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Sorption characteristics of heavy metal ions by aquatic weed

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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 cause of severe health and environmental problems. The prevailing purification technologies used to remove these contaminants are so costly and sometimes non-eco-friendly. Several aquatic weeds were found to be capable of sorbing these metal ions from their solution and could be one of the cheapest sources for the treatment of wastewater. The present study deals with the characteristics of this sorption process for chromium, lead, zinc and iron with macrophyte *Eichhornia crassipes* and data obtained is mathematically modeled with the help of statistical analysis. All the modeling results and statistical analysis is found to be very much concurrent to expectation. *Eichhornia crassipes* is found to have great efficiency in removing metal ions from the sample and could be used as one of the best sources of water treatment for metal ions.

Keywords: Sorption; Aquatic weed; *Eichhornia crassipes*; Heavy metals; Mathematical modeling; Statistical analysis; SSE; R^2; RMSE

1. 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 human body. These heavy metals are discharged from various industries like textile, dyeing, metal plating, mining, painting or agricultural sources like fertilizers or fungicidal sprays. These metals are toxic and have carcinogenic effect when they exceed the tolerance level. In order to minimize this problem, the search for new technologies to remove metals from wastewaters has become a major topic of research.

One promising option is to make use of locally available and cost-effective eco-friendly materials like aquatic plant *Eichhornia crassipes*. It is commonly known as common water hyacinth, is an invasive species of plant which is native to the Amazon basin. It can be found in all types of Florida freshwater habitats and has been introduced to tropical and subtropical regions around the world [1]. Large, dense *Eichhornia crassipes* mats can degrade water quality and can choke waterways. Plant respiration and biomass decay can result in oxygen depletion and fish kills (FDEP undated).The documented negative economic impacts of water hyacinth invasion worldwide have included the clogging of irrigation channels, choking off of navigational routes, smothering of rice paddies, loss of fishing areas, increase in breeding habitat available to disease-transmitting mosquitoes, and others [2].The costs associated with removal and maintenance control of water hyacinth are significant. But this specie has 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 depend-

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ing upon their affinity towards that particular metal [3]. If utilized in an efficient manner it could prove to be one of the cheapest and most feasible sources for wastewater treatment in industries producing wastewater containing these metal ions.

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

Weeds were grown in various concentrations of the above mentioned heavy metals. Heavy metal absorption and physiological changes were observed weekly.

2. Experimental study

To find out the heavy metal removal efficiency of *Eichhornia* the above mentioned study was conducted on a laboratory scale. The four heavy metals namely chromium, iron, lead and zinc were identified for the purpose of the study, the earlier studies conducted by Dixit et al. [4,5] have shown the presence of these metals in the lakes taken for the study. The initial concentrations of all the four heavy metals taken were 1.0, 5.0, 10.0 and 20.0 ppm as taken by Mishra et al. [6] in a similar study. For each experimental set 2.00 L solution of required concentration of heavy metal was taken. *Eichhornia crassipes* and *Hydrilla verticillata* of same size were collected; 100 g of both macrophytes were taken for each experimental set. One of the sets was controlled, in a 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 [7] by filtering the sample with Whatmann 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 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 has taken only two important parameters in detail viz. exposure time and concentration of metals to which the plants were exposed as taken by Hasan et al. [8] and Sudhira et al. [9] in a similar type of experimental setup.

3. Analysis of results and discussion with statistical validation

3.1. Sorption characteristics for lead

Samples of lead were taken with initial concentration 1 ppm, 5 ppm, 10 ppm and 20 ppm and changes in concentration were observed at constant interval of 1 week with the help of atomic absorption spectrophotometer. Table 1 shows the variation of concentration observed with time. Separate samples were also taken which were not subjected to any weed and variation in concentration of metal ions naturally was observed which is shown in column designated by controlled (4th week) and we observed negligible reduction in concentration as shown. Last column in the table shows the total percentage reduction in concentration with respect to the initial concentration taken.

These values were fitted by suitable curves by the method of linear least square with the help of a computer application and an equation having first order reaction characteristics with respect to the metal ion concentration shown as

$$C = C_{\text{in}} \cdot \exp(-b \cdot t) \tag{1}$$

is found to be most suitable in describing the relation. Symbols used in above equation describe C — concentration of metal ions present at time t; C_{in} — initial concentration; b — rate constant; t — time.

Table 2 shows the values of various parameters obtained. This equation shows that the rate of sorption is

Table 1
Weekly change in concentration of lead after treating with *Eichhornia crassipes*

Heavy metal concentration (mg/l)	Sample introduction	1st week	2nd week	3rd week	4th week	Controlled (4th week)	Total pollutant reduction percentage (%)
Lead (Pb)	1	0.48	0.24	0.16	0.10	0.99	90
Lead (Pb)	5	2.28	1.36	1.05	0.90	4.89	82
Lead (Pb)	10	4.24	2.36	2.16	2.00	9.70	80
Lead (Pb)	20	16.32	12.4	Plant died	Plant died	18.96	38

Table 2
Various parameters obtained for lead and *Eichhornia crassipes*

Initial lead concentration (ppm)	C_{in}	b	SSE	R^2	Adjusted R^2	RMSE
1	1	0.09511	0.01147	0.9787	0.9787	0.5354
5	5	0.0862	0.6543	0.9433	0.9433	0.4044
10	10	0.09105	3.993	0.9132	0.9132	0.9992

directly proportional to the concentration of metal present at that time or sorption process and it follows the first order kinetics.

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

Various statistical parameters for the equation are calculated which is designated by SSE — sum of squares due to error.

This statistics 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.

$$\text{SSE} = \sum_{i=1}^{n} w_i \left(y_i - \dot{y}_i \right)^2 \tag{2}$$

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.

3.2. R^2 — *coefficient of determination*

This statistics measures how successful the fit is in explaining the variation of the data. In another way, R^2 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^2 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

$$\text{SSR} = \sum_{i=1}^{n} w_i \left(\dot{y}_i - \overline{y} \right)^2 \tag{3}$$

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

$$\text{SST} = \sum_{i=1}^{n} w_i \left(y_i - \overline{y} \right)^2 \tag{4}$$

where SST = SSR + SSE. Given these definitions, R^2 is expressed as

$$R^2 = \frac{\text{SSR}}{\text{SST}} = 1 - \frac{\text{SSE}}{\text{SST}} \tag{5}$$

R^2 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^2 value of 0.8234 means that the fit explains 82.34% of the total variation in the data about the average.

3.3. *Adjusted* R^2*: degree-of-freedom adjusted coefficient of determination*

This statistics uses the R^2 statistics 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.

$$v = n - m \tag{6}$$

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 the 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^2 statistics 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.

$$\text{Adjusted } R^2 = 1 - \frac{\text{SSE}(n-1)}{\text{SST}(v)} \tag{7}$$

3.4. *RMSE — root mean squared error (standard error)*

This statistics 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

$$\text{RMSE} = s = \sqrt{\text{MSE}} \tag{8}$$

where MSE is the mean square error or the residual mean square

$$\text{MSE} = \frac{\text{SSE}}{v} \tag{9}$$

As shown by the table average value of '*b*' is found to be near about 0.09 and SSE values near to 0, R^2 value near to 1 which shows a very good concurrence of the process with the equation obtained. Deviation in the 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.

A similar analysis was also done for chromium, iron, zinc results for which are shown in Tables 3–8.

The values in Table 3 have fitted in similar mathematical model and results obtained are shown in Table 4.

Here all values for the goodness of curve are found to be very near to their ideal states but variation in rate constant is more with change in initial concentration.

Various curves obtained are shown in Fig. 2.

We have found similar results for iron as found in the case of zinc but values of rate constant have decreased. All statistical parameters are very much concurrent to there expected values for good fitting.

Curves obtained are shown in Fig. 3.

Table 8 shows very good response for the chromium at lower concentrations but at higher concentrations plant died after certain level of sorption.

Curves obtained are shown in Fig. 4.

4. Conclusion

Results obtained for various metals shows that *Eichhornia crassipes* has very good ability to remove metals

Table 3
Weekly change in concentration of zinc after treating with *Eichhornia crassipes*

Heavy metal concentration (mg/l)	Sample introduction	1st week	2nd week	3rd week	4th week	Controlled (4th week)	Total pollutant reduction percentage (%)
Zinc (Zn)	1	0.46	0.23	0.08	0.02	0.98	98
Zinc (Zn)	5	3.05	1.88	0.83	0.50	4.87	90
Zinc (Zn)	10	6.06	3.74	2.10	1.60	9.59	84
Zinc (Zn)	20	14.24	10.12	7.18	4.40	18.72	78

Table 4
Various parameters obtained for zinc and *Eichhornia crassipes*

Initial zinc concentration (ppm)	C_{in}	b	SSE	R^2	Adjusted R^2	RMSE
1	1	0.1116	0.001243	0.998	0.9974	0.02035
5	5	0.07652	0.07574	0.9944	0.9925	0.1589
10	9	0.07052	0.07672	0.9984	0.9978	0.1599
20	20	0.050	0.3539	0.9976	0.9969	0.3435

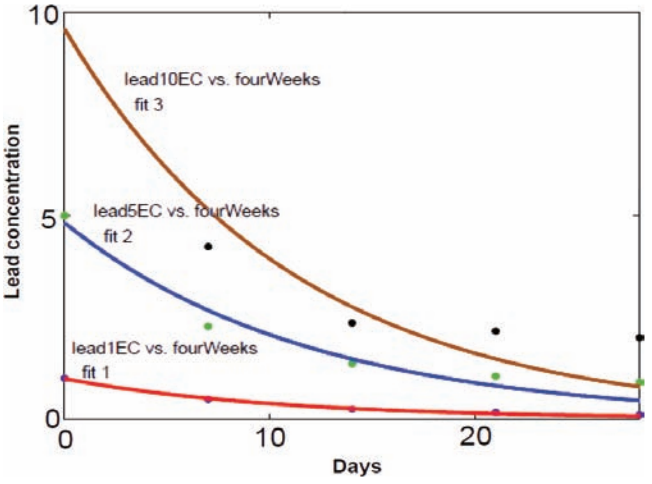

Fig. 1. Variation in concentration of Pb with time.

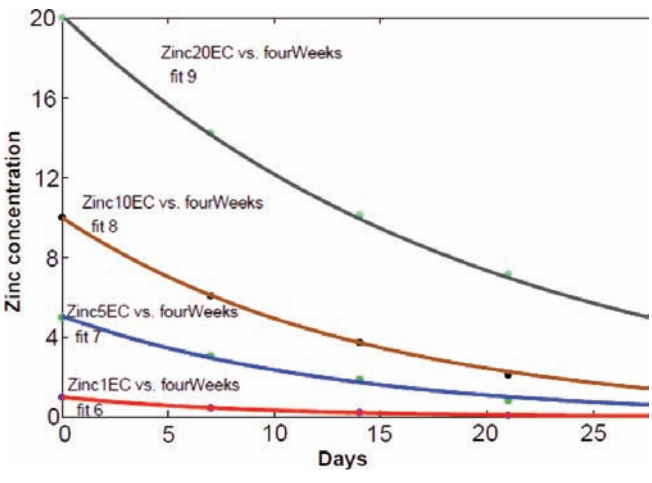

Fig. 2. Variation in concentration of Zn with time

Table 5
Weekly change in concentration of iron after treating with *Eichhornia crassipes*

Heavy metal (mg/l)	Sample introduction (09.02.2008)	1st week (15.02.2008)	2nd week (22.02.2008)	3rd week (01.03.2008)	4th week (08.03.2008)	Total pollutant reduction percentage (%)
Iron (Fe)	1	0.54	0.38	0.23	0.10	90
Iron (Fe)	5	3.24	2.31	1.44	0.70	86
Iron (Fe)	10	6.54	4.26	2.80	1.80	82
Iron (Fe)	20	14.61	10.60	6.70	4.40	78

Table 6
Various parameters obtained for iron and *Eichhornia crassipes*

Initial iron concentration (ppm)	C_{in}	b	SSE	R^2	Adjusted R^2	RMSE
1	1	0.07458	0.004375	0.991	0.988	0.03819
5	5	0.06089	0.0776	0.9931	0.9908	0.1608
10	10	0.06089	0.0006711	1.000	1.000	0.01496
20	20	0.05059	0.9594	0.9938	0.9918	0.5655

Table 7
Weekly change in concentration of chromium after treating with *Eichhornia crassipes*

Initial chromium concentration	1st week	2nd week	3rd week	4th week	Controlled (4th week)	Total pollutant reduction percentage (%)
1	0.52	0.39	0.22	0.11	0.982	89
5	3.34	2.20	1.30	0.80	4.89	84
10	6.48	4.22	2.70	2.10	9.68	79
20	16.26	13.14	Plant died	Plant died	19.10	34

Table 8
Various parameters obtained for chromium and *Eichhornia crassipes*

Initial chromium concentration (ppm)	C_{in}	b	SSE	R^2	Adjusted R^2	RMSE
1	0.9815	0.07478	0.006565	0.9863	0.9817	0.04678
5	5.048	0.06212	0.02697	0.9976	0.9968	0.09481
10	9.952	0.06016	0.08656	0.9979	0.9972	0.1699

from solutions and process of sorption nearly follows the first order kinetics with exponentially decreasing concentration. At lower concentration percentage reduction is higher than that at higher concentration but total reduction increases with increase in concentration. In the case of toxic metals like zinc and chromium plant died after certain high amount of sorption which clearly predicts that plant can not sustain more than a certain amount of these toxic metals. A negligible amount of reduction was also found in samples which were not subjected to any plant which may be either due to sorption on container walls or some other natural decomposition process but this reduction is small enough to be neglected. Rate constant for the first order kinetics decreases with increase in initial concentration and this reduction is more considerable in case of iron and zinc than lead and chromium. Statistical parameters obtained are very much satisfactory, SSE values are nearly equal to zero and most satisfactory at lower concentrations than at higher concentrations, R^2 values are also found to be very close to 1 which shows that kinetics obtained is very much satisfactory to regression, RMSE values are also found to be very satisfactory.

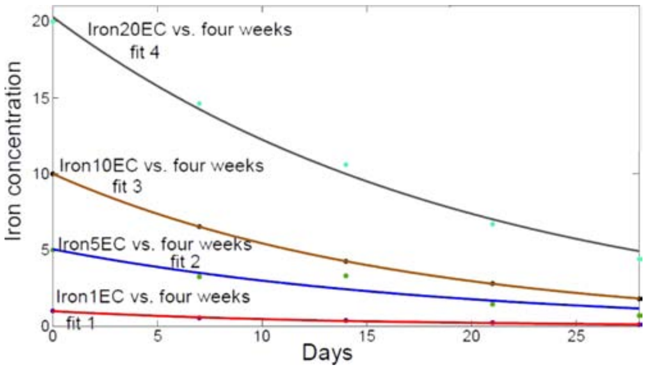

Fig. 3. Variation in concentration of Fe with time.

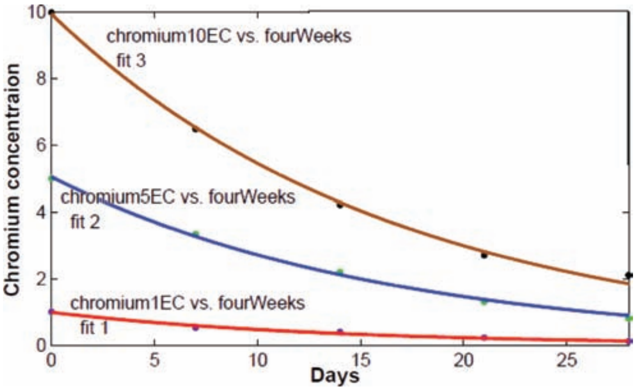

Fig. 4. Variation in concentration of Cr with time.

The above analysis shows that *Eichhornia crassipes* could be a very suitable alternative for the industries producing these harmful metals dissolved in water. It is easily available through out the world so very cost effective in comparison to the conventional methods.

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