Heavy Metal Ions Uptake Properties of the Aquatic Weed Hydrilla verticillata: Modeling and Experimental Validation

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Abstract: Heavy metals are one of the prominent sources of pollution in industrial wastewater and excessive presence of these metals is causing severe health and environmental problems. The prevailing purification technologies used to remove these contaminants are costly and sometimes not eco-friendly, so industries often try to escape from their responsibilities that, in turn, creates severe problems for existence of life. There is a great need to put intense and expeditious efforts into the search for more feasible and effective technologies to mitigate this problem.

Several aquatic weeds are capable of sorbing metal ions from their solution and could be utilized as one of the cheapest sources for the treatment of waste water. Our study deals with the characteristics of this sorption process for chromium, lead, zinc and iron with macrophyte Hydrilla verticillata. The data are mathematically modeled with statistical analysis. H. verticillata is found to have great efficiency in removing metal ions from the sample of water. The process is eco-friendly and if applied in an efficient manner, would prove to be the best method to tackle the problem growing metal ion pollution in water bodies.

Key words: Sorption, aquatic weed, Hydrilla verticillata, heavy metals, mathematical modeling, statistical analysis

Nomenclature

C- Concentration of metal ions present at time t
C_{in}-Initial concentration
b - Rate constant
t- Time

Introduction

Heavy metals are very harmful because of their non-biodegradable nature, long biological half-lives and their potential to accumulate in various parts of the human body. Environmental pollution due to the discharge of these heavy metals from various industries like textile, dyeing, metal plating, mining and painting, or from agricultural sources like fertilizers or fungicidal sprays cause a big concern because of their carcinogenic or toxic effects on humans, especially when tolerance levels are exceeded. These metals are toxic and having a carcinogenic effect when they exceed the tolerance level. Prevailing technologies, which mainly use an ion exchange method, ultrafiltration membranes and electrode ionization, are very costly. This, in turn, induces the industries to escape from proper treatment of their waste. In order to minimize this problem, the search for new technologies to remove metals from wastewaters has become a major topic of research.

Aquatic plants have a tremendous capacity to absorb materials from water (Boyd 1970) and hence bring the pollution load down. One promising option for mitigation of the heavy metal problem is to make use of locally available and cost-effective eco-friendly materials like the aquatic plant *Hydrilla verticillata*. H. verticillata, a submerged aquatic plant found widely in India, is listed as one of the most productive plants on earth (Rajeskannan, Rajamohan and Rajasimman 2008). It exhibits a degree of phenotypic plasticity (variable physical appearance) in response to age, habitat conditions, and water quality (Kay 1992). Branching is generally sparse in submerged portions of the plant, tending to become profuse at the surface (Langeland 1996). The costs associated with removal and maintenance control of *Hydrilla* are significant. But this species has been found to have great affinity to accumulate metal ions in its bulk. This aquatic weed absorbs the metallic ions and deposits them in various parts of macrophyte depending upon their affinity towards that particular metal (Tiwari, Dixit and Verma 2007). If utilized in an efficient manner it could prove to be one of the cheapest and most feasible source for waste water treatment in industries producing waste water containing these metal ions.

Hydrilla verticillata plant

In the present study the characteristics of sorption process of iron, zinc, lead and chromium metal ions with aquatic weed plant *Hydrilla verticillata* are presented, and the equation for the process and statistical analysis of results obtained are developed. When fitting data that contain random variations, there are two important assumptions made about the error:

1. The error exists only in the response data, and not in the predictor data.
2. The errors are random and follow a normal (Gaussian) distribution with zero mean and constant variance.

Hydrilla verticillata was grown in various concentrations of above mentioned heavy metals. Heavy metal absorption and physiological changes were observed weekly during the study.

Materials and Methodology

To find out the heavy metal removal efficiency of Hydrilla the above mentioned study was conducted in laboratory scale. Four heavy metals, namely chromium, iron, lead and zinc, were identified for the purpose of the study. Earlier studies have shown the presence of these metals in lake water taken for study (Dixit, Gupta and Tiwari 2005, Dixit et al 2007). The initial concentrations of the four heavy metals taken were 1.0, 5.0, 10.0 and 20.0 ppm as reported by Mishra and Tripathi (2009) in a similar study. For each experimental set a 2.00 liter solution of required concentration of heavy metal was taken. Hydrilla verticillata was collected from a nearby lake; 100 gm of the macrophyte was taken for each experimental set up. One of the set was controlled, in controlled experiment; where no macrophyte was introduced and 1.0, 5.0, 10.0 and 20.0 ppm concentrations were taken for each set of experiments. The duration of the experiment was four weeks. Duplicate samples were collected weekly from each set. Samples were collected and preserved as mentioned in APHA (1995) by filtering the sample with Whatman filter paper No.42 and adding 5.0 ml of concentrated nitric acid in one liter of sample to maintain the pH below 2.0.

Heavy metal analysis was performed with an atomic absorption spectrophotometer. The uptake of the metal by the plant and its tissue are affected by several parameters; e.g., pH, temperature, flow, evaporation, solar radiations, chemical constituent such as chlorides, sulphates, phosphates, nitrogen, BOD, COD, TOC, DO, TDS, TSS and metals. But the researchers have taken only two important parameters in detail; viz. exposure time and concentration of metals to which the plants were exposed (as taken by Hasan and Rai 2007 and Sudhira and Kumar 2000 in a similar type of experimental setup).

Statistical Parameters

Various statistical parameters for the equation are calculated which is designated by the following.

SSE - Sum of squares due to error

This statistic parameter measures the total deviation of the response values from the fit to the response values. It is also called the summed square of residuals and is usually labeled as SSE.

$$SSE = \sum_{i=1}^{n} w_i (y_i - \hat{y}_i)^2$$

A value closer to 0 indicates that the model has a smaller random error component, and that the fit will be more useful for prediction.

R2 - Coefficient of determination.

This statistic measures how successful the fit is in explaining the variation of the data. Put another way, R-square is the square of the correlation between the response values and the predicted response values. It is also called the square of the multiple correlation coefficients and the coefficient of multiple determinations. R-square is defined as the ratio of the sum of squares of the regression (SSR) and the total sum of squares (SST). SSR is defined as

$$SSR = \sum_{i=1}^{n} w_i (\hat{y}_i - \bar{y})^2$$

SST is also called the sum of squares about the mean, and is defined as

$$SST = \sum_{i=1}^{n} w_i (y_i - \bar{y})^2$$

Where SST = SSR + SSE. Given these definitions, R-square is expressed as

$$\text{R-square} = \frac{SSR}{SST} = 1 - \frac{SSE}{SST}$$

R-square can take on any value between 0 and 1, with a value closer to 1 indicating that a greater proportion of variance is accounted for by the model. For example, an R-square value of 0.8234 means that the fit explains 82.34% of the total variation in the data about the average.

Adjusted R-square - Degree-of-freedom adjusted coefficient of determination

This statistic uses the R-square statistic defined above, and adjusts it based on the residual degrees of freedom. The residual degrees of freedom is defined as the number of response values n minus the number of fitted coefficients m estimated from the response values.

$$v = n - m$$

The letter 'v' indicates the number of independent pieces of information involving the 'n' data points that are required to calculate the sum of squares. Note that if parameters are bounded and one or more of the estimates are at their bounds, then those estimates are regarded as fixed. The degrees of freedom are increased by the number of such parameters.

The adjusted R-square statistic is generally the best indicator of the fit quality when you compare two models that are nested — that is, a series of models each of which adds additional coefficients to the previous model.

$$\text{adjusted R-square} = 1 - \frac{SSE(n-1)}{SST(v)}$$

RMSE- Root mean squared error (standard error).

This statistic is also known as the fit standard error and the standard error of the regression. It is an estimate of the standard deviation of the random component in the data, and is defined as

$$RMSE = s = \sqrt{MSE}$$

Where MSE is the mean square error or the residual mean square $$MSE = \frac{SSE}{v}$$

Results and Discussions

Sorption Characteristics for Iron

Samples of iron were taken with initial concentrations of 1ppm, 5ppm, 10ppm and 20ppm, and weekly changes in concentration were observed with the help of atomic absorption spectrophotometer. Table 1 shows the variation of concentration observed over time. Separate samples were also taken that were not subjected to any weed. Variation in the concentration of metal ions in this sample was observed, shown in the column designated by Controlled 4th week. A negligible reduction in concentration, which may be due to sorption on container walls or some natural decomposition process, was observed. The last column in the table shows the total percentage reduction in concentration with respect to initial concentration taken.

Heavy Metal Concentration (mg./l)	Initial concentration	1st week	2nd week	3rd week	4th week	Controlled 4th Week	Total pollution reduction
Iron (Fe)	1.00	0.50	0.32	0.21	0.16	0.98	84.00
Iron (Fe)	5.00	3.21	2.11	1.18	1.10	4.87	78.00
Iron (Fe)	10.00	5.98	4.34	3.33	3.30	9.41	68.00
Iron (Fe)	20.00	15.40	12.62	10.45	9.30	18.96	54.00

Table 1. Weekly Change in Concentration of Iron after Treating with Hydrilla verticillata.

Several mathematical relations were found to fit these values by the method of linear least square. The following mathematical relation showing first order reaction characteristics was found to be best suited:

C=Cin*exp (b*t).

Table 2 shows the values of various statistical parameters obtained. This equation shows that rate of sorption is directly proportional to the concentration of metal present at that time, or sorption process follows the first order kinetics.

Most suitable values of constants for the equation and various statistical parameter for the results obtained are shown below in Table 2.

Average value of 'b' is found to be at an average of 0.05 while SSE values approaches 0, except in case of 10 ppm

Iron Initial concentration	Value of C_{in}	Value of b	SSE	R-Square	Adjusted R-square	RMSE
1ppm	1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
5ppm	5	-0.06174	0.0879	0.9934	0.9898	0.1641
10ppm	10	-0.05455	1.717	0.9463	0.9284	0.7565
20ppm	20	-0.02917	0.0878	0.9881	0.9842	0.544

Table 2. Various Parameters Obtained for Iron and HV.

concentration which might be due to some observational error. R-square value was found to be near to 1 which shows a very good concurrence of the process with the obtained equation. Deviation in parameters from their ideal values is observed as the concentration of metal increases, but even then results obtained are quite acceptable and satisfactory.

Curves obtained by the equation are shown in Fig. 1.

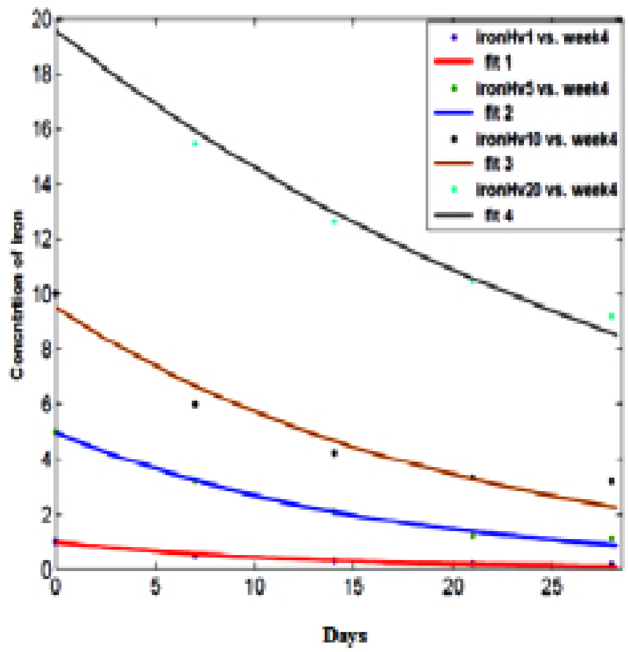

Figure 1. Variation in Concentration of Fe with Time.

A similar analysis was also done for chromium, lead and zinc, the results for which are shown in tables below.

Sorption Characteristics for Zinc

Heavy Metal Concentration (mg./l)	Initial concentration	1st Week	2nd week	3rd week	4th week	Controlled 4th Week	Total Pollution Reduction
Zinc(Zn)	1.00	0.64	0.34	0.16	0.14	0.98	86.00
Zinc(Zn)	5.00	3.20	2.00	1.10	1.00	4.87	80.00
Zinc(Zn)	10.00	7.40	5.40	3.81	2.40	9.58	76.00
Zinc(Zn)	20.00	15.68	12.42	9.75	6.40	18.72	68.00

Table 3. Weekly Change in Concentration of Zinc after Treating with Hydrilla verticillata.

These values have fitted in similar mathematical model and results obtained are shown in Table 4.

Table 4. Various Parameters Obtained for Zinc and HV.

Zinc initial concentration	Value of C_{in}	Value of b	SSE	R-Square	Adjusted R-square	RMSE
1ppm	1	-0.07602	0.004704	0.9911	0.9882	0.0396
5ppm	5	-0.06418	0.07093	0.9936	0.9915	0.1538
10ppm	10	-0.04683	0.1858	0.9948	0.9931	0.2488
20ppm	20	-0.03764	0.7359	0.9935	0.9913	0.4953

Various curves obtained are shown Figures.

Sorption Characteristics for Lead

Results obtained for lead are shown in the table below.

Heavy Metal Concentration (mg./l)	Initial concentration	1st Week	2nd week	3rd week	4th week	Controlled 4th Week	Total Pollution Reduction
Lead (Pb)	1.00	0.73	0.48	0.28	0.20	0.99	80.00
Lead (Pb)	5.00	3.46	2.52	1.61	1.40	4.89	72.00
Lead (Pb)	10.00	6.94	4.77	3.58	Lethal Dose	9.70	64.00
Lead (Pb)	20.00	16.88	Lethal Dose			18.56	15.60

Table 5. Weekly Change in Concentration of Lead after Treating with Hydrilla verticillata.

Values of various parameters obtained for general equation type used above are given in the following table.

Lead initial concentration	Value of C_{in}	Value of b	SSE	R-Square	Adjusted R-square	RMSE
1ppm	1	-0.05633	0.003884	0.9933	0.9911	0.03101
5ppm	5	-0.0495	0.05153	0.9941	0.9921	0.1311
10ppm	10	-0.04703	0.3443	0.9888	0.9832	0.3495

Table 6. Various Parameters Obtained for Lead and HV.

We have found similar results for lead as in the case of zinc, but values of rate constant have converged more. All statistical parameters are very much concurrent to their expected values for good fitting.

At initial concentration of 20ppm, the plant died in 14 days. So, the data obtained were not significant to be put into the model. Curves obtained are shown in fig. 3

Sorption Characteristics for Chromium

Results obtained for chromium are shown in Table 7.

Heavy Metal Concentration (mg./l)	Initial concentration	1st Week	2nd week	3rd week	4th week	Controlled 4th Week	Total Pollution Reduction
Chromium(Cr)	1.00	0.62	0.52	0.37	0.20	0.982	80.00
Chromium(Cr)	5.00	3.12	1.96	1.54	1.40	4.89	72.00
Chromium(Cr)	10.00	6.55	4.57	3.69	plant died	9.60	63.10
Chromium(Cr)	20.00	13.48	plant died			19.10	37.60

Table 7. Weekly Change in Concentration of Chromium after Treating with Hydrilla verticillata.

Values of various parameters obtained for general equation type used above are given in Table 8.

Chromium initial concentration	Value of C_{in}	Value of b	SSE	R-Square	Adjusted R-square	RMSE
1ppm	1	-0.05178	0.006849	0.9821	0.9761	0.04778
5ppm	5	-0.05643	0.2989	0.9671	0.9561	0.3156
10ppm	10	-0.05186	0.2919	0.9876	0.9814	0.382

Table 8. Various Parameters Obtained for Chromium and HV.

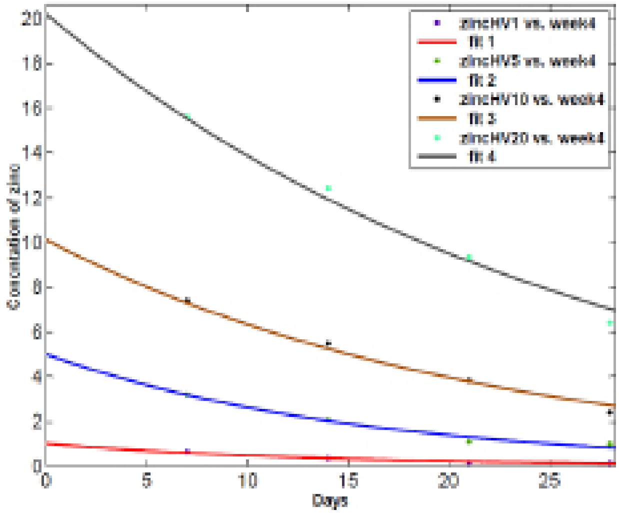

Figure 2. Variation in Concentration of Zn with Time.

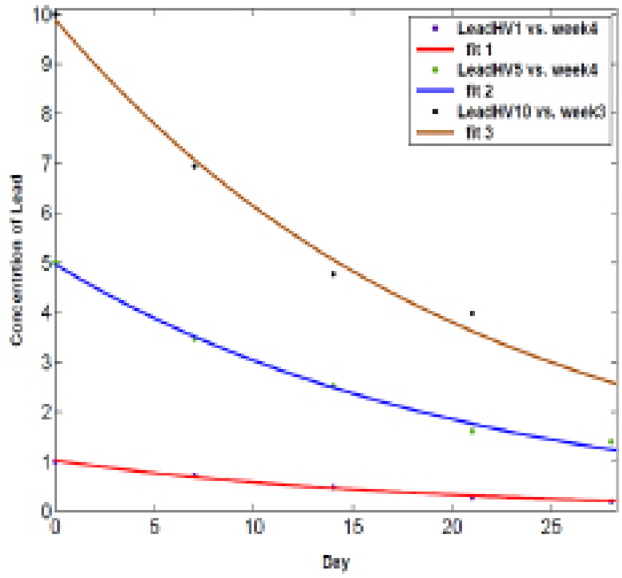

Figure 3. Variation in Concentration of Pb with Time.

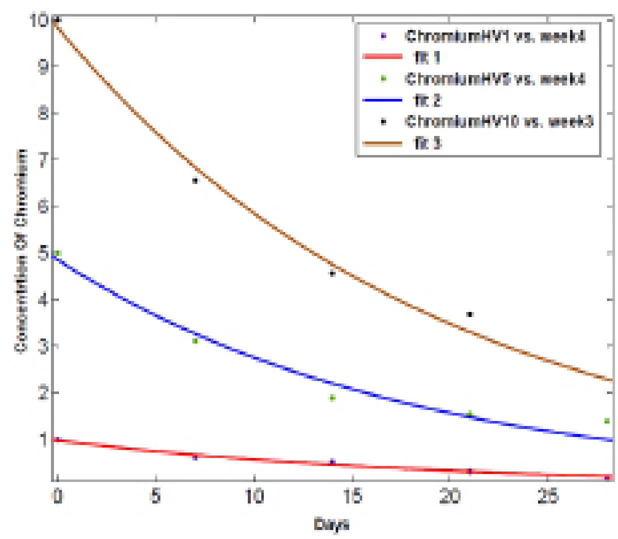

Figure 4. Variation in Concentration of Cr with Time.

Results obtained for chromium are most satisfactory because the values have converged again and found nearly equal to 0.05. Other parameters of SSE, R-Square, adjusted R-square, and RMSE are also very satisfactory.

Curves obtained are shown in Fig. 4

In case of toxic metals like Zn and Cr, the plant died after a certain high amount of sorption manifesting that plants have a permissible value for toxic metal ions.

Conclusion

In this study, heavy metal ions uptake properties of aquatic weed Hydrilla verticillata were analysed. Solutions of Fe, Zn ,Pb and Cr were prepared with initial concentrations of 1, 5, 10, 20 ppm, and 100 gm of macrophyte added to it. Weekly readings of remaining metal ion concentrations were calculated. An equation representing experimental observations was derived using statistical analysis. The sorption process was found to follow first order kinetics. SSE values were nearly equal to zero, R-square values were found to approach 1, RMSE values were also very satisfactory. Variation in rate constant for Fe and Zn is considerable, but for Pb and Cr it is nearly constant at 0.05. The proposed model was found to well describe the experiment results.

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