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Kinetic equations of the biological removal of lead from industrial wastewater using aquatic plants of Khuzestan province

Saeed Taheri Ghannad [1,*], Ali Afrous [2]

[1]*Department of Water Engineering, Dezful Branch, Islamic Azad University, Dezful, Iran*
[2]*Department of Engineering, Andimeshk Branch, Islamic Azad University, Andimeshk, Iran*

Abstract: Lead is among the most important environmental pollutants that contaminate soil and water resources from different ways. This element is including the most toxic heavy metals in the United States Environment Organization. Therefore refining of soil and water contaminated with this element is from most important environmental policies of developing countries and industrial countries. In this study, the kinetic of Lead removal was examined using Phytoremediation of the aquatic plants. Plants used in this study consisted of common Reed, Typha and Bermudagrass that after planting and vegetative stage were irrigated with the synthetic wastewater in different concentrations 5, 10 and 15 mg-pb/l. Then from the pots soil was sampled every 5 to 10 days. The obtained results were fitted with the four models of the zero-zero-order kinetic, first-order kinetic, power model and exponential association model. The results showed that the best correlation coefficients were obtained in priority order with the exponential association model, power model, first-order kinetic and zero-order kinetic. Power and exponential models had higher precision entire duration experiment. Whereas kinetic models of the first-order and zero-order were not accurate at the initial and final times of experiment. In addition, the results showed that the reaction rate constant for the three species varied in the range 0.0014 to 0.0071 day^{-1} that this amount was higher for Reed than the other species so that removal rate of soil Lead by cultivation Reed was faster than the other two species and this constant coefficient in all cases was decreasing with the increasing different concentration levels of the wastewater.

Key words: *Phytoremediation; Kinetic model; Lead removal; Aquatic plants*

1. Introduction

Water pollution by heavy metals is a worldwide environmental problem due to the increasing exploitation of mining activities, industrialization and urbanization has increased around the world. Lead is among the most important environmental pollutants that contaminate soil and water resources from different ways (Rostami et al., 2002). This element is including the most toxic heavy metals in the United States Environment Organization. Therefore refining of soil and water contaminated with this element is from most important environmental policies of developing countries and industrial countries. Lead metal is unnecessary for the body, so that trace amount in the body, indicating contamination with this element. Lead substitute with calcium in the cells and disrupt the activities of the body. Also cause liver and kidney dysfunction, genital organs and reproductive system, anemia, loss of intelligence interest and occurrence of the metabolic complications (Yasaie et al., 2000). Remove and control pollution of heavy metals is very difficult due to their multiple and different sources of pollutions. Because each pollutant requires its own refining process. Until now, many methods have been developed for the purification of wastewater including can be pointed to the chemical precipitation, reverse osmosis and ion exchange of organic (Jadia and Fulekar, 2009). Each of which has its own advantages and disadvantages (Hashemian et al., 2014). Including the optimal method of biological for the removal of pollutants is the use of plants and other expression, Phytoremediation. In this way, different species of plants can had an important role in the removal of environmental pollutants as biological filters (Hazrat et al., 2013). In previous studies, less has been discussed on the modeling and mechanisms of the Lead removal from soil and wastewater. Thus, in this study were examined kinetic models of the Lead removal by cultivating the aquatic species of Khuzestan province in Iran.

2. Mathematical models

Soil is as a medium that can effectively store organic compounds and heavy metals using the adsorption mechanism. Various models for the study of soil absorption rate have been studied by researchers. Which can be named such as Langmuir, Frendolich and linear adsorption isotherm? It is worth noting that the adsorption phenomenon in itself would not be able to reduce the concentration

* Corresponding Author.

of organic contaminants and merely delays the movement and transport of pollutants mass (Abedi et al., 2014).

2.1. Zero-Order Kinetic model

In the kinetics model of zero-order, decomposed pollutants plot versus time.

$Y=k.t$ (1)

At this model Y is pollitant decomposed and k is reaction constant in 1/day and t is time in day.

2.2. First-order kinetic model

Using the kinetic equation of first-order can estimated the decomposition rate of water and soil pollutants.

$U=K/Y_0$ (2)

In Eq. 2, Y_0 is initial concentration of soil pollutants in mg/kg and U is pollutant decomposition rate and k also is rection constant of first-order model in 1/day.

$Y=Y_0.e^{-k.t}$ (3)

In this equation, Y is the residual concentration of pollutants in water or soil and Y_0 also is initial concentration of the pollutant and k also is the constant of biological uptake rate. According equation 2, if residual mass of the pollutants is determined at any given time. The require time to absorb or break down pollutants will be obtained from the following equation [1].

$t=-(\ln(Y/Y_0)/k$ (4)

3. Materials and methods

In order to implement this study, plastic pots were prepared with 60 cm in diameter and 40 cm in height. Therefore pots were filled from sand with grains diameter of 1 to 5 mm and a depth of 30 cm was. After preparing the pots and planting, were placed a suitable interval each other. Selected plants included common Reed, Typha and Bermudagrass selected due to their abundance in the Khuzestan province. Young plant samples were collected from margins of Dez river immediately were transferred to the site of the research in experimental field of Islamic Azad University of Dezful branch (48° 25´E, 32° 16´ N) under ambient conditions. After preparation of bed and adding nutrients to the cultivation medium, each pot was randomly assigned to a treatment in three replicates. The youngest seedlings were selected for cultivation in each medium sample. After washing of seedlings with water, three plants were cultivated at regular intervals, with the minimum distance of 5 cm from wall of the pots at a depth of 10 cm (density of 25 plants per square meter). After preparing the pots and planting the desired species were irrigated with the irrigation water for 40 days because irrigation with synthetic wastewater in the early stages of cultivation caused stress to the plant due to lack of root stability and compatibility with the new culture medium. So after the elapse of this period, irrigation with simulated wastewater was performed in the different concentrations 5, 10 and 15 mg-pb/l.

3.1. Sampling and measuring

Considering that the pots used in this study had not drain, therefore, the reduction of Lead in the soil represents the cumulative uptake by plant with the refraining from volatilization. To this end, during the experimental period was sampled from the pots soil every five to ten days. Soil samples were taken at 0 , 41, 52, 62, 72 , 82, 92 , 102 days after planting. By measuring the concentration of Lead in the substrate, it was possible to calculate the cumulative uptake of plants using mass balance approach. Then, the reduction trend of soil-extractable Lead and plants uptake in time were examined according to the measurements then selected models were plotted using software $\text{Curvexpert}_{1.4}$. After examining the above, appropriat plant were selected between plant species and appropriate model to simulate the Lead removal was introduced.

4. Results and discussion

4.1. Exponential association regression model

Exponential Association regression model using curve expert software was used in order to simulate the kinetics of uptake in different treatments. The general form of this model is as $Y = a.(1 - e^{-b.t})$. In this equation, t in day and Y Lead uptake in milligram per kilogram soil was defined. Lead absorption curves have been showed for Bermudagrass, Reed and Typha in the treatments of average level of Lead concentration in Fig.1, 2, 3. In these diagrams, the regression coefficients and b are variable constants for the different species and under different levels of concentration. According to this model, the adsorption kinetic was highly correlated. Therefore, these equations can be used to simulate the Lead removal at different concentrations. The results showed that with the increasing concentration levels, the correlation coefficient increased. So this model in the medium and high levels had high precision. Comparison of model in the studied species showed correlation coefficient of Reed was much higher than the other two species so had better fit to this plant. Therefore, these equations can be used to simulate the Lead absorption at different times and in different plant species, especially Reed with the high correlation coefficients. Goudarzi and Afrous (2012) used this function in order to modeling the absorption of nickel and cadmium in sewage sludge by cultivation aquatic plants. They concluded that there was a high correlation between the uptake of nickel and cadmium in time and suggested this model can be used to simulate the removal mechanism of nickel and cadmium (Goudarzi and Afrous, 2012).

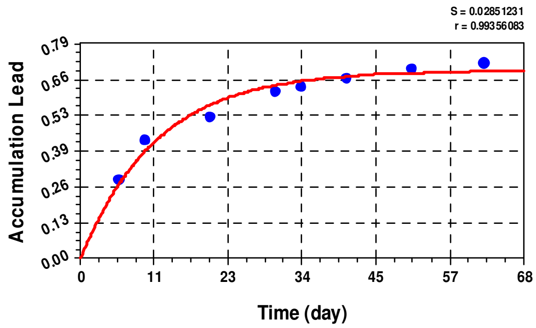

Fig.1: Absorption curve of Bermudagrass at concentration10 mg/l pb in ppm.

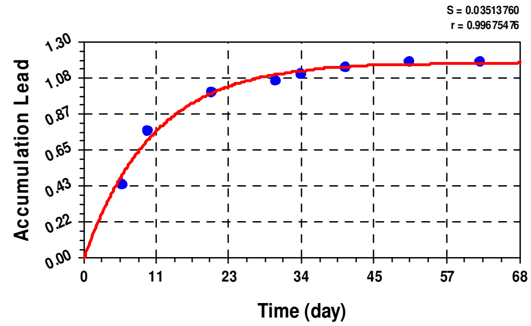

Fig.3: Absorption curve of Typha at concentration 10 mg/l pb in ppm.

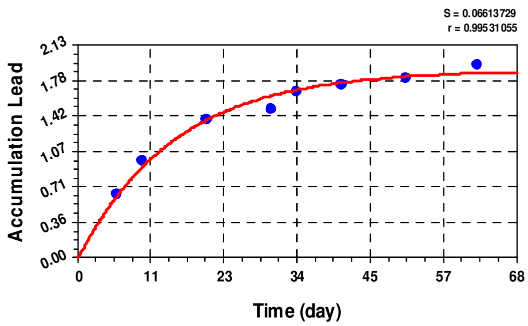

Fig.2: Absorption curve of common Reed at concentration 10 mg/l pb in ppm.

Table 2: Regression Coefficients of the EXP. Association model in different plant species and different levels of wastewater concentration

Regression Coeficients		Eq. Coeficients		Concentration Levels	Aquatic plants
S	R^2	B	a		
0.0375	0.974	0.0676	0.468	5 mg/l	Bermudagrass
0.028	0.99	0.0855	0.69	10 mg/l	
0.02	0.998	0.135	1.075	15 mg/l	
0.041	0.99	0.0496	0.778	5 mg/l	Reed
0.035	0.996	0.0925	1.175	10 mg/l	
0.12	0.99	0.123	2.45	15 mg/l	
0.035	0.986	0.0498	0.608	5 mg/l	Typha
0.0416	0.995	0.119	1.146	10 mg/l	
0.044	0.998	0.127	1.864	15 mg/l	

4.2. Fitting with other models of the kinetic

The use of appropriate models to simulate and calculate the necessary time for refining the soil and reach the optimal level is essential due to the lengthy process of phytoremediation. For this purpose, models of zero-order kinetic (linear function), first order kinetic and power function were selected and with the data collected were fitted. On this basis, removal kinetic of the soil Lead during experiment was fitted using software curvexpert$_{1.4}$ whose the results have been showed in Table 3. Results showed the first-order kinetic model in all treatments had a higher correlation coefficient (R^2) and consequently the lower standard error (s) than the linear model. Comparison first-order kinetic model with Power model showed that power function had a higher correlation coefficient. Therefore, it is suggested that power model be used to simulate the Lead removal with the high correlation coefficient. Example of fitting with this model has been shown in Fig.4-6. With this Figures was concluded that the power model had higher accuracy than other models at all times of sampling and kinetics models of first-order and zero-order were not accurate in the initial and final times. In addition, the equilibrium time was calculated to reach half the initial concentration in soil which based on the model of first-order kinetic, the equilibrium time was 384, 190 and 100 days by cultivation Bermudagrass, Typha and Reed, respectively at the average-level concentration (10 mg-pb/l). This indicates that the reed has more potential than the other species for phytoremediation So that the substrate concentration need to less time for half the initial concentration of Lead in soil. This may be due to more uptake and more activity microorganisms around the roots and rhizomes of Reed. Results showed that the reaction rate constant for the three aquatic species was in a range 0.0014 to 0.0071 that this amount also was higher for reed than other plants. Therefore, the rate of Lead removal in soil by cultivation Reed significantly faster than the other two species. Comparison these three models with the exponential association model also showed exponential association model had higher correlation coefficient than other models at different levels of the wastewater concentration and it can be used to simulate the kinetic of Lead removal from the industrial wastewater. Gunther et al (1996) found that the decomposition of hydrocarbon pollutants in soil planted with Ryegrass was higher compared to unplanted soil due to the increase microbial activity and microorganisms. They found that plant roots leads to microbial growth and removal of the soil pollutants (Gunther et al., 1996). Reilley et al (1996) also found similar results (Reilley et al., 1996). Hutchinson et al (2001) showed that enough time for establishment and growth of plants in the soil is an important factor in the process of phytoremediation (Hutchinson et al., 2001). Vinas et al (2005) based on similar studies, reported that the removal kinetic of organic compounds complies with a biphasic pattern. They examined biological degradation of contaminated soils with kerosene within a 200-day period (Vinas et al., 2005). Abedi Koupaie et al (2014) studied phytoremediation potential of Ryegrass in the petroleum-contaminated soil in Iran. They found contaminants removal in the soil was increasing until 50 days and then decreased the rate of pollutants decomposition and ultimately fixed at the end of the 80-day period and changes trend followed the model of first-order kinetic (Abedi et al., 2014). In a study conducted by Dalalyan et al (2010) simulated phytoremediation potential of soils contaminated with cadmium and copper. The results showed that the rate of phytoremediation of cadmium and copper by sage was compatible with zero-order model (Dalalyan and Homae, 2010). According to the results this study and other studies, the kinetic model should be simulated based on plant species, different levels of wastewater concentration and pollutant type.

Table 3: The results of zero-order, first-order and power kinetic equations

Zero-order kinetic			First-order kinetic			Concentration Levels	Aquatic plants
S	R^2	Eq.	S	R^2	Eq.		
0.07	0.91	Y=0.134+0.0068.t	0.06	0.93	$y = 1.975.e^{-0.00392.t}$	5 mg/l	Bermudagrass
0.125	0.87	Y=0.382+0.0138.t	0.12	0.88	$y = 5.895.e^{-0.00176.t}$	10 mg/l	
0.245	0.77	Y=0.482+0.0133.t	0.24	0.78	$y = 11.52.e^{-0.0014.t}$	15 mg/l	
0.09	0.94	Y=0.169+0.0113.t	0.07	0.96	$y = 2.016.e^{-0.00713.t}$	5 mg/l	Reed
0.29	0.91	Y=0.517+0.0276.t	0.26	0.93	$y = 5.56.e^{-0.0062.t}$	10 mg/l	
0.51	0.82	Y=1.01+0.0325.t	0.5	0.83	$y = 11.14.e^{-0.0332.t}$	15 mg/l	
0.08	0.93	Y=0.127+0.009.t	0.07	0.944	$y = 1.99.e^{-0.0054.t}$	5 mg/l	Typha
0.24	0.83	Y=0.417+0.0162.t	0.23	0.85	$y = 5.611.e^{-0.0033.t}$	10 mg/l	
0.43	0.77	Y=0.817+0.0233.t	0.42	0.78	$y = 11.23.e^{-0.00228.t}$	15 mg/l	

Table 3: The results of zero-order, first-order and power kinetic equations

S	R^2	Power Kinetic	Concentration Levels	Aquatic plants
0.04	0.97	$Y=0.067.t^{0.5}$	5 mg/l	Bermudagrass
0.07	0.95	$Y=0.104.t^{0.5}$	10 mg/l	
0.18	0.86	$Y=0.17.t^{0.5}$	15 mg/l	
0.017	0.997	$Y=0.102.t^{0.5}$	5 mg/l	Reed
0.15	0.97	$Y=0.268.t^{0.5}$	10 mg/l	
0.36	0.9	$Y=0.387.t^{0.5}$	15 mg/l	
0.04	0.98	$Y=0.08.t^{0.5}$	5 mg/l	Typha
0.15	0.93	$Y=0.178.t^{0.5}$	10 mg/l	
0.32	0.87	$Y=0.294.t^{0.5}$	15 mg/l	

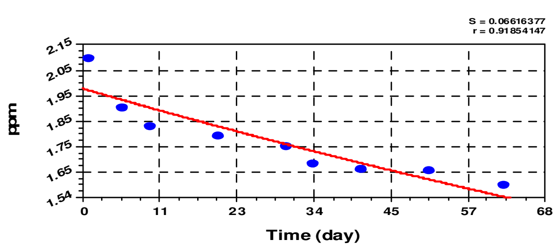

Fig.4: Fitting with first-order kinetic model (soil Lead in time)

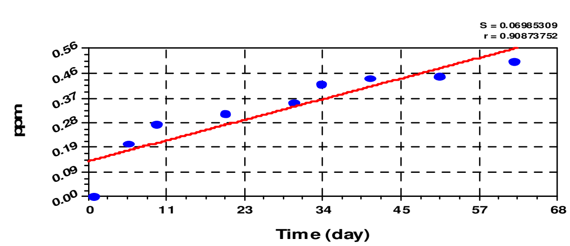

Fig.5: Fitting with zero-order kinetic model (plant Lead in time)

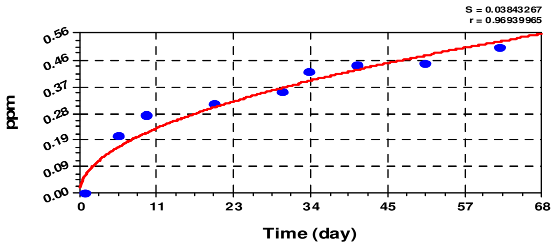

Fig.6: Fitting with power- kinetic model (plant Lead in time)

5. Conclusions

Experimental results showed that the kinetic of the Lead removal in soil was mainly in the form of an association exponential model and then power model had the best correlation coefficient compared to the other models. The results showed that these two models had better performance and matching during the period of experiment. Whereas zero-order and first-order kinetics models were not accurate at the initial and final times. The calculation results of the equilibrium time to achieve half the initial concentration in the soil (y/2) showed that base on the first-order kinetics model, the equilibrium times 384, 190 and 100 days was achieved respectively by cultivation of Bermudagrass, Typha and Reed in treatments of the mean level of wastewater concentration. This result implies that Reed had greater potential for Phytoremediation than the other two species. Therefore, soil concentration was reached in less time by half the initial concentration of the soil Lead. The results showed that the reaction rate constant for the three species varied in the range 0.0014 to 0.0071 day^{-1} that this amount was higher for Reed than the other species. Thereby the rate of Lead removal by Reed cultivation was faster than the other two species and this constant coefficient in all cases was decreasing with increasing the concentration levels of wastewater. In the end it was concluded that the kinetics of phytoremediation should be simulated based on plant type, concentration levels of wastewater and pollutant type.

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