

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

Savita Dixit, Sangeeta Dhote, Ranajyoti Das, Rajat Dubey, and Harsh Vaidya



Savita Dixit



Sangeeta Dhote

**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



*Hydrilla verticillata* plant

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.

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.

### *R<sup>2</sup> - 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

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

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	0.90	0.82	0.75	0.68	0.98	14.00
Iron (Fe)	5.00	3.91	3.11	2.41	1.90	4.87	78.00
Iron (Fe)	10.00	6.90	4.94	3.53	2.50	8.61	68.00
Iron (Fe)	20.00	15.40	12.63	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:

$$C = C_{in} * \exp(b * t).$$

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 <sub>in</sub>	Value of b	SSE	R-Square	Adjusted R-square	RMSE
1ppm	1	-0.07807	0.007366	0.9932	0.9940	0.08596
5ppm	5	-0.06174	0.00079	0.9924	0.9890	0.11661
10ppm	10	-0.04899	1.717	0.9863	0.9884	0.1304
20ppm	20	-0.02817	0.0070	0.9881	0.9840	0.164

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.

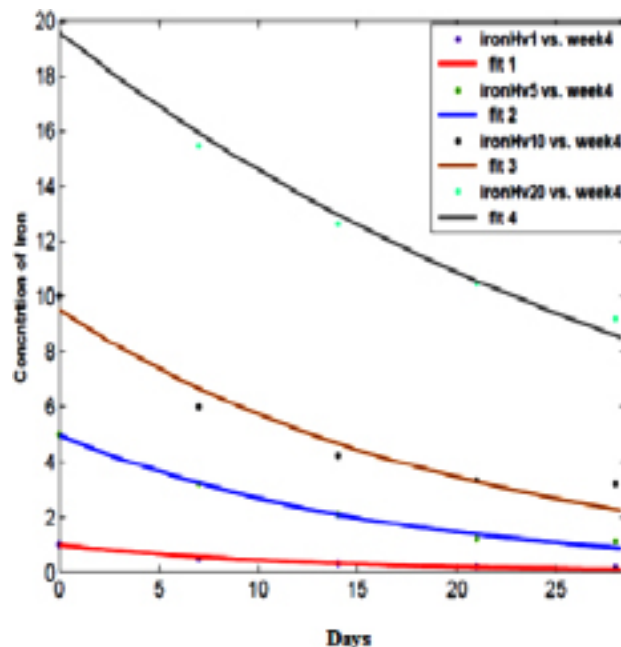


Figure 1. Variation in Concentration of Fe with Time.

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	0.84	0.74	0.76	0.74	0.98	16.00
Zinc(Zn)	5.00	3.20	2.18	1.70	1.00	4.87	88.00
Zinc(Zn)	10.00	7.40	5.48	3.87	2.40	9.58	76.00
Zinc(Zn)	20.00	15.68	12.42	9.79	6.60	18.77	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.

Disc Initial concentration	Value of $C_{in}$	Value of $b$	SSR	R-Square	Adjusted R-square	RMSE
1ppm	1	-0.00632	0.000004	0.9911	0.9881	0.0096
5ppm	5	-0.00611	0.00003	0.9906	0.9902	0.0138
10ppm	10	-0.00603	0.00001	0.9908	0.9901	0.0088
20ppm	20	-0.00584	0.00007	0.9905	0.9902	0.0093

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	0.38	0.28	0.78	88.00
Lead (Pb)	5.00	3.46	2.03	1.61	1.40	4.09	72.00
Lead (Pb)	10.00	6.94	4.07	3.08	plant died	9.29	68.00
Lead (Pb)	20.00	14.08	plant died			18.76	15.00

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 $b$	SSR	R-Square	Adjusted R-square	RMSE
1ppm	1	-0.05632	0.000004	0.9903	0.9911	0.0101
5ppm	5	-0.0495	0.00133	0.9941	0.9911	0.0101
10ppm	10	-0.04932	0.00001	0.9908	0.9902	0.0093

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	0.67	0.52	0.37	0.26	0.62	80.00
Chromium(Cr)	5.00	3.12	1.90	1.54	1.40	4.09	72.00
Chromium(Cr)	10.00	6.55	4.57	3.69	plant died	9.68	62.00
Chromium(Cr)	20.00	11.48	plant died			18.76	31.00

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 $b$	SSR	R-Square	Adjusted R-square	RMSE
1ppm	1	-0.05078	0.000009	0.9921	0.9761	0.0071
5ppm	5	-0.05643	0.00006	0.9971	0.9561	0.0086
10ppm	10	-0.05186	0.00007	0.9976	0.9624	0.0082

Table 8. Various Parameters Obtained for Chromium and HV.

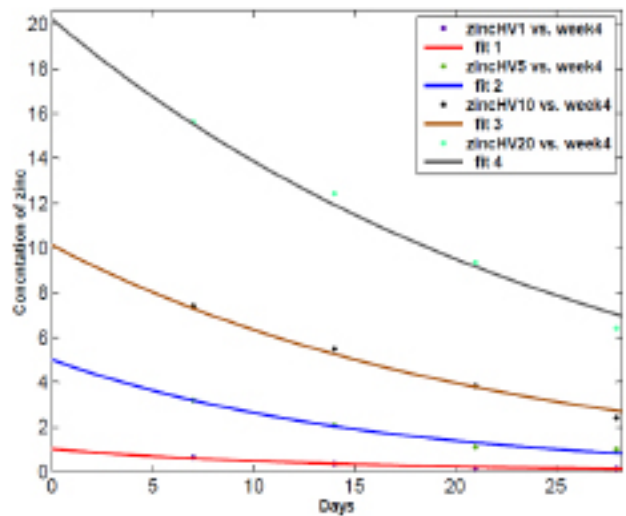


Figure 2. Variation in Concentration of Zn with Time.

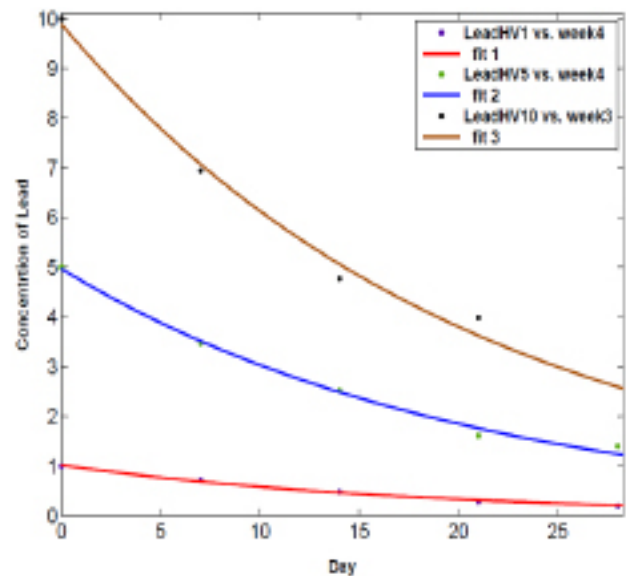


Figure 3. Variation in Concentration of Pb with Time.

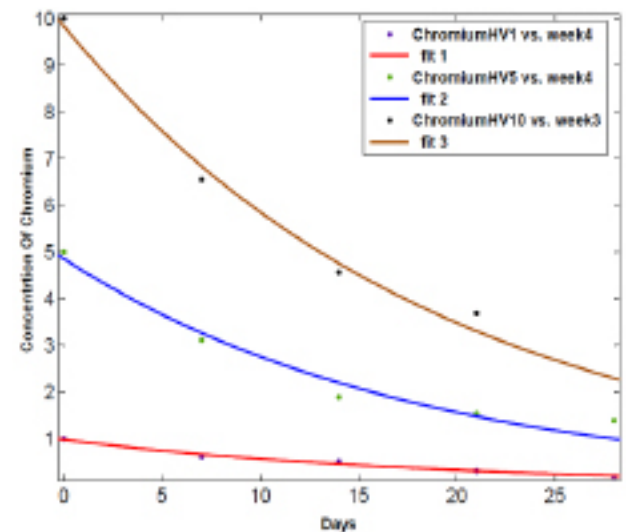


Figure 4. Variation in Concentration of Cr with Time.

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.

--

**Savita Dixit**, PhD, is a Assistant Professor of Applied Chemistry in MANIT, National Institute of Technology at Bhopal, India, and has more than 20 years of teaching experience at graduate and post graduate levels in Indian universities. She is actively involved in research activities in environmental sciences. She has also guided PhD and M. Tech. candidates towards their degrees.

Corresponding address: savitadixit1@yahoo.com

**Dr. Sangeeta Dhote** is Assistant Professor (Contract) in Department of Chemistry in MANIT, Bhopal, INDIA. She has teaching as well as research experience in the field of environment chemistry. She has completed her Ph.D. in water purification through macrophytes. She has a vast knowledge in the field of water purification and treatment. Along with research experience she also published research papers in various international journals. Corresponding address: sangeetadhote@yahoo.com

**Ranajyoti Das**, B. Tech 3rd year, Chemical Engineering (MANIT-Bhopal).

Corresponding address: rana.nitb@gmail.com

**Rajat Dubey**, B. Tech 3rd year, Chemical Engineering (MANIT-Bhopal).

Corresponding address: rajatdubey1110@gmail.com

**Harsh Vaidya**, B. Tech 3rd year, Chemical Engineering (MANIT-Bhopal).

Corresponding address: harsh.dj@gmail.com

### References

- APHA, 1995, *Standard Methods for the Examination of Water and Wastewater* (19th ed.), Washington, DC: American Public Health Association, American Water Works Association, and Water Pollution Control Federation.
- Boyd C.E., 1970, 'Vascular aquatic plants for mineral nutrient removal from polluted water,' *Economic Botany* 24:95-103.
- Dixit, S., N. Verma, S. Tiwari and D.D. Mishra, 2007, 'An innovative technique for lake management with reference to aeration unit installed at Lower Lake, Bhopal, India,' *Journal of Environmental Monitoring Assessment* 124:33-37.
- Dixit, S., S.K. Gupta and S. Tiwari, 2005, 'Nutrient overloading of Fresh Water Lake of Bhopal, India,' *Electronic Green Journal*, Issue 21.
- Hasan, S.H., M. and S. Rai, 2007, 'Sorption of cadmium and zinc aqueous solutions by water hyacinth (*Eichhornia crassipes*),' *Bio-Resource Technology* 98:912-928.
- Kay, S.H., 1992, 'Hydrilla: A rapidly spreading aquatic weed in North Carolina.' AGRIS: *International Information System for the Agricultural Sciences and Technology* 449.
- Langeland K.(1996). '*Hydrilla verticillata* (L.F.) Royle (*Hydrocharitaceae*), "The Perfect Aquatic Weed", 'Castanea (Southern Appalachian Botanical Society) 61(3):293-304.
- Mishra, V.K. and B.D. Tripathi, 2009, 'Accumulation of chromium and zinc from aqueous solutions using water hyacinth (*Eichhornia crassipes*),' *Journal of Hazardous Materials* 164(2-3):1059-1063.
- Rajeshkannan R., N. Rajamohan and M. Rajasimman, 2009, 'Removal of malachite green from aqueous solution by sorption on *Hydrilla verticillata* biomass using response surface methodology,' *Frontier of Chemical Engineering (China)* 3(2):146-154.
- Sudhira, H.S. and V.S. Kumar, 2000, 'Monitoring of lake water quality in Mysore city,' *Proceeding of International Symposium on Restoration of Lakes and Wetlands*, 27-29 November, Indian Institute of Science, Bangalore, pp.1-10.
- Tiwari, S., S. Dixit and N. Verma, 2007, 'An effective means of bio-filtration of heavy metal contaminated water bodies using aquatic weed *Eichhornia crassipes*.' *Environmental Monitoring and Assessment* 129:253-256.