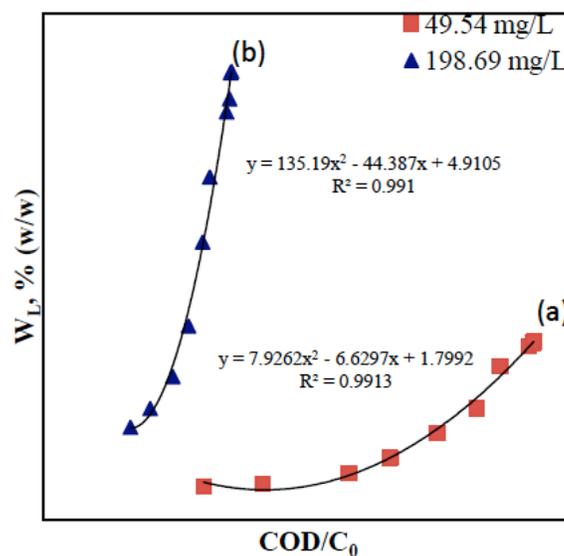
Dimensionless approach has rarely been applied in the modelling of adsorption phenomenon as well as in the analysis of soluble lignin and tannin contents in the

batch test filtrate. In the present work, a dimensionless approach using Buckingham  $\pi$  theorem has been applied to model the soluble lignin ( $W_L$ ) and tannin ( $W_T$ ) contents (%). Various dimensionless groups  $t/T$ ,  $COD/C_0$ ,  $W_{ad}/V.C$ ,  $pH_e/pH_i$  have been developed for  $W_L$  and  $W_T$ . The behaviour of  $W_L$  and  $W_T$  have been observed through plots with dimensionless groups i.e.  $t/T$ ,  $COD/C_0$ ,  $W_{ad}/VC$  and  $pH_e/pH_i$ .

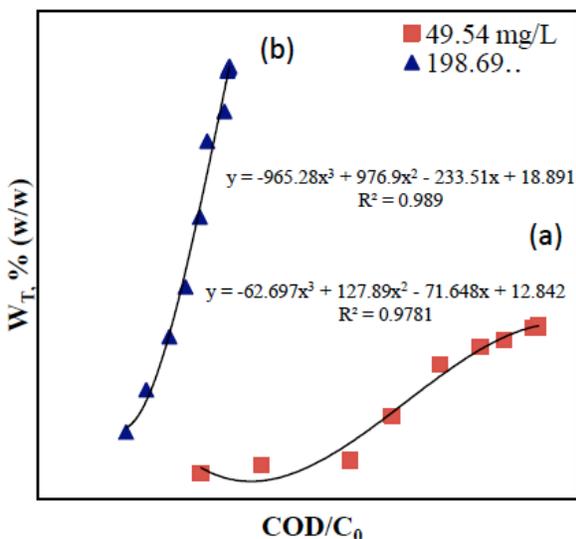


**Figure 10:** Variation of  $W_T$  with  $C$ , mg/L in batch test filtrate [ $C_0 = 49.54$  and  $198.69$  mg/L;  $M = 2.5$  and  $6.0$  g/L respectively].

Variations of  $W_L$  and  $W_T$  (%) are plotted against  $COD/C_0$  and are shown in Figures 11 and 12 respectively. The nature of the curves represent a definite trend and follow a polynomial of degree 2 with  $R^2$ -values above 0.98 for both the Cr(VI) concentrations studied.

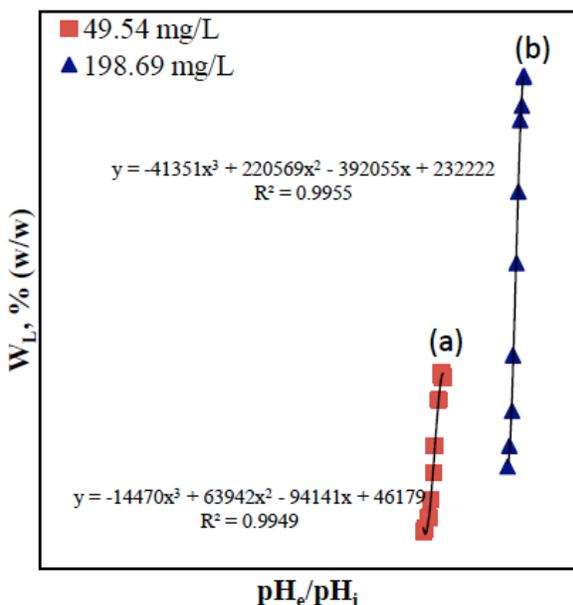


**Figure 11:** Variation of  $W_L$  with  $COD/C_0$  in batch test filtrate [ $C_0 = 49.54$  and  $198.69$  mg/L;  $M = 2.5$  and  $6.0$  g/L respectively].



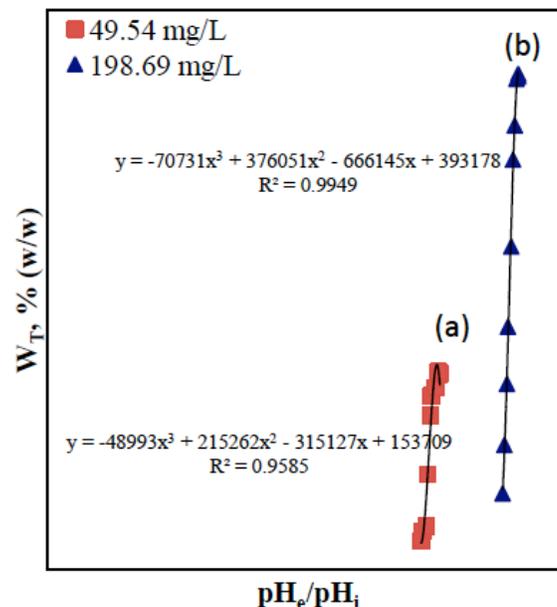
**Figure 12:** Variation of  $W_T$  with  $COD/C_0$  in batch test filtrate [ $C_0 = 49.54$  and  $198.69$  mg/L;  $M = 2.5$  and  $6.0$  g/L respectively].

While acquisition of data on pH, it was observed that the pH of the filtrate after batch adsorption is changed to higher values with increase in dose of EOLP. Due to this reason, it was felt necessary to observe the variations of the  $W_L$  and  $W_T$  with dimensionless pH i.e.  $pH_e/pH_i$  as shown in Figures 13 and 14. The experimental data best corresponds to polynomial of degree 3 with  $R^2$  values above 0.96.



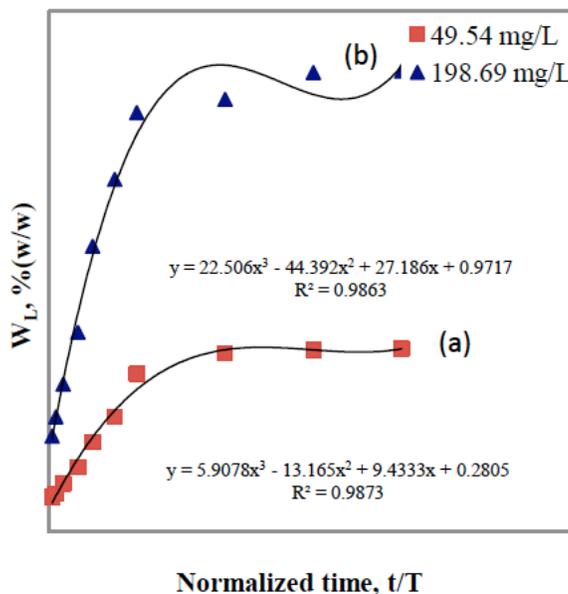
**Figure 13:** Variation of  $W_L$  with  $pH_e/pH_i$  in batch test filtrate [ $C_0 = 49.54$  and  $198.69$  mg/L;  $M = 2.5$  and  $6.0$  g/L respectively].

Experimental results of Tables 1 and 2 clearly show that soluble lignin or tannin contents (%) are highly dependent on the time of contact for which the



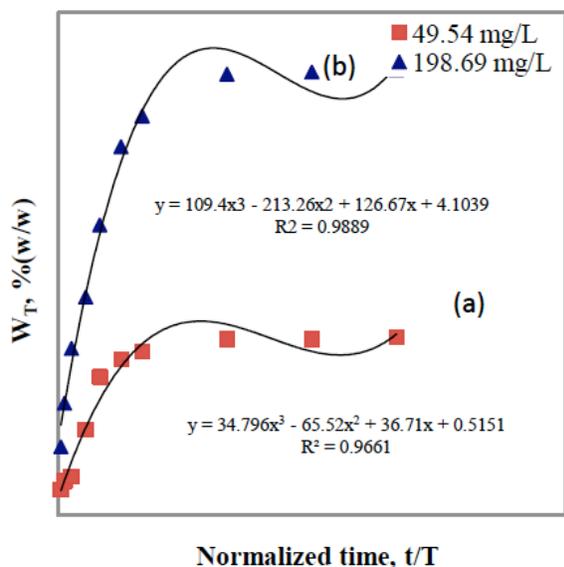
**Figure 14:** Variation of  $W_T$  with  $pH_e/pH_i$  in batch test filtrate [ $C_0 = 49.54$  and  $198.69$  mg/L;  $M = 2.5$  and  $6.0$  g/L respectively].

adsorbent is in contact with Cr(VI) solution. Therefore, in order to observe the behaviour of  $W_L$  or  $W_T$  with normalized time ( $t/T$ ), i.e. time of contact per unit time of total duration of experiments, the curves were drawn in Figures 15 and 16. The experimental data are fitted well with polynomial of degree 3 with  $R^2$ -value above 0.97.



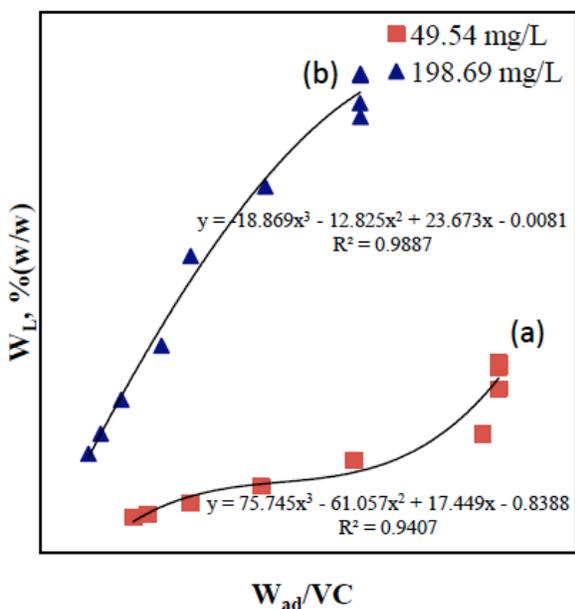
**Figure 15:** Variation of  $W_L$  with normalized time in batch test filtrate [ $C_0 = 49.54$  and  $198.69$  mg/L;  $M = 2.5$  and  $6.0$  g/L respectively].

Experimental results further demonstrate that Cr(VI) concentration varies with time of contact and hence the



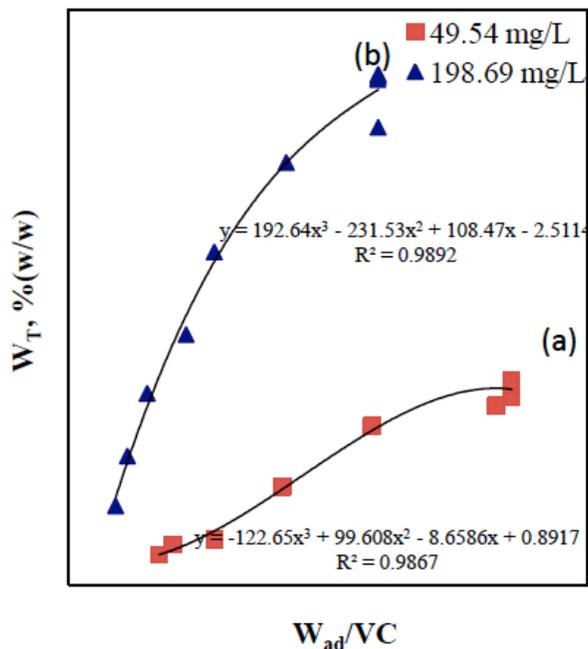
**Figure 16:** Variation of  $W_T$  with normalized time in batch test filtrate [ $C_0 = 49.54$  and  $198.69$  mg/L;  $M = 2.5$  and  $6.0$  g/L respectively].

mass of Cr(VI) remained in the filtrate (VC) may be responsible for increase in colour concentration with higher adsorbent doses. In order to observe the role of residual mass of Cr(VI) in the filtrate, both  $W_L$  and  $W_T$  were plotted against a dimensionless parameter ( $W_{ad}/VC$ ) as shown in Figures 17 and 18 respectively. A definite trend is seen in both these figures and the data are fitted with polynomial of degree 3 with  $R^2$ -values higher than 0.94. The behaviour of the curves show that both the soluble lignin and tannin contents



**Figure 17:** Variation of  $W_L$  with ratio  $W_{ad}/VC$  in batch test filtrate [ $C_0 = 49.54$  and  $198.69$  mg/L;  $M = 2.5$  and  $6.0$  g/L respectively].

have dependency on the residual Cr(VI) concentrations and the doses of adsorbent added during experiments. From these plots (Figures 1 to 18), it is evident that both soluble lignin and tannin contents (%) have certain dependency on the various dimensionless variables studied.



**Figure 18:** Variation of  $W_T$  with ratio  $W_{ad}/VC$  in batch test filtrate [ $C_0 = 49.54$  and  $198.69$  mg/L;  $M = 2.5$  and  $6.0$  g/L respectively].

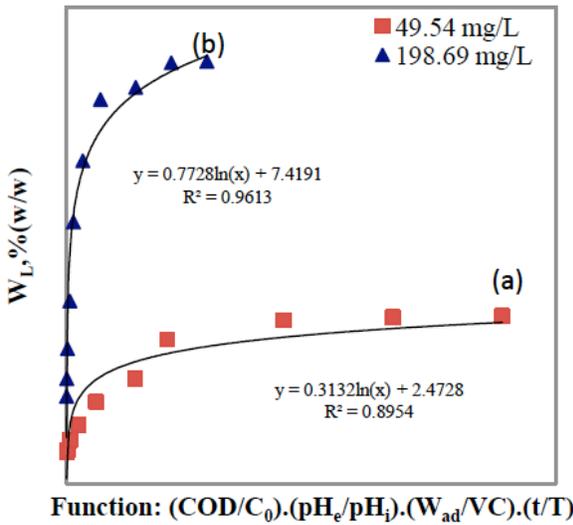
### Kinetics of Leaching of Lignin and Tannin

In order to evaluate the kinetics of leaching of soluble lignin and tannin contents during batch adsorption experiments, the combined influence of various dimensionless parameters i.e.  $COD/C_0$ ,  $pH_e/pH_i$ ,  $t/T$  and  $W_{ad}/VC$  on  $W_L$  and  $W_T$  was studied using a dimensionless multiplier function ( $F$ ) as expressed below:

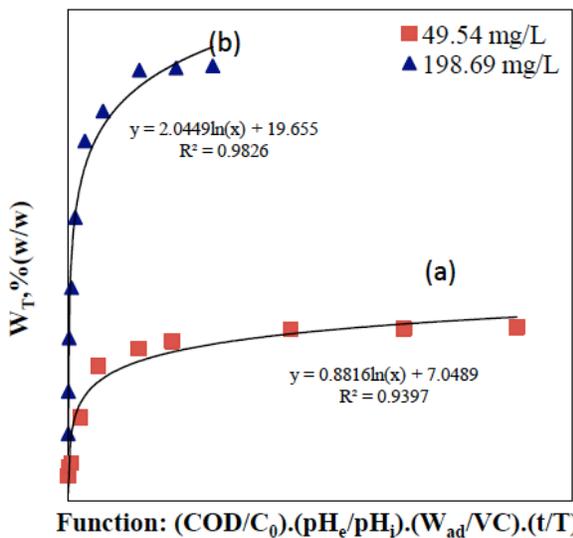
$$F = \frac{COD}{C_0} \cdot \frac{pH_e}{pH_i} \cdot \frac{t}{T} \cdot \frac{W_{ad}}{VC} \tag{4}$$

Variation of  $W_L$  and  $W_T$  (%) with function ( $F$ ) are shown in Figures 19 and 20 respectively. These plots show a definite trend of variations of  $W_L$  or  $W_T$ . From the nature of plots in these figures, it is evident that the variation of  $W_L$  or  $W_T$  with function ( $F$ ) follows a pseudo second order type behaviour. The experimental data are best fitted with logarithmic function having  $R^2$ -values above 0.90 for  $W_L$  and above 0.94 for  $W_T$  as can be seen from Figures 19 and 20 respectively. A pseudo second order expression for  $W_L$

and  $W_T$  with respect to function (F) can be respectively expressed as:



**Figure 19:** Variation of  $W_L$  with function  $[(COD/C_0) \cdot (pH_e/pH_i) \cdot (W_{ad}/VC) \cdot (t/T)]$  in batch test filtrate [ $C_0 = 49.54$  and  $198.69$  mg/L;  $M = 2.5$  and  $6.0$  g/L respectively].



**Figure 20:** Variation of  $W_T$  with function  $[(COD/C_0) \cdot (pH_e/pH_i) \cdot (W_{ad}/VC) \cdot (t/T)]$  in batch test filtrate [ $C_0 = 49.54$  and  $198.69$  mg/L;  $M = 2.5$  and  $6.0$  g/L respectively].

$$\frac{dW_T}{dF} = k_{2T} (W_{T_e} - W_T)^2 \quad (5)$$

$$\frac{dW_L}{dF} = k_{2L} (W_{L_e} - W_L)^2 \quad (6)$$

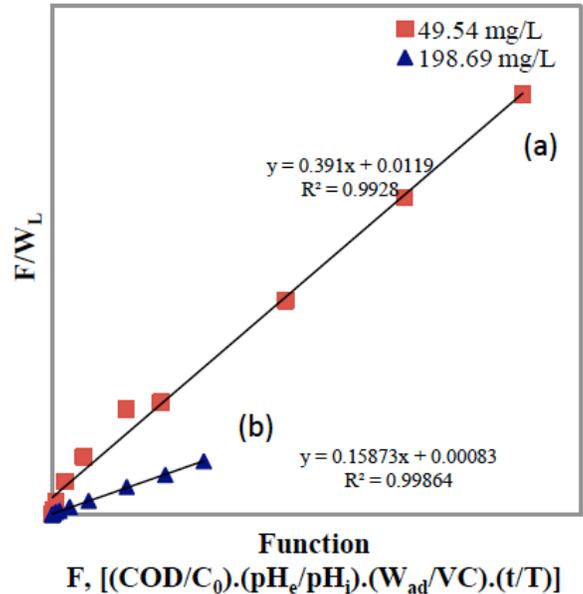
Where,  $k_{2L}$  = pseudo second order rate constant for leaching of soluble lignin;  $k_{2T}$  = pseudo second order rate constant for leaching of tannins;  $W_{L_e}$  = soluble lignin content at equilibrium (%);  $W_{T_e}$  = Tannin content

at equilibrium (%) and  $W_L$  and  $W_T$  are soluble lignin and tannin content at time,  $t$  (%)

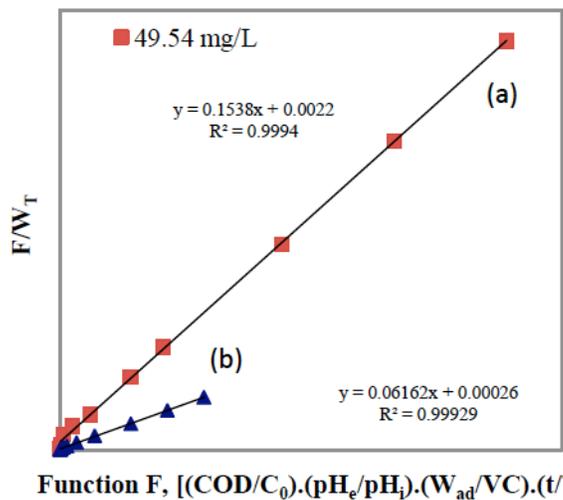
The solution of Eq. (5) and (6) and the corresponding linear forms can be expressed as:

$$\frac{F}{W_L} = \frac{1}{k_{2L} W_{L_e}^2} + \frac{F}{W_{L_e}} \quad (7)$$

and,



**Figure 21:** Linear model for the ratio  $(F/W_L)$  using dimensionless function  $F = [(COD/C_0) \cdot (pH_e/pH_i) \cdot (W_{ad}/VC) \cdot (t/T)]$  [ $C_0 = 49.54$  and  $198.69$  mg/L;  $M = 2.5$  and  $6.0$  g/L respectively].



**Figure 22:** Linear model for the ratio  $(F/W_T)$  using dimensionless function  $F = [(COD/C_0) \cdot (pH_e/pH_i) \cdot (W_{ad}/VC) \cdot (t/T)]$  [ $C_0 = 49.54$  and  $198.69$  mg/L;  $M = 2.5$  and  $6.0$  g/L respectively].

**Table 3: Linear Functions for Estimation of Soluble Lignin and Tannin Contents**

S.No.	Initial Cr(VI) concentration (mg/L)	Adsorbent dose (g/L)	Linear models for estimation of Lignin and Tannin	Kinetic constants	R <sup>2</sup>
1.	49.54	2.5	$F/W_L=0.391F+0.011$	$W_{Le}=2.45$ $k_{2L}=1.20$	0.992
2.	198.69	6	$F/W_L=0.15873F+0.00083$	$W_{Le}=6.16$ $k_{2L}=1.94$	0.998
3.	49.54	2.5	$F/W_T=0.153F+0.002$	$W_{Te}=6.36$ $k_{2T}=0.85$	0.999
4.	198.69	6	$F/W_T=0.06162F+0.00026$	$W_{Te}=15.92$ $k_{2T}=0.99$	0.999

$$\frac{F}{W_T} = \frac{1}{k_{2T}W_{T_e}^2} + \frac{F}{W_{T_e}} \quad (8)$$

Curves have been plotted between  $F/W_L$  or  $F/W_T$  as a function  $F$ , for two different initial Cr(VI) concentrations and are shown in Figures 21 and 22 respectively for soluble lignin and tannin contents (%). Excellent linear fits are observed in both these figures with R<sup>2</sup>-values greater than 0.99. This clearly shows a better correlation of multiplier function 'F' with both soluble lignin and tannin contents in batch test filtrate. The simple linear expressions for soluble lignin and tannin contents (%) along with kinetic constants of leaching of lignin and tannins and R<sup>2</sup>-values are presented in Table 3.

These expressions can be easily used to estimate the soluble lignin and tannin contents in the batch test filtrate after batch adsorption with a fair degree of accuracy.

## CONCLUSIONS

Raw *Embllica officinalis* leaves impart lignin and tannin in filtrate of batch adsorption tests. Both lignin and tannin contents are found related to pH, chemical oxygen demand(COD), initial Cr(VI) concentration (C<sub>0</sub>) residual Cr(VI) concentration in batch test filtrate (C), amount of adsorbent (W<sub>ad</sub>) and time of contact (t). Dimensionless parameters are developed and the lignin and tannin contents are found correlated with dimensionless parameters. From the study conducted on rate of leaching of soluble lignin and tannins, the kinetics of leaching of soluble lignin and tannin follow a pseudo second order rate kinetics. Linear mathematical models are derived based on pseudo second order kinetics for determination of lignin and tannin contents in batch test filtrate. However, these findings need to be verified in future studies.

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## NOTATIONS

- Abs = Absorbance value (%)
- C = Residual Cr(VI) concentration in batch test filtrate (mg/L)
- COD = Chemical oxygen demand in filtered sample (mg/L)
- C<sub>0</sub> = Initial Cr(VI) ion concentration (mg/L)
- C<sub>SL</sub> = Concentration of soluble lignin content (g/L)
- F = Multiplier function (-)
- k<sub>2L</sub> = Pseudo second order rate constant for leaching of soluble lignin
- k<sub>2T</sub> = Pseudo second order rate constant for leaching of tannins
- pH<sub>e</sub> = pH of the filtered sample after adsorption
- pH<sub>i</sub> = Initial pH of Cr(VI) solution
- R<sup>2</sup> = Coefficient of determination
- T = Time of total duration of experimental run (min)
- t = Time of contact (min)
- V = total volume of the filtrate (ml)
- V<sub>f</sub> = Final volume of solution (ml)

- $V_i$  = Initial volume of the solution (ml)
- $V'$  = Volume of 0.1 N aqueous solution of  $KMnO_4$  for the titration of the sample (ml)
- $V_O$  = Volume of titrant 0.1 N  $KMnO_4$  used for blank (ml)
- $W_{ad}$  = Mass of adsorbent (g)
- $W_L$  = Soluble lignin content (% w/w)
- $W_{Le}$  = Soluble lignin content at equilibrium (%)
- $W_T$  = Tannin content (% w/w)
- $W_{Te}$  = Tannin content at equilibrium (%)

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