Removal of Lead Ions from Aqueous Solutions by a Novel *Ficus Carica* L.-Zeolite-Alginate Biocomposite

Kadriye ESEN ERDEN, Ibrahim DORUK, Meruyert KAYGUSUZ, Cem GÖK*

Pamukkale University, Denizli Vocational School of Technical Sciences, 20070, Denizli, Turkey

Short Title: *Removal of Lead (II) by a Novel Tricomponent Biocomposite*

****Corresponding author:*** M. KAYGUSUZ, E-mail: meruyertk@pau.edu.tr. Tel: +90-258-2123788 / Fax: +90-258-2113865. Address: Pamukkale University, Denizli Vocational School of Technical Sciences, 20070 Kinikli, Denizli, Turkey.

Abstract

In this study, fig leaves, zeolite and alginate were used to prepare a biocomposite for biosorption of Pb(II) ions from aqueous solutions. Effects of various parameters on the biosorption process such as pH, temperature, initial lead concentration and contact time have been investigated. Under optimum conditions the amount of adsorbed lead per gram of adsorbent (q_e) was found to be approximately 10 mg/g. Results have suggested that the prepared biosorbent possesses promising biosorption potential. Maximum uptake of Pb(II) ions (95%) has been achieved at pH 8, with 25 mg/L of initial concentration and at a temperature of 288.15 K. Among the applied Freundlich, Langmuir and D-R models, the data correlated well with Freundlich and D-R models and it was established that the biosorption was physical in nature. Thermodynamic parameters showed the exothermic heat of biosorption and the feasibility of the process.

Keywords: biosorption, lead, biosorbent, alginate, *Ficus Carica* L.

1. INTRODUCTION

Among the heavy metals, lead is one of the major pollution sources which discharged into the environment from metal finishing, ceramics, pulp, lead smelters, electroplating, mining and battery manufacturing industries (Isaac et al., 1997). In addition, to provide best colour matches and finishes textile and leather industries widely use pigments which contain mostly lead and cadmium (Aslan and Üzüm, 2015). Lead is a well-known highly toxic metal considered as a priority pollutant (Mondal, 2009). The presence of high levels of lead in the environment may cause long-term health risks to humans and ecosystems. Therefore, it is necessary to remove the lead ions before they are released into the environment.

The removal of heavy metals from contaminated waters has been investigated employing a wide variety of methods including chemical precipitation, ion-exchange, membrane filtration, reverse osmosis, etc. Due to the expensive costs of the so-called methods, the most promising alternative method for the removal of metal ions is adsorption. There is a growing demand to find low-cost and efficient, locally available adsorbent for the adsorption of heavy metals.

In current study, biocomposite was prepared from natural materials such as zeolite, alginate and fig leaves. Fig (*Ficus carica* L.) is among the oldest fruits and is known to manhood from ancient times. *F. carica* L., belonging to the Moraceae family, is a deciduous tree native to South-western Asia and the Eastern Mediterranean (Uğurlu et al., 2016). Figs are an important traditional crop in Turkey, due to the wide adaptability to the soil and climatic conditions (Aksoy et al., 2001). Natural zeolites have been known by their high ion-exchange capacity, relatively high specific surface areas and, more importantly, their relatively low prices (Chmielewská et al., 2011). The adsorptive properties of alginate based on the presence of carboxylic acid and hydroxyl functional groups that have a high affinity towards heavy metals. On the other hand, it is highly porous and allows an extended use of the surface (Navarro et al., 2014).

The objective of this study was to investigate the use of environmentally friendly cost effective biocomposite to recover lead from waste water. Effects of various parameters on the adsorption process such as pH, temperature, initial lead concentration and contact time have been investigated.

2. MATERIALS AND METHODS

Materials and Instrumentation

Zeolite and alginic acid sodium salt were purchased from Sigma-Aldrich, USA. Lead chloride ($PbCl_2$) was supplied from Merck. All chemicals used in the experiments were of analytical reagent grade. Inductively coupled plasma optic emission spectroscopy (Spectro, Germany) was used for the determination of lead ions.

Preparation and characterization of biocomposite adsorbent

Harvested fresh *Ficus carica* L. leaf samples were extensively washed with tap and distilled water to remove impurities. Then, samples were dried at room temperature and not exposed to direct sunlight. The leaf samples were transferred to oven and dried at 50°C for 24 hours using an oven (Test, Turkey). The dried samples were ground in a mortar with pestle and sieved using a standard mesh (<120 µm) sieve (Jeotest, Turkey). *Ficus carica* L. leaves powder and zeolite were encapsulated into sodium alginate beads in aqueous calcium chloride solution to prepare a biocomposite material. For this purpose, a required amount of sodium alginate (%2) was dissolved in 100 ml distilled water with constant stirring at 50ºC until a gelous solution was obtained. Zeolite (0.5 g) and *Ficus Carica* L. leaves powder (1 g) were mixed carefully under continuous stirring until the mixture became homogeneous. The suspension was injected drop wise into a 0.5 M solution of calcium chloride with the help of injection syringe. Fine biocomposite beads of alginate–zeolite–*Ficus Carica* L. leaves powder were formed. The hydrogel beads were separated from the solution by filtration and dried for overnight in an oven maintained at 50º C. Dried mass of the beads was used as adsorbent for lead ion removal.

Fourier Transform Infrared Spectroscopy (FT-IR) was used to determine the vibration frequency changes in the functional groups in the prepared biosorbent. The FT-IR spectra within the range of wave-number of 4400–400 cm^{-1} using KBr pressed disk technique were obtained by Agilent Infrared spectrometer (USA). Scanning Electron Microscope (SEM) was used to analyse the surface properties and the morphology of the prepared biocomposite beads (Quanta FEG 250, USA).

Batch experiments

Stock solution of lead ions (500 ppm) was prepared by dissolving calculated amount of $PbCl_2$ in distilled water and working standards of required strength were prepared by diluting the reserve solution.

The biosorption experiments of lead with the prepared biocomposite were carried out by the batch equilibrium biosorption experiments using a thermostated shaker bath. Parameters such as pH, initial concentration of lead solution, contact time and temperature were investigated. Most of the biosorption experiments were performed using the 0,1g of adsorbent which was suspended in 25 mL of $PbCl_2$ in a polyethylene (PE) flask at selected pH. The pH was adjusted by adding diluted HCl and NaOH to the solutions at the each experiment. The solution was separated from the solids by filtration after biosorption experiments. The lead concentration remained in aqueous solution was determined with ICP-OES. The amount of adsorbed lead (q_e, mg/g) was calculated by a mass balance relationship:

$$q\,(\mathrm{mg/g}) = \frac{(\mathrm{C_i} - C_e)V}{m} \qquad (1)$$

where C_i and C_e are the initial and equilibrium concentrations of lead ions (mg/L) in solutions, respectively. m is the weight of the adsorbent (g), V is the volume of the aqueous phase (L).

Sorption Isotherms

Langmuir, Freundlich and Dubinin-Radushkevich-Kaganer (DRK) isotherms are applied to describe the sorption characteristics of Pb(II) on the biosorbent.

Langmuir isotherm

The Langmuir isotherm is the most widely used model and traditionally used to quantify and contrast the performance of different biosorbents. This model's theory presumed monolayer coverage of adsorbate over a homogeneous sorbent surface (Langmuir, 1918). Langmuir model linearized equation is expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b_L} + \frac{\mathrm{C_e}}{Q_0} \qquad (2)$$

where q_e is the amount of lead ions adsorbed onto adsorbent, C_e is the equilibrium concentration of lead in solution, and Q_0 and b_L are Langmuir constants related to biosorption capacity and biosorption energy, respectively.

Freundlich isotherm

The Freundlich model assumes a logarithmic decrease in the enthalpy of biosorption with the increase in the fraction of occupied sites. In other words, this model is also an empirical expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies (Freundlich, 1906).This model can be given as follows:

$$\log q_e = \log K_F + \frac{1}{n_F} \log C_e \qquad (3)$$

where K_F represents the biosorption capacity (mg/g), n_F is a constant related to biosorption intensity (dimensionless).

Dubinin-Radushkevich (D-R) isotherm

The other widely used isotherm is Dubinin–Radushkevich (D–R) model, used to estimate the apparent free energy of adsorption, was proposed an equation to find out the adsorption mechanism on the basis of the potential theory assuming a heterogeneous surface (Dubinin et al., 1947). The linearized equation of the D-R isotherm is given as:

$$\ln C_{ads} = \ln X_{\mathrm{m}} - \beta\varepsilon^{2} \qquad (4)$$

where C_{ads} (mmol/g) is the amount of solute sorbed per unit weight of solid, X_m (mg/g) is the biosorption capacity, β (mol/K)^2 is a constant related to energy and ε is the Polanyi potential. Polanyi potential can be computed by following equation:

$$\varepsilon = RT\ln\left(\frac{1}{1+C_e}\right) \qquad (5)$$

where R is a gas constant in kJ/mol and T is the temperature in Kelvin. If $\ln C_{ads}$ is plotted against ε^2, β and X_m can be obtained from the slope and intercept, respectively. The mean energy of biosorption (E) is calculated by the following equation using the constant β.

$$E = \frac{1}{\sqrt{-2\beta}} \qquad (6)$$

3. RESULTS AND DISCUSSION

Characterization of biosorbent

The images of the dried and powdered fig leaves, the as-prepared and dried biocomposite are given in Figure 1. As it could be seen from Fig. 1, the prepared biocomposite beads have characteristic green color which came from the fig leaves origin and became darker after drying. The biocomposite beads appeared spherical in shape and uniform in size (µm) which reduced with drying (µm).

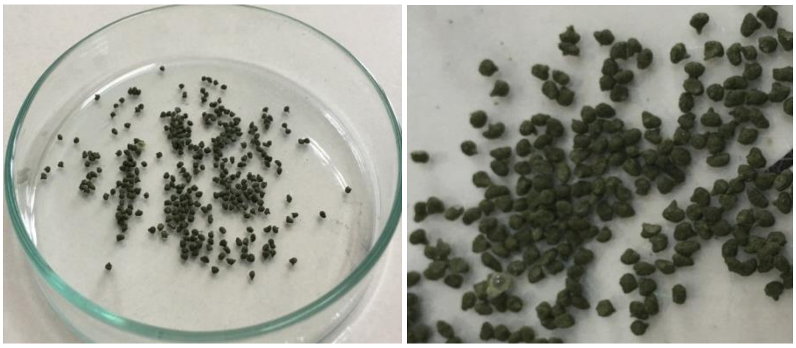

Figure 1. Dried (a) and powdered fig leaves (b), the as-prepared (c) and dried biocomposite (d, e)

FT-IR Analysis

F. carica-zeolite-alginate biocomposite was analysed using a Fourier transform infrared spectrometer as shown in Figure 2. The absorption peak at 3326 cm^{-1}and 2923 cm^{-1}indicated the presence of both free and hydrogen-bonded –OH groups on the surface of the biosorbent. The other peaks observed at 1597, 1077, and 942 cm^{-1} may be due to C–C, C–O, and C–N stretching, respectively (Boufi and Alila, 2011). The broad peak at 629 cm^{-1} and 819 cm^{-1} indicate the presence of–OH bending due to β-glycosidic linkage. The appearance of smaller peaks at 1313-1559 cm^{-1} may be attributed to -CH, -CH_2 and -C-OH bending (Sharma et al., 2013). The hydrogel displays absorbance peaks of COOH at 1419 cm^{-1} and SiO_4 tetrahedral stretching at 1008 cm^{-1}(Bayomi et al., 2015). The peaks located at 2041, 2168 and 2185 cm^{-1} can be assigned to stretching vibration of C-O, C≡C bondor gas-phase species, respectively (Ma et al., 2016; Li, 2005).

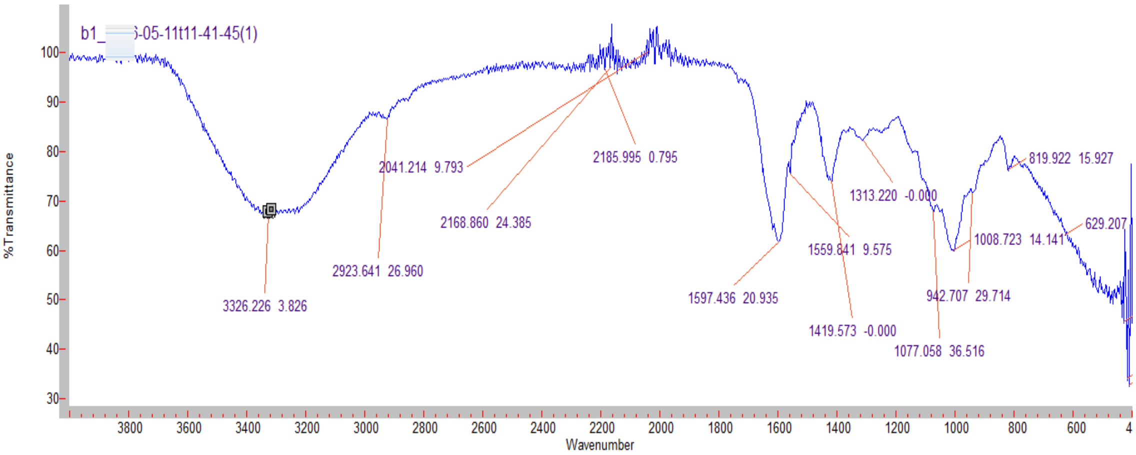

Figure 2. The Fourier Transform Infrared Spectroscopy spectra of biocomposite

SAF BİTKİ-ALJİNAT VE ZEOLİT BİOCOMPOSİTE İLE BİRLİKTE FTIR GRAFİĞİ VERİLİP EKLENECEK

Microscope Analysis

The microscopic images obtained by a scanning electron microscope clearly depicted the surface topography and internal architecture of the biosorbent (Figure 3). The prepared biocomposite bead has irregular and porous structure with latitudinal cavities. When the surface morphology was examined under power of magnification 2500x a lot of pores and wrinkles were appeared. Encapsulated fig leaves powder and zeolite were seen as stretched to the alginate matrix and it changed the morphology of surface due to grafting of the matrix with the amorphous and crystalline particles of fig leaves and zeolite, respectively. This led to physical and possibly to chemical cross-linking in the biocomposite structure which enhanced the biosorption process.

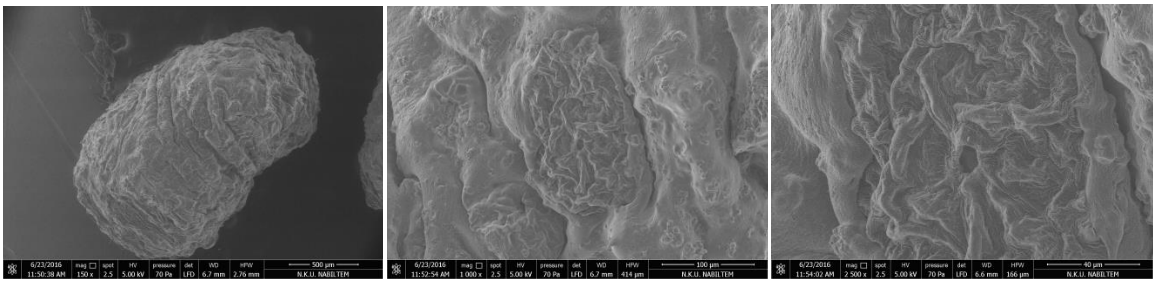

Figure 3.SEM micrographs of the prepared biocomposite

Studies on optimum bioremoval conditions

In order to compare the efficiency of the prepared biosorbent, the biosorption of lead ions were performed using separately *Ficus Carica* L powder and alginate. The batch biosorption experiments were investigated under the conditions of 0,1 g of biosorbent, 25 mL and 100 mg/L of lead solution at pH 4, 25°C for 2 h at 200 rpm agitation speed. The obtained results show that adsorption capacity of *Ficus Carica* L powder and alginate were 24% ve 12%, respectively. However, at the same conditions maximum uptake of lead ions by the biocomposite was 40%.

Effect of initial pH

pH has been known as an important parameter affecting the sorption process. In order to determine the effect of pH on the biosorption of Pb(II) ions onto biosorbent, the batch biosorption studies at different pH values were carried out. Experiments were investigated under the conditions of 0,1g of biosorbent, 25 mL and 10 mg/L of lead solution at 25°C for 2 h at 200 rpm agitation speed. Figure 3 shows that lead removal changes in a pH range of 2–8.

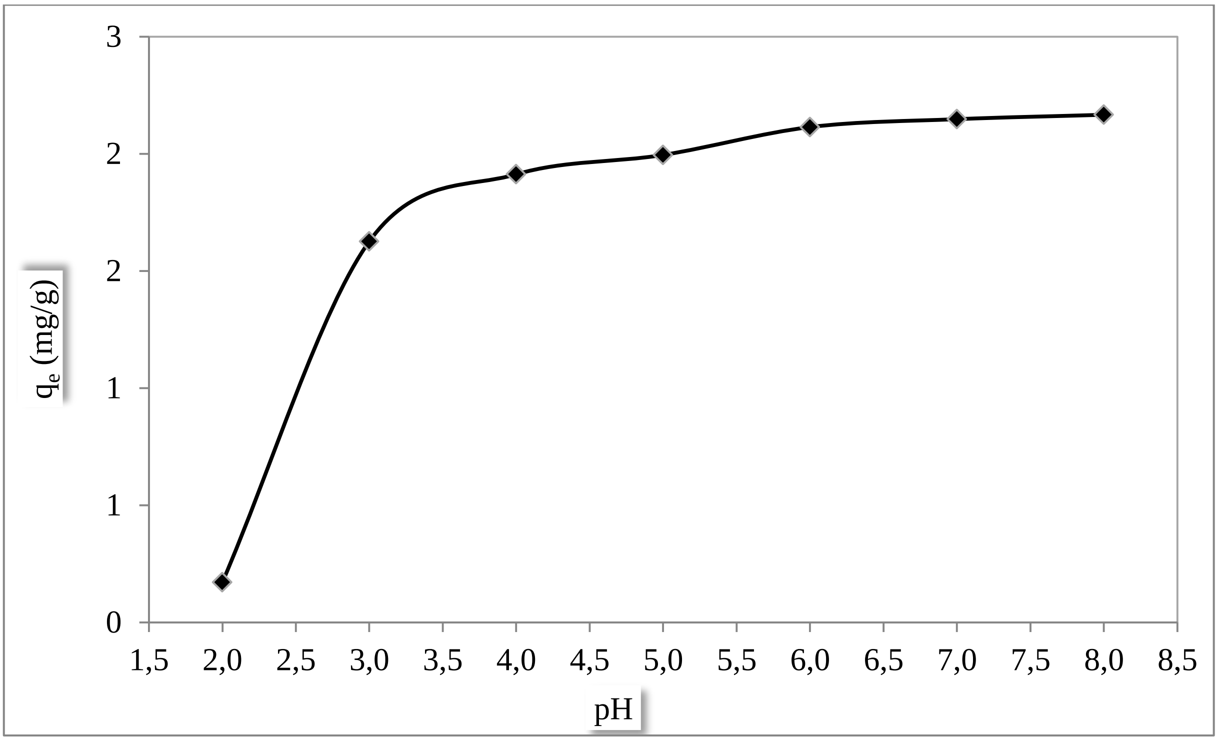

Figure 3. The adsorbed lead efficiency as a function of pH

As can be seen from the Fig. 3, the maximum biosorption of Pb(II) ions on the biosorbent was observed at pH 8.00 with 86.67%.

The effect of initial Pb(II) concentration

The biosorption of Pb(II) was studied as a function of initial Pb(II) concentration. Biosorption efficiencies of the biocomposite as a function of the initial concentration of lead between 5 and 200 mg/L were presented in Figure 4. The biosorption experiments were carried out under the conditions of pH 4.0, 0.1 g biosorbent, 25 mL of lead solution, 25 °C temperature, 2 h of contact time at 200 rpm agitation speed.

As seen in Fig. 4, the Pb(II) sorption increased from 52.0 to 64.7 % with an increase of the initial lead concentration in solution from 5 to 25 mg/L and then decreased to 33.70% at 200mg/L of lead concentration. As noticed the biosorption efficiency decreases by increasing Pb(II) concentration in solution. The biosorbent has a maximum lead sorption at 25mg/L initial lead concentration.

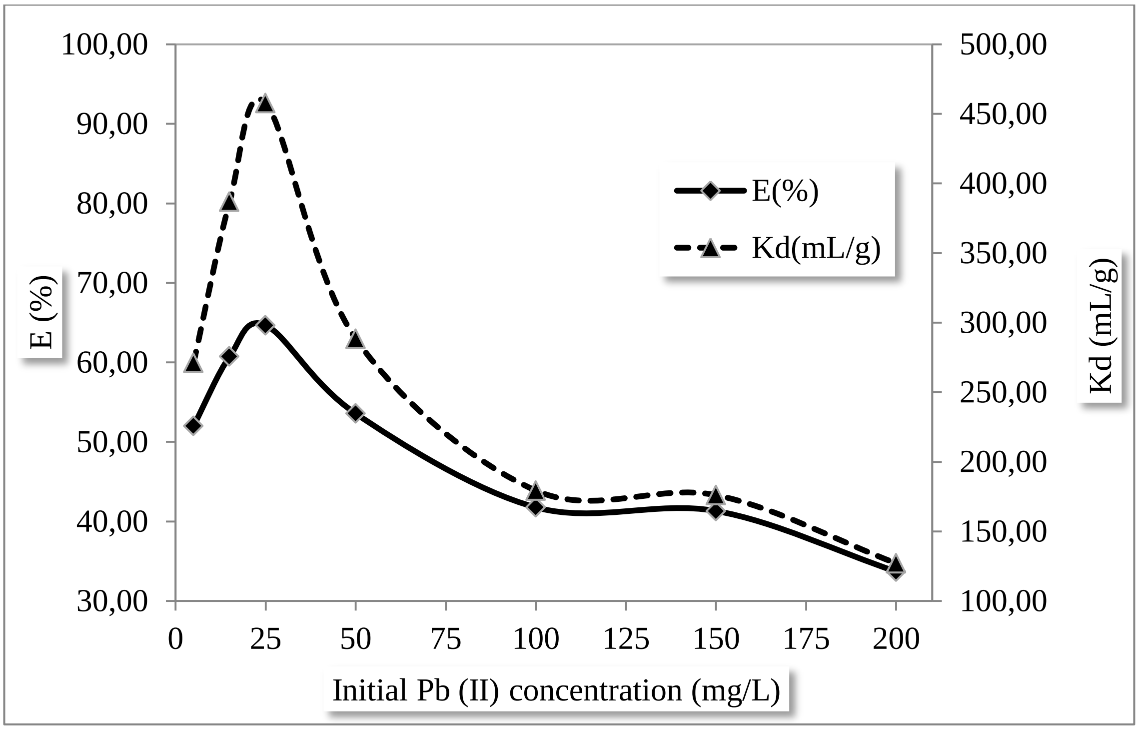

Figure 4. The adsorbed lead efficiency as a function of initial Pb(II) concentration

Effect of contact time

The contact time between the metal ions and adsorbent has great importance for designing biosorption processes. The effect of contact time on the lead biosorption in the range of 30-1440 min was investigated with 25mL and 100 mg/L of lead solution, 0.1 g of biosorbent at pH 4.0,25 °C at 200rpm agitation speed. Figure 5 shows adsorbed lead efficiency as a function of contact time.

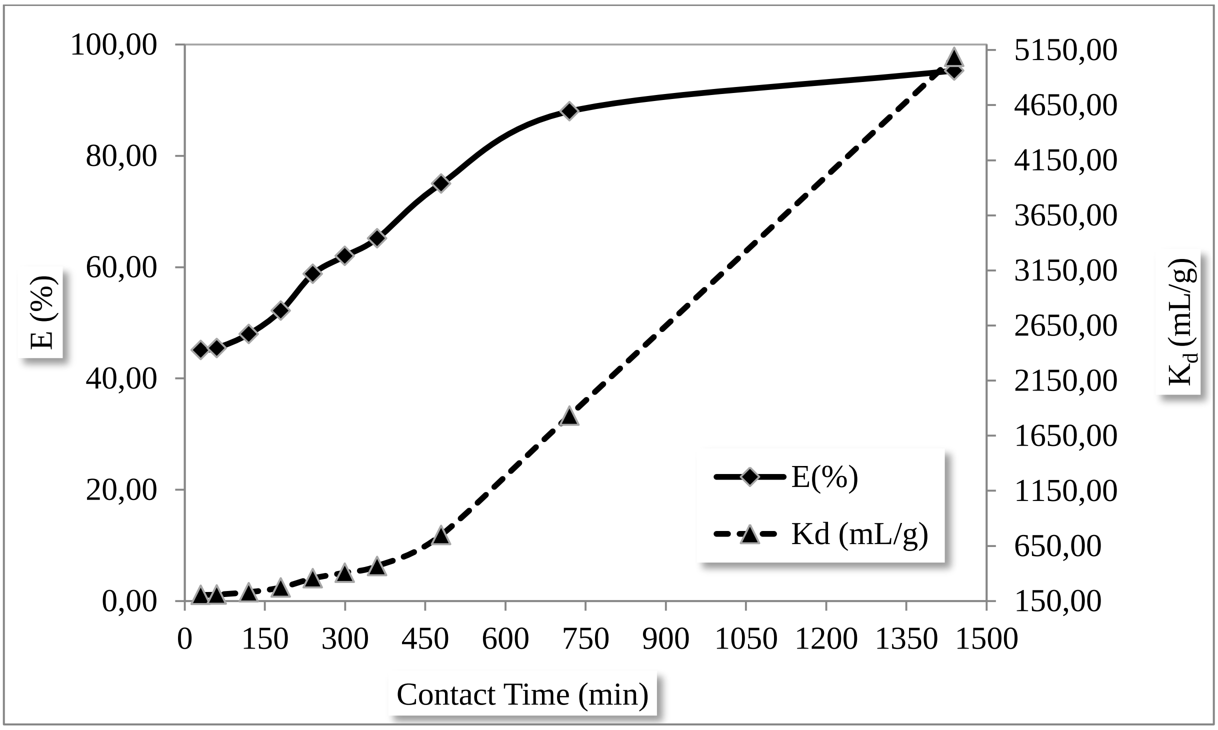

Figure 5. The adsorbed lead efficiency as a function of contact time

As clearly seen from Fig. 5, high removal percentage of lead is obtained even at the beginning of the sorption. The biosorption efficiency increases rapidly over 65% at the first 300 min. After 1440minutes, 95% of lead ions have been removed from the solution.

Effect of temperature and thermodynamic studies

The effect of temperature on the biosorption of Pb(II) was studied varying 5 different temperature from 288.15 to 328.15 K while the other parameters were kept constant(0,1g of biosorbent in 25 mL and 50 mg/L of standard lead solution at pH 4.0 and 2 h of contact time at 200rpm agitation speed). The influence of different temperatures was examined using biosorption of lead ions on the biosorbent appeared to be temperature dependent over the temperature range tested as shown in Figure 6. According to results, biosorption of lead ions was exothermic in nature.

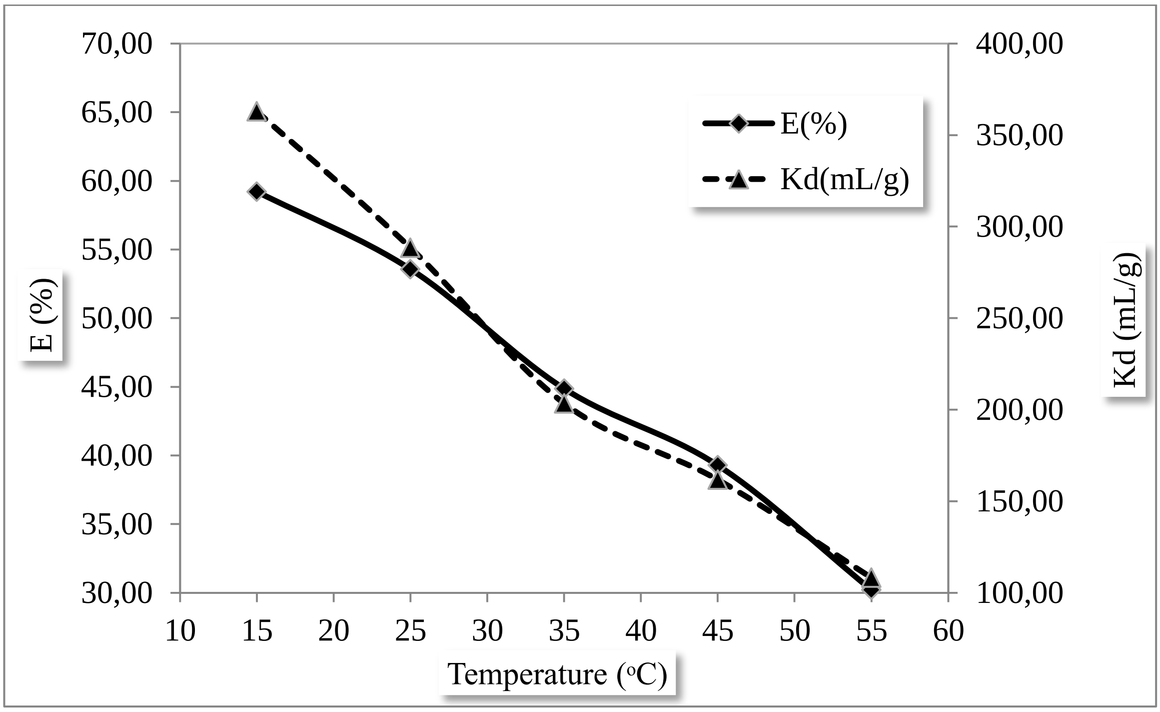

Figure 6. The adsorbed lead efficiency as a function of temperature

Thermodynamic parameters(enthalpy, $\Delta H°$, entropy, $\Delta S°$, Gibbs energy change, $\Delta G°$) were calculated by using the following equation:

$$lnK_{\mathrm{d}} = \left(\frac{\Delta S^{\mathrm{o}}_{\mathrm{ads}}}{R}\right) - \left(\frac{\Delta H^{\mathrm{o}}_{\mathrm{ads}}}{RT}\right) \qquad (7)$$

where$K_d$is distribution coefficient, R is the gas constant (8.314 J/mol.K), T is temperature in Kelvin,$\Delta H^{\mathrm{o}}_{\mathrm{ads}}$, $\Delta S^{\mathrm{o}}_{\mathrm{ads}}$, and T are the enthalpy and entropy, respectively. The plot of ln K_d against 1/T is created and the values of enthalpy and entropy were obtained from the slope and intercept of the plot (Fig. 7). The following well-known equation was used to calculate Gibbs free energy:

$$\Delta G = \Delta H - T\Delta S \qquad (8)$$

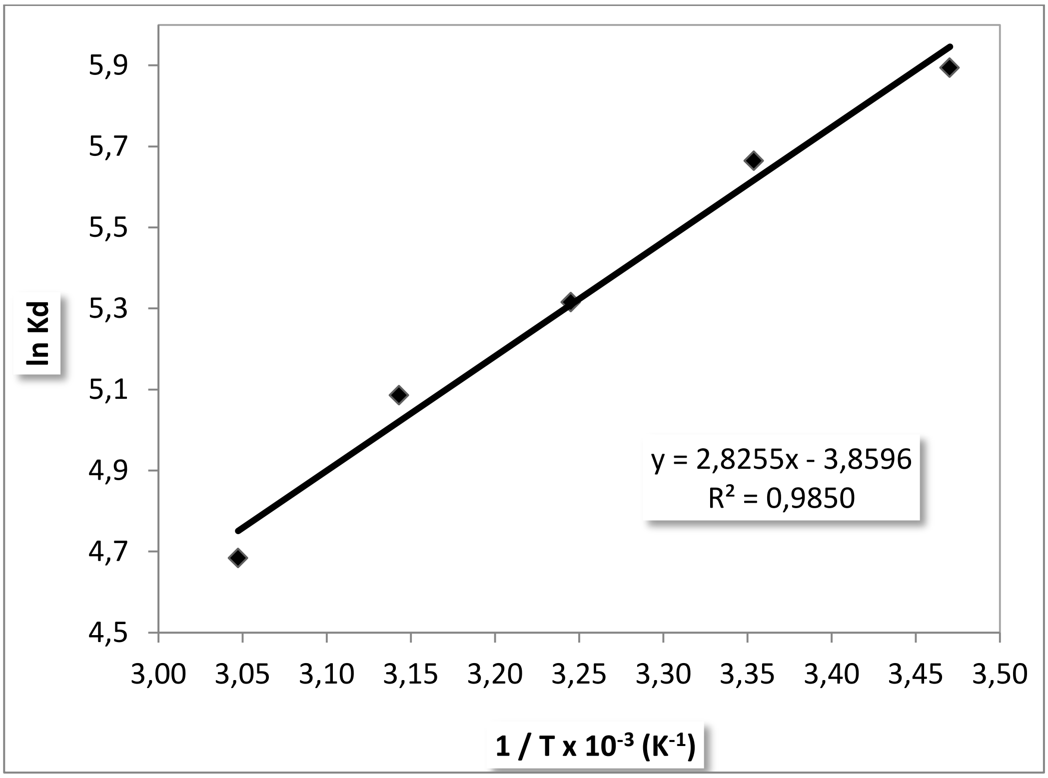

Figure 7. Influence of temperature on the thermodynamic behavior of biosorption of Pb(II)on biocomposite

The negative value of enthalpy change, ΔH, shows that the biosorption of lead is exothermic process. The value of ΔG for these processes becomes less negative with increasing temperature which shows that sorption is less favoured at high temperatures as shown in Table 1. The reaction is spontaneous and more favorable at lower temperatures. The negative value of biosorption entropy is a harmonious result with the general information of decreasing entropy when ions pass solid phase from solution.

Table 1. Thermodynamic parameters for biosorption of Pb(II)

ΔH° (kJ/mol)	ΔS° (J/molK)	R^2	ΔG° (kJ/mol) 288.15 K	298.15 K	308.15 K	318.15 K	323.15 K
-23.491	-32.089	0.9850	-14.245	-13.924	-13.603	-13.282	-12.961

Adsorption Isotherms

To acquire more insight into the biosorption of lead on to alginate-zeolite-*Ficus Carica* L. biocomposite, the results of equilibrium batch sorption experiments were evaluated with isotherm models. The biosorption of lead on to biocomposite is a mass transfer operation that can be described mathematically. The equilibrium is established between the concentration of the metal ions dissolved in aqueous phase and that bound to the adsorbent (Gok, 2014; Bayramoglu, 2003). In order to analyze this process, the experimental data have been subjected to different sorption isotherms namely Freundlich, Langmuir and Dubinin–Radushkhevich models. Biosorption equilibrium in the concentration range of 5–200 mg/L was studied with 100 mg of Alginate-*Ficus Carica* L. biocomposite at 25°C, pH 4.0 and 120 min contact time. The constants and correlation coefficients (R^2) of isotherm models have been calculated from the plots for biosorption of lead on the biocomposite and the results are given in Table 2. By increasing the initial lead concentration in solution, the amount of sorbed metal gradually increases.

Table 2. Constants of isotherm models for lead biosorption onto biocomposite

Isotherm models	Parameters	
Langmuir	Q_o(mg/g)	370,4
	b_L (L/mg)	0,006
	R^2	0.8324
Freundlich	K_F (mg/g)	2.68
	n_F	1.16
	R^2	0.9845
Dubinin–Radushkevich	X_m(mg/g)	150,3
	β (mol/kJ)^2	2,97x10^{-8}
	E (kJ/mol)	4,10
	R^2	0.9817

Lagmuir Isotherm: The equilibrium data for Pb(II) ions over the concentration range from 5 to 200 mg/L at 298.15 K has been correlated with the Langmuir isotherm (Fig. 8).Q_0 and b_L were calculated from the slope and intercept of linear plots of C_e/q_e versus C_e. Considering the comparative magnitudes of correlation coefficients together with the isotherm constants suggests that the Langmuir isotherm does not provide a particularly good model for the biosorption of lead.

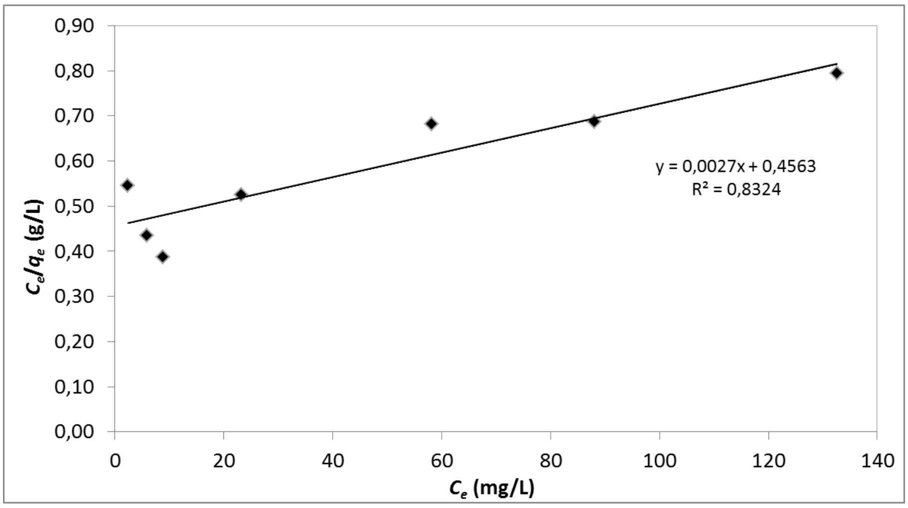

Figure 8. Linear isotherm models of Langmuir for lead biosorption on Alginate-*Ficus Carica* L. biocomposite.

Freundlich isotherm: Linear plot of log q_e versus log C_e shows the applicability of Freundlich isotherm for lead biosorption onto biocomposite (Fig. 9). According to the correlation coefficients, the biosorption process could be well described by Freundlich equation.

The values of n are bigger than 1, reflecting the beneficial biosorption. The numerical value of 1/n <1 indicates that sorption capacity is only slightly suppressed at lower equilibrium concentration and suggests multiple binding sites, with the highest strength sites binding the sorbate first. This isotherm predicts saturation of the sorbent by the sorbate thus infinite surface coverage is predicted mathematically, indicating a multilayer sorption of the surface (Aytas et al., 2009).The value of $K_{F,}$ signify the sorption capacity, is also founded as 2.68 mg/g.

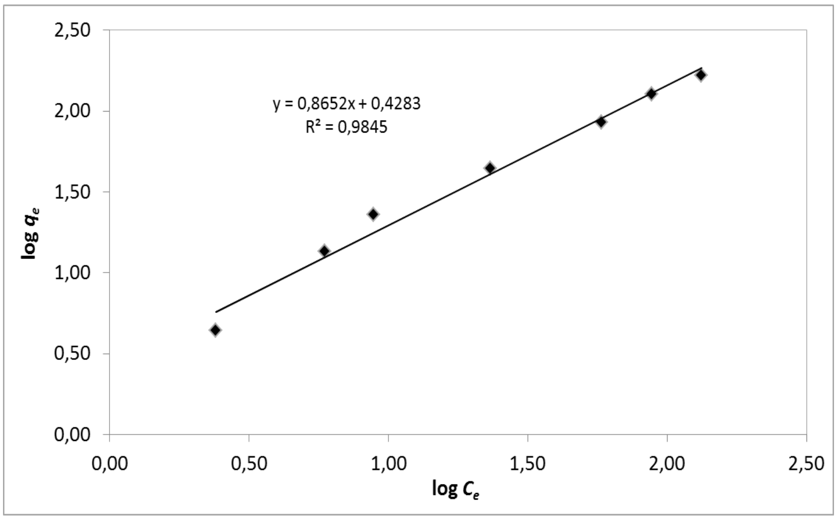

Figure 9. Linear isotherm models of Freundlich for lead biosorption on alginate-zeolite-*Ficus Carica* L. biocomposite.

Dubinin-Radushkevich-Kaganer (DRK) isotherm: The plot of ln C_{ads} against $\varepsilon^2$is a straight line as shown in Fig. 10.β and X_m can be obtained from the slope and intercept, respectively. The calculated constants of Dubinin–Radushkevich isotherm and mean free energies are given in Table 2. The biosorption capacity (X_m) of the D–R model is 150.31 mg/g for lead ions. The magnitude of *E* is used to estimate the reaction mechanism of biosorption process. If value of *E* is between 1 and 8 kJ/mol, it indicates a physical biosorption. If value of *E* is higher than 8 kJ/mol, the biosorption process is of a chemical nature. Hence, the value of E, 4.10 kJ/mol shows that the process is in the range of physical biosorption. It is also assumed to be heterogeneous in the structure of prepared biocomposite.

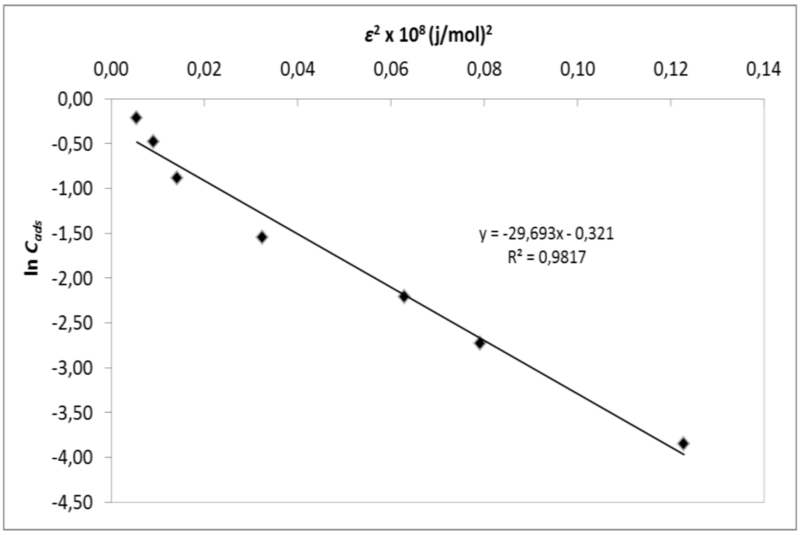

Figure 10. Linear isotherm models of Dubinin–Radushkevich (D–R) for lead biosorption on alginate-zeolite-*Ficus Carica* L. biocomposite.

Comparison of alginate-zeolite-Ficus Carica L. biocomposite with other biosorbents

Several studies have been performed on biosorption of lead in literature for recent years. A comparison of the lead metal uptake capacities (Q_0, *mg/g*) of this study with those of other adsorbents reported in the literature is given in Table 3. Although a direct comparison of our study with other reported biosorbents is difficult due to the varying experimental conditions employed in those studies, in general, alginate-zeolite-*Ficus Carica* L. biocomposite exhibits reasonable adsorption capacity in comparison with other biosorbents.

Table 3. Comparison of lead uptake capacities Q_o(mg/g) of various adsorbents

Biosorbent	Q_o(mg/g)	Reference
Olive stone waste	4.47×10^{-5}mol/g = 9.30mg/g	Fiol et al. 2005
Sulfured orange peel (MOP)	164mg/g	Liang et al. 2011
Cinnamomum camphora leaves	75.82mg/g	Chen et al. 2010
Modified lentil husk	81.43mg/g	Basu et al. 2015
Australian marine algae	1.55mmol/g = 322mg/g	Matheickal and Yu 1999
Alginate-zeolite-*Ficus Carica* L. biocomposite	370,4 mg/g	Present study

The last few decades, development of new low cost biosorbents that have metal binding capacities and modification of the performance of existing ones has been intensified. Plants have been known by their heavy metal accumulation properties and have recognised as bioindicators. The study was performed under heavy metal accumulation level of *Ficus carica* bark and leaves (Ugurlu et al., 2016). Sasikala and Muthuraman (2015) used *Ficus carica* seeds for the adsorption of Cr (III) and found the average percentage of adsorption as 94.6% that indicated the occurrence of a strong interaction between the metal and adsorbent. *Ficus carica* bast fiber was used for the adsorption of Cr(VI) and maximum adsorption capacity was found as 19.68 mg/g (Gupta et al., 2013). Sharma et al. (2013) chemically modified the *Ficus carica* bast fiber with acrylic acid and found 56% of adsorption of Cr(VI) for this sorbent. To the best of our knowledge, there is no study performed on the biosorption of lead ions on the biocomposite containing *Ficus carica* L. leaf powder.

4. CONCLUSION

Natural adsorbents are basically biodegradable that consists mainly of degradable organic matter. The prepared biocomposite in this study was consisted of natural materials such as fig leaves, alginate and zeolite. The adsorption process was lead ion concentration and pH dependent. The maximum biosorption of Pb(II) ions on the biosorbent was observed 86.67% at pH 8.00 with 10 mg/L initial Pb(II) concentration. The negative value of enthalpy change ΔH (-23.491kJ/mol), shows that the biosorption of lead is exothermic process. The reaction is spontaneous and more favorable at lower temperatures. The biosorption process could be well described by Freundlich and D-R equations. The value of the sorption capacity is founded as 2.68 mg/g. The mean energy of biosorption calculated as 4.10 kJ/mol shows that the process is in the range of physical biosorption. It is also assumed to be heterogeneous due to the structure of the prepared biocomposite. The results of present study have suggested that the prepared biosorbent is suitable for the removal of Pb(II) ions from aqueous solutions. The prepared biocomposite can be considered as a new approach to improve the quality of the treated effluent and to clean up a polluted aqueous ecosystem.

Acknowledgements

This study was financially supported by General Directorate of Agricultural Research and Policies (TAGEM) of Republic of Turkey Ministry of Food, Agriculture and Livestock under the project number of TAGEM 14-ARGE44. The authors are also grateful to Assoc.Prof.Dr. Abdulah AKDOGAN and research team members of Suzan ERDOGAN, Buket OZTURK, Saner ASLAN and Mesut Tunay ONURMAN

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