Biosorption Behaviour of an Arid Land Plant, *Euphorbia rigida*, Towards to Heavy Metals: Equilibrium, Kinetic and Thermodynamic Studies

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ABSTRACT

The potential of an arid-land plant, *Euphorbia rigida* (*E. rigida*), for the removal of heavy metals [Pb(II), Zn(II), Cu(II), Cd(II), Ni(II)] from aqueous solutions was studied in the current work. Batch sorption experiments were conducted to investigate the effects of pH, particle size, initial metal ion concentration, contact time and temperature. Besides, biosorption data was analysed by different isotherm and kinetic models. Equilibrium studies showed that the biosorption closely follows the Langmuir and Freundlich isotherms. From the kinetic point of view, pseudo-second order model gave the best fitting with the experimental results. The evaluated thermodynamic parameters showed that biosorption onto *E. rigida* was a feasible, spontaneous and endothermic process. The affinities of metal ions onto *E. rigida* decreased as Pb(II) > Zn(II) > Cd(II) > Cu(II) > Ni(II) in single metal biosorption. Besides, binary and ternary metal sorption studies were conducted to investigate the co-ion effect. Experimental results showed that *E. rigida* can be used as an alternative and effective low cost biosorbent for the removal of heavy metals from aqueous solutions.

Keywords:
Euphorbia rigida; Single-multi heavy metal biosorption; Equilibrium; Kinetics; Thermodynamics

INTRODUCTION

High release of heavy metals from industries like metal processing, refining, paint, battery industry and mining causes serious wastewater contamination because of the non-degradable nature of metals. Released metal ions become poisonous for both plants and living organisms after certain concentrations since they tend to pile up in living organisms and cause various disturbances and disorders [1-4]. Hence, various physical and/or chemical treatment techniques have been applied for many years, such as chemical reduction, precipitation, solvent extraction, coagulation, flocculation and filtration, membrane processes [5-7]. However, feasible applications of the mentioned techniques are limited due to high operational and initial capital costs, low efficiency and production of undesirable sludge. Many of the mentioned techniques have substantial penalties, such as demand for high-priced equipment, high reagent consumption, high energy requirement, inadequate metal removal, and generation of toxic sludge. On the other hand, adsorption systems are rapidly gaining prominence in water treatment processes because of advantages such as easy design, control and operation [8]. The versatility and simplicity of adsorption directed researchers to search alternative sorbents to the time-honored sorbents. Therefore, the biosorption study of metal ions on natural adsorbents which are abundant in nature and require little processing is important for finding low-cost adsorbents [9-11]. Biosorption involves metal binding by ionic and covalent bonds to the surface matrix of the biomass [12]. It is known as an alternative technique to treat dilute heavy metal wastewaters because of availability of unlimited bio sources, high efficiency and surface porosity of biomass [13]. To this end, agricultural wastes and non-edible plants are considered as a viable option for utilization in biosorption processes.

In the literature, different biomass samples like nutshells [14], sawdust [15], algae [16] and their modified forms [17] were reported as alternative biosorbents. However, attention should be should be drawn on naturally

growing land plants considering both their abundancies and biosorption abilities. Among various types of biomass species, terpene hydrocarbons could be an effective candidate for biosorption processes. A well-known terpenoid biomass is the Euphorbiaceae family and *Euphorbia rigida*, a member of Euphorbiaceae, grows on the arid lands of Middle Anatolia in abundant quantities and without requiring special labour. About 2000 species of *E. rigida* is known all along the world and it is reported that 80 species of *Euphorbia* are found in Turkey. This biomass drew the attention of several researchers interested in converting it to petroleum substitute oil by pyrolysis [18]. Also, in another study, highly porous activated carbons were produced from *E. rigida* by chemical activation [19]. But direct utilization of *E. rigida* without applying any thermal treatment process for the removal of hazardous species has not been sufficiently studied. It is believed that usage of *E. rigida* as a biosorbent would lead to a new evaluation route for the other non-edible biomass species. In biosorption processes, it is also well known that interpretation and representation of multi-metallic systems is more complex than that of monometallic systems because of competition phenomena and hence there are limited published works on it. Therefore, the scope of this study was to determine the sorption characteristics of *E. rigida* for the removal of Pb(II), Zn(II), Cu(II), Cd(II) and Ni(II). Batch biosorption experiments were focused on to investigate the effects of solution pH, particle size, initial metal ion concentration, contact time and temperature. Equilibrium and kinetic studies together with the thermodynamic analysis were made with the obtained data. In addition, experiments were conducted in multi-metal solutions to investigate the co-ion effect.

METHODS

Biomass Preparation and Characterization

Raw *E. rigida* (leaves and stalks) samples were obtained from South-western Anatolia. Before biosorption experiments, *E. rigida* was washed to remove contaminants and dried at room temperature. Proximate, ultimate and component analysis of *E. rigida* were performed to determine characteristics of the biomass and all the results were summarized in Table 1.

In order to characterize surface chemistry of *E. rigida* modified Boehm titration was performed and surface acidic and basic groups were quantified. For this purpose, 0.5 g of biomass samples were placed to a series of flasks which include 50 mL of 0.05 N $NaHCO_3$, Na_2CO_3, NaOH and HCl. The flasks were shaken for 24 h and then filtered and titrated with 0.05 N NaOH or HCl depending on the nature of surface groups. By observing the end points in the presence of phenolphthalein and methyl red indicators, amount of the surface groups was determined quantitatively.

The pH point of zero charge (pHpzc) of *E. Rigida* was also determined by pH drift method. For this purpose, 0.15 g of biomass sample was added 50 mL solution of 0.01 M NaCl whose initial pH had been measured and adjusted by 0.01 M NaOH or HCl. The pH values of the solutions were measured after 48 h. The pHpzc of biosorbent is noted as the point where $pH_{initial}$ equals to pH_{final}.

The surface microstructure of E. rigida was also characterized using scanning electron microscope combined with Energy Dispersive X-ray Spectroscopy , SEM-EDX (Zeiss Supra 50VP).

Biosorption Experiments

The salts used were $Pb(NO_3)_2$, $N_2O_6Zn.6H_2O$, $Cu(NO_3)_2.3H_2O$, $Cd(NO_3)_2.4H_2O$ and $Ni(NO_3)_2.6H_2O$, for Pb(II), Zn(II), Cu(II), Cd(II), Ni(II), respectively. Stock solutions of 1000 mg/L were prepared by analytical grade salts in double deionized water which has a conductivity of 18.2 MΩ/cm. Then, stock solutions were diluted to acquire desired concentrations. The initial pH values were regulated to the required value with 0.1 mol/L and/or 0.01 mol/L of NaOH and HCl solution. Batch biosorption experiments were performed by mixing metal solutions with *E. rigida* in a temperature programmed shaker and by taking samples at different time intervals. Each experiment is performed twice and average values were considered. The effects of biosorption parameters such as, pH (3-9), particle size (0.112-0.850 mm), biosorbent dosage (1-10 g/L), initial metal ion concentration (10-50 mg/L), contact time (up to 24 h) and temperature (20-40 °C) were investigated in a batch mode. After sorption process, biomass separated from the samples by filtering and the filtrate was analysed by atomic adsorption spectrometer (Varian Spectra A240 FS)

The amount of metal biosorbed per unit mass of the biosorbent at equilibrium (q_e) and at each time interval (q_t) were calculated by the following equations,

$$q_e = \frac{(C_i - C_e)\, V}{w} \qquad (1)$$

$$q_t = \frac{(C_i - C_t)\, V}{w} \qquad (2)$$

where C_i is the initial and C_e is the equilibrium concentration of the metal ion (mg/L). In the equations, C_t is the concentration of the metal ion at any time (mg/L), V is the volume of aqueous solution (L), and w is the mass of biosorbent (g).

In the last stage of the study, binary and ternary biosorption experiments were conducted to conclude whether *E. rigida* is applicable for the treatment of solutions including the combination of heavy metals.

Theoretical Approach

Biosorption Isotherms

For convenient design and fundamental knowledge of the process, biosorption isotherm, the specific relationship between sorbate and sorbents in equilibrium, is necessary. In order to gain information about the mutual effects of sorbent and sorbate, different isotherm models should be applied to experimental data. In this study, Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) models were used to investigate the biosorption equilibrium between the metal ions and the biosorbent.

Langmuir model assumes that sorption occurs by distribution of sorbate molecules in a single layer throughout the sorbent surface and dynamic equilibrium exists between sorbed and non-adsorbed free molecules [20-22]. The linearized form of the Langmuir is given as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{3}$$

where q_m is the monolayer adsorption capacity of the activated carbon (mg/g), and K_L is the constant (L/mg).

Freundlich model accepts multilayer adsorbate uptake on the sorbent surface and heterogeneous sorbate surface with active sites [23]. The linearized Freundlich equation is given by;

$$\ln qe = \ln K_F + \frac{1}{n} \ln C_e \tag{4}$$

where K_F ((mg/g)(L/mg)1/n) is a constant related with the adsorption capacity and n is an empirical parameter indicating the adsorption intensity.

Dubinin-Radushkevich (D-R) model designates the adsorption on uniform pores and a variable adsorption potential throughout a heterogeneous surface [24]. The linear D-R isotherm equation is as follows:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{5}$$

where β is a constant related to the adsorption energy (mol²/kJ²), q_m is the theoretical saturation capacity, and ε is the Polanyi potential.

The last isotherm model used in the study, Temkin [25] considers the effects of indirect sorbent/sorbate interactions and assumes non-uniformly distributed binding energies of sorbate molecules. The linear form of Temkin isotherm equation is expressed as:

$$q_e = B \ln K_T + B \ln C_e \tag{6}$$

Biosorption Kinetics

The biosorption processes can be controlled by different mechanisms and various kinetic models (pseudo-first order, pseudo-second order, intraparticle diffusion and Elovich) were used to look into the mechanism and influential parameters of the sorption.

The pseudo-first order model expresses the rate equation by assuming the rate of change of solute uptake with time is related with the difference in saturation concentration and instantaneous concentration [26]. The pseudo-first order equation is formulized as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{7}$$

where k_1 is the rate constant which is belonging to pseudo-first order model (1/min). Integration of this equation is turned out a linearized form as:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \tag{8}$$

Apart from the first order equation, the rate of change of solute uptake with time varies with the square of the difference in saturation concentration and the quantity of solid uptake in pseudo-second order equation as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{9}$$

where k_2 is the rate constant of pseudo-second order model (g/mg.min) [27]. Integration of this equation also resulted in a linearized form as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{10}$$

Although pseudo-first order together with pseudo-second order are convenient to describe sorption kinetics, they don't take into account the diffusion effect. At this point, intraparticle diffusion model [28] is beneficial for in-depth investigation of transportation process of sorbate molecules. The intraparticle diffusion equation expresses variation of solute uptake proportional with $t^{1/2}$ and is written by the following equation:

$$q_t = k_p t^{1/2} + C \tag{11}$$

where k_p is the intraparticle diffusion rate constant (mg/g min¹ᐟ²) and C is the intercept of intraparticle model plot which gives an opinion about the thickness of the boundary layer. Accordingly, if intraparticle diffusion is included in the sorption, the model plot should be linear. Either, intraparticle diffusion is the rate-controlling step in the case of model lines go across the origin then. Otherwise, some other mechanisms are accepted to be present which effects the boundary layer [29, 30].

On the other hand, Elovich kinetic model [31] may be suitable when there is a chemical interaction between sorbate ions and surface sites. The linear Elovich equation can be represented by:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \tag{12}$$

Table 1. Characteristics of *E. rigida*

Proximate analysis (%)		Ultimate analysis (%)		Component analysis (%)	
Moisture	3.00	C	49.56	Extractive	12.55
Ash	6.40	H	5.16	Lignin	37.92
Volatiles	76.80	N	1.20	Hemicellulose	29.50
Fixed C*	13.80	O+inorganics*	44.08	Cellulose inorganics *	19.17

*Calculated as difference
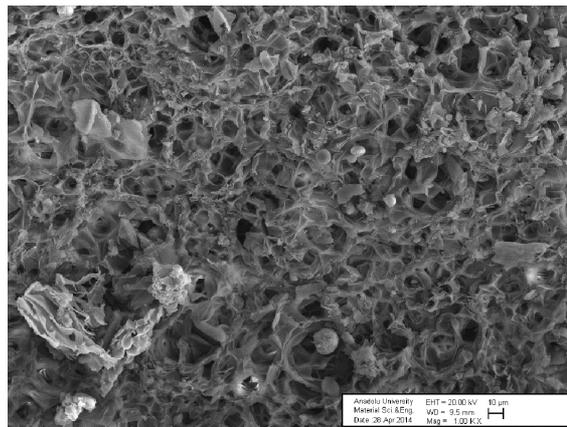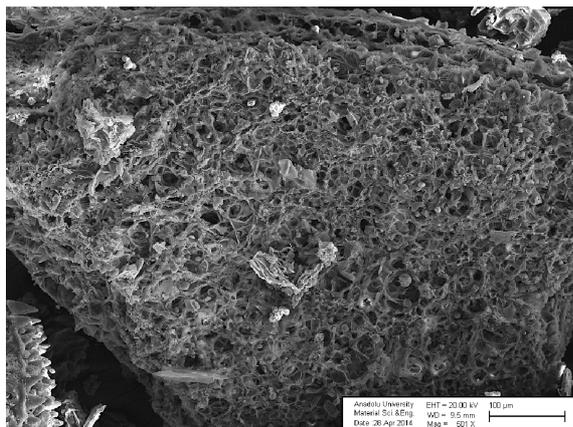
Figure 1. SEM micrographs of raw *E. rigida*

Biosorption Thermodynamics

For detection of the effects of temperature, spontaneity and feasibility of sorption process, thermodynamic parameters (Change in Gibbs free energy, enthalpy and entropy) should be interpreted.

The Gibbs free energy change (ΔG°) of biosorption process can be determined from the given equation:

$$\Delta G^{o} = -RT \ln K_{L} \tag{13}$$

where R is the gas constant (8.314 J/mol.K), K_{L} is equilibrium Langmuir constant and T is the temperature (K). Relationship between ΔG°, enthalpy change (ΔH°) and entropy change (ΔS°) can be demonstrated by:

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} \tag{14}$$

and manipulation of Eq.13 is resulted in a linear equation for calculating thermodynamic parameters as:

$$\ln K_{L} = -\frac{\Delta G^{o}}{RT} = -\frac{\Delta H^{o}}{RT} + \frac{\Delta S^{o}}{R} \tag{15}$$

RESULTS AND DISCUSSION

Characteristics of *E. rigida*

Fig 1 presents two electron micrograph examples of the *E. rigida* with a magnification of 500x and 1000x. According to secondary electron images, surface of raw *E. rigida* seems heterogeneous which includes some interconnected pores and channels. This topographical feature of E. rigida shows that it can be useful for sorption of metal ions. According to EDX analysis C and O are the main atomic constituents with minor amounts of Si, Mg, Ca. Ultimate analysis results given in Table 1 also supports that the main constituent of *E. rigida* is C which is 50 wt.% approximately.

Surface chemistry of E. rigida (Table 2) was studied by determination of pHpzc and surface functional groups using Boehm titration. According to the results, quantity of acidic surface groups are more than basic surface groups. Approximately 90 % of acidic surface groups are determined as phenolics.

Biosorption of single-metal solutions

Effect of pH

Since pH affects solubility of metal ions metal binding sites by dissociation of active functional groups and surface charges, it is one of the important factors that should be considered throughout the biosorption process. The effect of pH on heavy metal sorption was determined by performing the experiments in a pH range of 3-9 with a constant particle size range as 0.112-0.224 mm. The results are given in Fig. 2 and pHpzc and amount of surface functionalities were summarized in Table 2. Accordingly, pHpzc, value of *E. Rigida* can be deduced close to 5.0 because of acidic surface groups. It is known that, when pH is less than pHpzc the surface of the biosorbent becomes positively charged, and metal sorption is hindered, because of electrostatic repulsion between ions and surface functional groups. On the contrary, in the case of higher pH values than pHpzc, the quantity of negative charges increases and hence metal sorption is frequently favou-

Table 2. Surface chemistry of *E. rigida*

PH_{PZC}	Carboxylic (meq/g)	Lactonic (meq/g)	Phenolic (meq/g)	Acidic (meq/g)	Basic (meq/g)
4.82	0.2662	0.0888	3.4510	3.8060	0.1443

red. The further increase in pH also causes an increase of the dissociation degree of functional groups from biosorbent surface and electrostatic interactions increases as a consequence. The amounts of Zn (II) and Cd(II) biosorbed onto *E. rigida* was found to increase with an increase in pH from 3 to 7. But further increasing pH caused to decreases in biosorption capacities of these two ions. According to this, optimum pH value for Zn (II) and Cd(II) ions was determined as 7. On the other hand, the highest Ni (II), Cu (II) and Pb(II) uptake were obtained at a pH value of 6. The differences in biosorption capacities of heavy metals onto *E. rigida* at different pH values could be due to the differences in the affinities of metal ions to the molecules on the biosorbent surface. At a pH value of 9, the biosorption capacity of all metal ions were at their lowest. This may be due to the formation of anionic hydroxide complexes. These complexations may decrease the dissolved metal ion quantity and their competition with active surface sites. Therefore, all the subsequent experiments were followed by adjustment of pH values of the solutions.

Effect of particle size of biosorbent

The contact surface of the biomass with metal ions in aqueous solution has a significant role in biosorption process due to the external mass transfer resistance. The effect of particle size (Dp) on heavy metal sorption was determined within the range of 0.112 mm to 0.850 mm and results are given in Fig. 3 using optimum pH values for each metal ion. Decreasing the particle size of the biosorbent increased the surface area available for metal ions and therefore increases the biosorption capacity. Hence, a particle size range between 0.112-0.224 mm were used at the rest of the study.
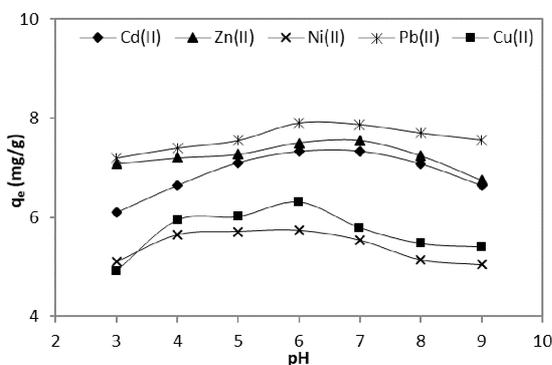
Effect of biosorbent dosage

It is well known that the initial metal concentration and the available sorption sites on the sorbent provide the driving force to sorption according to the mass transfer
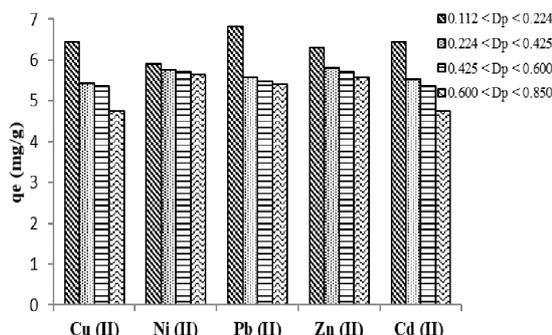
Figure 3. Effect of particle size on heavy metal biosorption (Dp, in mm)

phenomena. For biosorption to take place, mass transfer resistance between the solution and sorbate should be overcome. It is obvious that an increase in biomass dose generally increases the metal uptake because of the increases in active sites on the adsorbent surface. Whereas overlapping and partial aggregation of sorption sites may cause the decline in the amount of metal adsorbed. Such aggregation can cause to a decline in surface area of the biosorbent and increase in diffusional path. In order to investigate the effect of biomass dose for heavy metal removal, variable amounts of biosorbents (1-10 g/L) were added to solutions and the results are given in Fig.4. It is well understood that increasing the biosorbent dosage decreases the uptake amounts.

Effect of concentration, temperature and contact time

Biosorption capacities of all ions increased considerably by increasing the concentration from 10 to 50 mg/L. The explanation of this phenomenon is the driving force provided by metal ions that overcomes the mass transfer
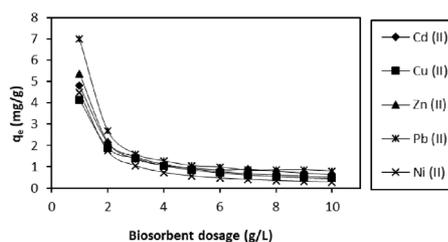
Figure 2. Effect of solution pH on heavy metal biosorption

Figure 4. Effect of biosorbent dosage on heavy metal biosorption

Table 3. Comparison of biosorption capacity (mg/g) on various sorbent materials

Biosorbent	Pb(II)	Zn(II)	Cu(II)	Cd(II)	Ni(II)	Reference
Wheat straw	-	-	11.4	14.5	-	[34]
Lichen (C. furcata)	12.3	-	-	-	7.9	[35]
Black carrot residues	-	-	8.8	-	5.7	[36]
Dye loaded groundnut shells	-	9.6	7.6	-	7.5	[37]
Tobacco dust	39.6	25.1	36.0	29.6	24.5	[38]
Grapefruit peel	-	-	-	42.1	46.1	[39]
Moringa pods	-	-	6.1	-	5.5	[40]
Corn cobs	8.3	-	7.6	-	13.5	[41]
Coconut dregs residue	9.7	-	2.8	-	5.9	[42]
E. rigida	18.5	14.2	12.1	11.9	10.9	Present work

resistance between the solution and solid surface. Thus quantity of metal ions adsorbed onto *E. rigida* enhanced the uptake amounts with increasing metal ion concentra-

Figure 5. Effect of contact time and temperature (Initial metal ion concentration= 50 mg/L)

tions. Fig. 5 shows the dependence of the q_t values versus contact time at different temperatures. Accordingly, q_t values increased rapidly at the initial stages with an increase in the contact time, then gradually increased and finally equilibrium was established for all metal ions. The contact time needed to reach equilibrium for all studied metal ions was found about 3 h. The obtained curves also confirm that biosorption occurred in two stages which were a very fast surface biosorption followed by a slower intracellular diffusion.

In general, there is no certain consensus about the temperature dependency of metal biosorption since surface interactions of each specific sorbate-sorbent pair effect nature of the process significantly. According to the results, biosorption capacities of *E. rigida* for all metal ions increased with an increase in the solution temperature. This indicates the endothermic nature of the biosorption. The affinities of metal ions onto *E. rigida* decreased as Pb(II) > Zn(II) > Cd(II) > Cu(II) > Ni(II) in single metal biosorption. In the applied experimental conditions, maximum capacities were determined as 18.5, 14.2, 12.1, 11.9 and 10.9 for Pb(II), Zn(II), Cu(II), Cd(II) and Ni(II) biosorption, respectively. The highest capacities obtained by using highest initial metal ion concentration (50 mg/L), temperature (40 °C) and contact time (24 h) as can be seen from Figure 5. Generally, biosorption behaviour biomass is attributed to the interactions of different functional groups found on the biosorbent surface with metal ions. And these interactions between biosorbent surface and ions and their complexation degrees are considered as the influential factors in biosorption process. Several authors concluded that soft ions (such as Pb(II)) can be adsorbed on biomass preferentially than the borderline (such as Ni(II)) and hard ions [32, 33]. This is due to the interactions of soft ions with the biomass ligands which are mainly by covalent bonding. On the other hand, hard ions interact biomass ligands exclusively by electrostatic attraction and borderline ions have intermediate properties between these two of them. Therefore, Pb(II) occupied the first position in the affinity ranking among the examined ions. Table 3 was given to make comparison between sorption capacity
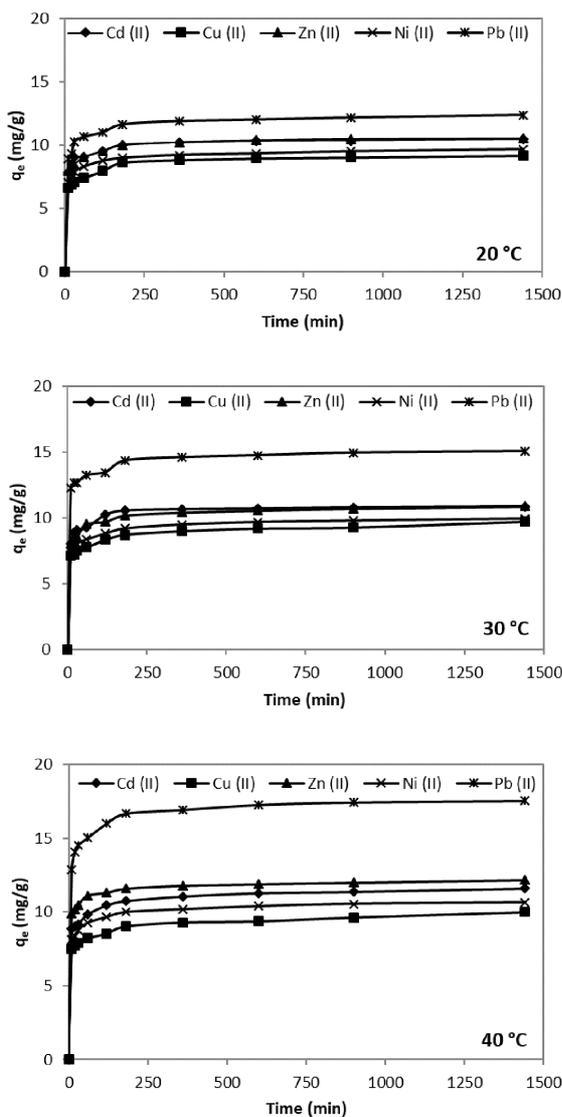
Table 4. Isotherm constants for heavy metal biosorption onto *E. rigida* at 20 °C

Isotherm	Pb(II)	Zn(II)	Cu(II)	Cd(II)	Ni(II)
Langmuir					
q_m (mg/g)	21.5939	14.4927	7.3964	17.8514	16.6389
K_L (l/mg)	0.0136	0.0074	0.0662	0.0434	0.0228
R^2	0.9788	0.9780	0.9784	0.9123	0.9918
MAPE (%)	1.0937	2.8040	4.4897	5.2486	1.3809
RMSE	0.0327	0.1031	0.2120	0.1189	0.0564
Freundlich					
K_F ((mg/g) (L/mg)$^{1/n}$)	0.6282	0.9421	0.8698	1.0394	0.5538
n	1.1806	1.5790	1.9527	1.4355	1.3552
R^2	0.9990	0.9950	0.9973	0.9942	0.9975
MAPE (%)	0.9588	1.7732	1.3823	2.1129	1.6477
RMSE	0.0162	0.0303	0.0191	0.0373	0.0231
Dubinin–Radushkevich					
q_m (mg/g)	8.7758	7.1499	4.4549	7.3294	6.3041
β	$7.00×10^{-6}$	$5.00×10^{-6}$	$4.00×10^{-6}$	$3.00×10^{-6}$	$8.00×10^{-6}$
E	$2.67×10^2$	$3.16×10^2$	$3.54×10^2$	$4.08×10^2$	$2.5×10^2$
R^2	0.8816	0.8837	0.8612	0.8609	0.8857
MAPE (%)	9.0071	7.7715	11.1695	12.1275	8.0527
RMSE	0.1783	0.1508	0.1400	0.1912	0.1581
Temkin					
B	4.6449	3.0825	1.6546	3.3839	3.0366
K_T	0.2971	0.4222	0.6268	0.5990	0.2979
R^2	0.9639	0.9777	0.9777	0.9442	0.9788
MAPE (%)	9.9911	5.5342	4.7086	10.4158	6.8005
RMSE	0.5494	0.3136	0.1799	0.5757	0.2798

of *E. rigida* and similar biomass samples that were found in the literature. It can be said that the capacity of *E. rigida* was found to be compatible with the reported studies.

Equilibrium, kinetic and thermodynamic studies

Isotherm parameters obtained from the Langmuir, Freundlich, D-R and Temkin models and their respective results are given in Table 4. According to the results, heavy metal biosorption onto *E. rigida* adsorption fitted well to the Freundlich model that considers multilayer adsorption of ions. Higher values of correlation coefficients (R^2) obtained by Freundlich model also indicate the acceptability of the model of heterogeneous sorption phenomena for the system. The performance of the constructed isotherms were also statistically measured by the MAPE (Mean absolute percentage error) and RMSE (Root mean squared error) and the results were given in Table 4.

Kinetic parameters related to applied models are given in Table 5. The statistical coefficients were compared for determining the suitable kinetic models for the biosorption process. Accordingly, for all metal ions pseudo-second order kinetic model fit better with the experimental data than

other kinetic models according to the calculated correlation coefficients (R^2) MAPE (Mean absolute percentage error) and RMSE (Root mean squared error) values. The fitted pseudo-second order model is useful for predicting behaviour over the whole range of biosorption. The best fittings with this model indicate that the rate-determining step consists of chemical adsorption including valence forces through the sharing or exchange of electrons between the surface of *E. rigida* and metal ions. The intraparticle diffusion model also was plotted in order to determine the effect of mass transfer resistance on the binding of metal ions on *E. rigida*. During kinetic analysis with intraparticle diffusion model, plots of the model did not pass through the origin for all metal ions. This observations indicate that the intraparticle diffusion was not the rate-limiting step of the process due to existence of some degree of boundary layers.

In order to get a better insight into the mechanism and to ascertain the temperature dependency, spontaneity and feasibility of the biosorption process, thermodynamic parameters are calculated and the corresponding results are given in Table 6. The positive value of enthalpy change (ΔH°) revealed that biosorption of metal ions is in endothermic

Table 5. Kinetic parameters for heavy metal biosorption onto *E. rigida*

Kinetic Model	Pb(II)	Zn(II)	Cu(II)	Cd(II)	Ni(II)
Pseudo-first order					
k_1	0.0237	0.0672	0.0207	0.0089	0.0115
q_e	1.3829	6.7623	3.9591	6.0436	2.3157
R^2	0.7661	0.9737	0.9928	0.9676	0.7324
MAPE (%)	70.2501	45.7410	12.2379	3.7638	50.6705
RMSE	0.2266	0.1905	0.0304	0.0282	0.1208
Pseudo-second order					
k_2	0.0451	0.0151	0.0075	0.0068	0.0284
q_e	10.7296	9.0744	5.8548	8.1169	7.0872
R^2	0.9998	0.9972	0.9957	0.9917	0.9986
MAPE (%)	1.6060	2.0243	3.2017	2.0617	3.8259
RMSE	0.0584	0.1560	0.3025	0.2700	0.2084
Intraparticle diffusion					
k_p	0.2030	0.3723	0.3799	0.4786	0.2403
C	8.6032	4.8315	0.988	2.0886	4.4403
R^2	0.7031	0.8428	0.9558	0.9552	0.8362
MAPE (%)	3.4446	5.0141	6.7588	5.8711	4.1403
RMSE	0.3618	0.4409	0.2240	0.2841	0.2916
Elovich					
α	28282.67	13.5386	0.5830	1.2689	41.4593
β	1.4271	0.8232	0.8137	0.6654	1.2505
R^2	0.8255	0.8848	0.9864	0.9837	0.9131
MAPE (%)	2.5268	4.5257	3.4209	3.0967	4.0550
RMSE	0.2774	0.3775	0.1241	0.1713	0.2832

nature. Also, positive value of entropy change (ΔS°) showed the randomness at the biosorbent–liquid interface because of the release of water molecules, ion exchange and binding of the metal ions. Moreover, negative values of Gibbs free energy change (ΔG°) showed that biosorption was spontaneous and confirmed the affinities of the *E. rigida* towards metal ions.

Multi-metal biosorption

Biosorption in multi-component systems is accepted as a much more complex process than single component systems due to solute-solute competition and the solute-surface interactions. Therefore, binary biosorption [Ni(II)-Zn(II), Cu(II)-Pb(II), Pb(II)-Cd(II)] and ternary biosorption of Cd(II)-Pb(II)-Cu(II) experiments were performed to explain co-ion effect in the removal process.

Fig. 6 shows the binary and ternary biosorption results of heavy metals. Comparing binary biosorption results with the single metal systems showed that, uptake amounts of Ni(II) and Zn(II) ions were decreased in binary systems (Fig.6.a). In binary solutions uptake amounts were decreased due to the competition of ions for sticking on the biosorbent surface and also due to the co-ion effect. On the other hand, the total heavy metal uptake on *E. rigida* is increased, because of the attraction of different metal ions on different surface sites. The obtained curves indicate that contact time presents a slightly increasing trend and 90 min contact time was found to be suitable for binary biosorption of Ni(II)-Zn(II). Besides, heavy metal removal was found as an endothermic process for binary biosorption as it was found for single metal systems. Analogue results were obtained for Cu(II)-Pb(II) binary system which are given in Fig. 6.b. Figure 6.c exhibits the results for Pb(II)-Cd(II) system. Likewise, the Ni(II)-Zn(II) and Cu(II)-Pb(II) binary systems, contact time increased the uptake amount to a certain value until equilibrium was established and 90 min was found to be the required time for the highest uptake amounts. Differently, Cd(II) uptake was not affected by adding Pb(II) ions into the solution. But, amount of Pb(II) biosorbed onto *E. rigida* decreased significantly in the presence of Cd(II) ion.

In order to investigate ternary metal ion biosorption, effects of initial heavy metal concentration, time and temperature were investigated. The biosorption of Cd(II)-Pb(II)-Cu(II) ions onto *E. rigida* as a function of metal ion concentrations were evaluated and uptake amounts were found lower than in the individual system, except Pb(II).

Table 6. Thermodynamic parameters calculated for heavy metal biosorption onto *E. rigida*

Metal ion	T (°C)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)	R²	MAPE (%)	RMSE
Pb(II)	20	-19.3604					
	30	-20.7203	20.17725	134.8863	0.9999	0.0256	0.0021
	40	-22.0576					
Zn(II)	20	-19.2236					
	30	-21.1083	38.7733	197.7568	0.9982	0.2697	0.0250
	40	-23.1828					
Cu(II)	20	-20.3364					
	30	-21.1669	8.3863	97.8252	0.9098	0.3144	0.0283
	40	-22.2994					
Cd(II)	20	-20.7013					
	30	-21.6591	15.9853	124.8357	0.9046	0.6034	0.0555
	40	-23.2110					
Ni(II)	20	-17.5471					
	30	-18.8666	14.6767	110.1605	0.9343	0.5285	0.0417
	40	-19.7405					

When the effect of contact time was analysed, the time to reach equilibrium for all metals was nearly same for single and binary systems as it is seen in Fig 6.d. For ternary metal biosorption, temperature showed a slightly increasing effect on the uptake amount of ions likewise single metal solutions. Consequently, competition among heavy metals affected uptake amounts of metals in binary and ternary metal systems significantly.

SEM-EDX Analysis

SEM-EDX is a beneficial method to determine the element existence by the help of characteristic X-ray energy. SEM–EDX analysis was performed on samples before and after biosorption to investigate textural properties and, thereafter, to understand binding of metal ions to the sorbent surface. Several sites on the *E. rigida* were analyzed after biosoption and their respective X-ray spectra are shown
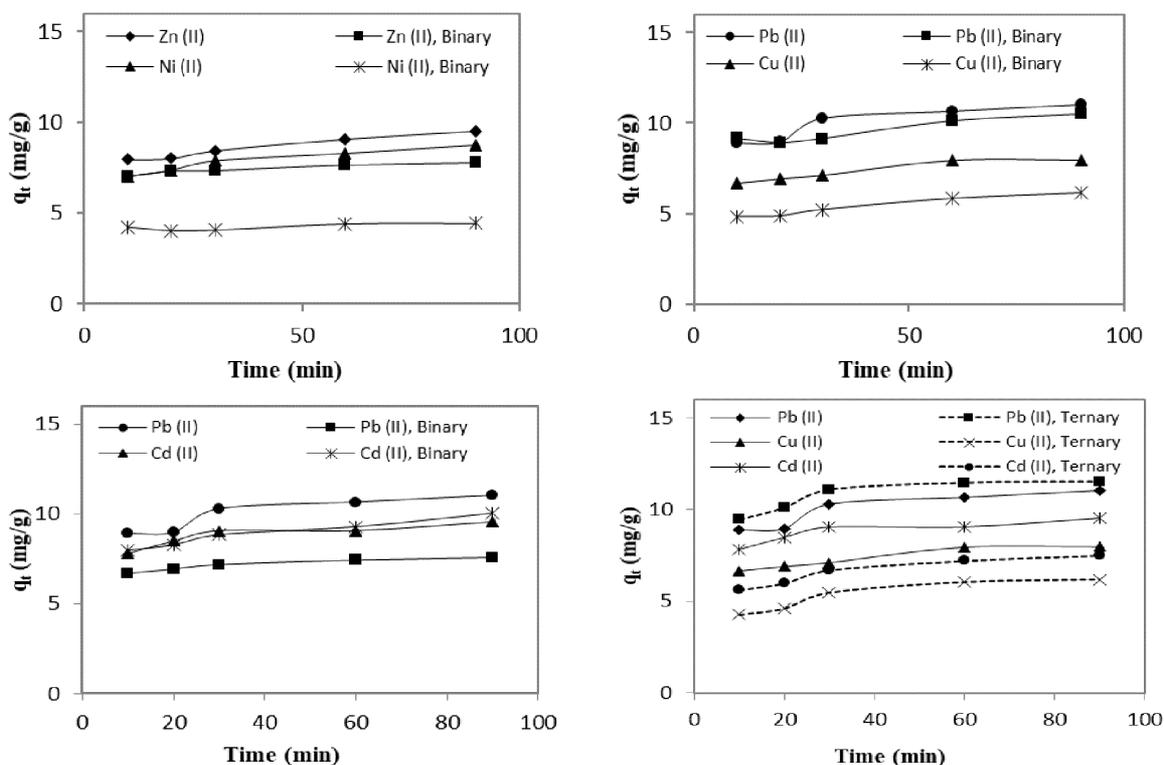

Figure 6. Effect of contact time for single, binary and ternary metal solutions (Initial metal ion concentration= 50 mg/L)

in Fig.7. From top to bottom, EDX spectra confirm that Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) ions stick on the surface and pores of *E.rigida* which can be understood from red dots seen in the micrographs. Furhermore, internal cavities after heterogeneous distribution of metal ions exist on the surface. These features were identical to the morphological descriptions of *E.rigida* regardless of the type of the ion.

CONCLUSIONS

This present study demonstrated the results of the biosorption process for the removal of Pb(II), Zn(II), Cu(II), Cd(II) and Ni(II) ions from aqueous solution using an arid land plant biomass. According to the uptake amounts, the affinities of the metal ions to adsorption sites decreased in the order of Pb(II) > Zn(II) > Cd(II) > Cu(II) > Ni(II) in single metal containing solutions. For the single metal containing systems, Freundlich isotherm gives the best correlation for heavy metal biosorption. Kinetic modelling showed that the data perfectly complied with pseudo-second order model. Thermodynamic analysis showed that process is endothermic and spontaneous. In multi-metal systems, the uptake amounts for both metals were significantly changed in the

presence of co-ions. But, presence of co-ions had no effect on equilibrium time and temperature dependency of the biosorption process. *E. rigida* proved itself as an alternative low cost biosorbent for removing heavy metals.Results suggested that non-edible biomass species can be incorporated in decentralized water treatment systems to offer a simple option for treating the low concentrations of heavy metals.

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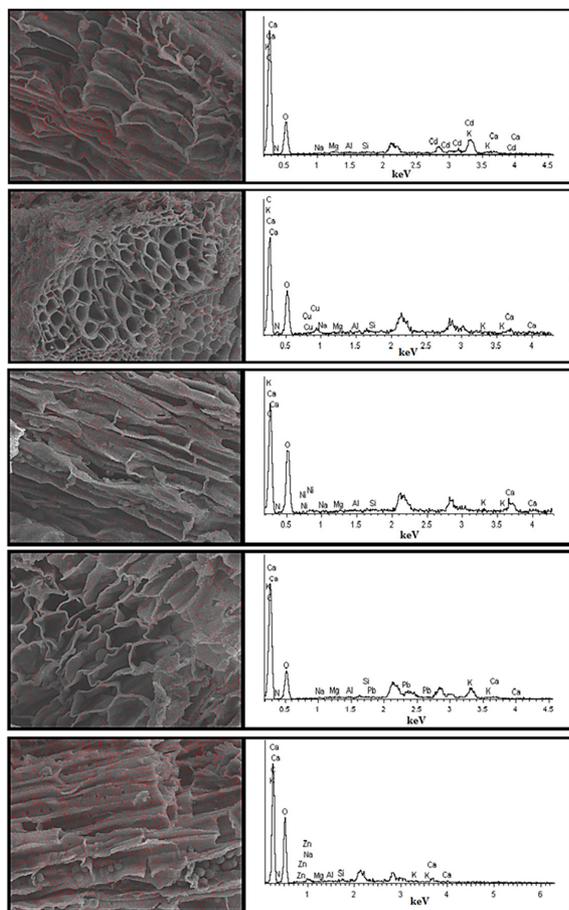[13] Semerjian L. Equilibrium and kinetics of cadmium adsorption

Figure 7. SEM micrographs and EDX spectra of *E. Rigida* after heavy metal biosorption

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