Article

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

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Abstract: In this study, fig leaves, zeolite and alginate were used to prepare a biocomposite for the adsorption 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. Maximum uptake of Pb(II) ions (85%) has been achieved at pH 6, with 25 mg/L of initial concentration and at a temperature of 288.15 K. Among the applied models, the data correlated well with Freundlich and D-R models and it was established that the biosorption was physical in nature. The amount of adsorbed lead per gram of sorbent was found to be 150.3 mg/g. Thermodynamic parameters showed the exothermic heat of biosorption and the feasibility of the process. Results have suggested that the prepared biosorbent possesses promising biosorption potential.

Keywords: adsorption; lead; biocomposite; 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 [1]. In addition, to provide best color matches and finishes textile and leather industries widely use pigments which contain mostly lead and cadmium [2]. Lead is a well-known highly toxic metal considered as a priority pollutant [3]. The presence of even low 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 [4]. Figs are an important traditional crop in Turkey, due to the wide adaptability to the soil and climatic conditions. Moreover, Turkey is a leader country in fig production in the world; hence, to evaluate the agricultural waste like fig leaves is noteworthy[5]. Natural zeolites have been known by their high ion-exchange capacity, relatively high specific surface areas and, more importantly, their relatively low prices[6].Rich zeolite deposits, especially of clinoptilolite, are located in Turkey [7]; therefore, it is rational to benefit from this abundant material. 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 [8].

In this study, the first attempt was to prepare biocomposite from fig leaves, zeolite and alginate; and benefit from not only the availability and low-cost of these compounds but also from the accumulative properties of fig leaves, the rigidity and thermal resistance of zeolite, and the high porosity and effective surface of alginate. In this regard, the main objective of the study was to investigate the use of environmentally friendly cost effective biocomposite to remove lead from aqueous media. For this purpose, the 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

2.1. Materials

Zeolite and alginic acid sodium salt were purchased from Sigma-Aldrich (USA). Lead chloride ($PbCl_2$), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were supplied from Merck (Germany).All chemicals used in the experiments were of analytical reagent grade.

2.2. Preparation and characterization of biocomposite

Harvested fresh *Ficus carica L.* leaf samples were extensively washed with tap and distilled water to remove impurities. Then, the leaf samples were dried at room temperature and not exposed to direct sunlight. The dried samples were ground in a mortar with pestle and sieved using a standard mesh (<120 μm) sieve (Jeotest, Turkey). F. carica L. leaves powder and zeolite (~30 μm) 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 F. 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–F. caricaL. leaves powder were formed. The hydrogel beads were separated from the solution by filtration and dried for overnight in an oven (Test, Turkey) maintained at 65ºC. The dried mass of the beads was used as a sorbent for lead ion removal. The dry weight is a value that is easy to standardize. In addition, taking into account the possible industrial applications this is relatively easy to transport and store the dried material.

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

2.3. Batch experiments

Stock solution of lead ions (500 mg/L) 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 adsorption experiments of lead with the prepared biocomposite were carried out by the batch equilibrium adsorption experiments using a thermostated shaker bath. Parameters such as pH, initial concentration of lead solution, contact time and temperature were investigated. Most of the adsorption experiments were performed using the 0.1g of biocomposite which was suspended in 25 mL of $PbCl_2$in a polyethylene (PE) flask at selected pH. The pH was adjusted by adding the diluted HCl and NaOH to the solutions at the each experiment. The solution was separated from the solids by filtration after adsorption experiments. The lead concentration remained in aqueous solution was determined with inductively coupled plasma optic emission spectroscopy (ICP-OES, Spectro, Germany).

95   The amount of adsorbed lead (qe, mg/g) was calculated by a mass balance relationship:
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97
$$q_e(mg/g) = \frac{(C_i - C_e)V}{m}$$ (1)
98
99   where C_i and C_e are the initial and equilibrium concentrations of lead ions (mg/L) in solutions,
100   respectively. m is the weight of the sorbent (g), V is the volume of the aqueous phase (L).

2.4. Sorption Isotherms

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

2.4.1. Langmuir isotherm

105   The Langmuir isotherm is the most widely used model and traditionally used to quantify and
106   contrast the performance of different sorbents. This model's theory presumed monolayer coverage
107   of adsorbate over a homogeneous sorbent surface [9]. Langmuir model linearized equation is
108   expressed as follows:
109
110
$$\frac{C_e}{q_e} = \frac{1}{Q_0 b_L} + \frac{C_e}{Q_0}$$ (2)
111
112   where q_e is the amount of metal ions adsorbed onto adsorbent, C_e is the equilibrium
113   concentration of lead in solution, and Q_0 and b_L are Langmuir constants related to adsorption
114   capacity and adsorption energy, respectively.

2.4.2. Freundlich isotherm

116   The Freundlich model assumes a logarithmic decrease in the enthalpy of adsorption with the
117   increase in the fraction of occupied sites. In other words, this model is also an empirical expression
118   encompassing the surface heterogeneity and the exponential distribution of active sites and their
119   energies [10]. This model can be given as follows:
120
121
$$\log q_e = \log K_F + \frac{1}{n_F} \log C_e$$ (3)
122
123   where K_F represents the adsorption capacity (mg/g), n_F is a constant related to adsorption
124   intensity (dimensionless).

2.4.3. Dubinin-Radushkevich (D-R) isotherm

126   The other widely used isotherm is Dubinin–Radushkevich (D–R) model, used to estimate the
127   apparent free energy of adsorption, was proposed an equation to find out the adsorption mechanism
128   on the basis of the potential theory assuming a heterogeneous surface [11]. The linearized equation
129   of the D-R isotherm is given as:
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131
$$\ln C_{ads} = \ln X_m - \beta \varepsilon^2$$ (4)
132   where C_{ads} (mmol/g) is the amount of solute sorbed per unit weight of solid, X_m (mg/g) is the
133   adsorption capacity, β(mol/K) is a constant related to energy and ε is the Polanyi potential. Polanyi
134   potential can be computed by following equation:
135
136
$$\varepsilon = RT \ \ln\left(\frac{1}{1 + C_e}\right)$$ (5)
137
138   where R is a gas constant in kJ/mol K and T is the temperature in Kelvin. If $\ln C_{ads}$ is plotted
139   against ε^2, β and X_m can be obtained from the slope and intercept, respectively. The mean energy of
140   adsorption (E) is calculated by the following equation using the constant β.
141
$$E = \frac{1}{\sqrt{-2\beta}}$$ (6)

3. Results and Discussion

3.1. Characterization of the biocomposite

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 insize (diameter~2 mm) which reduced with drying (~0,5 mm). However, the specific characteristic of the alginate beads is to swell repeatedly to the previous size in the liquid media.
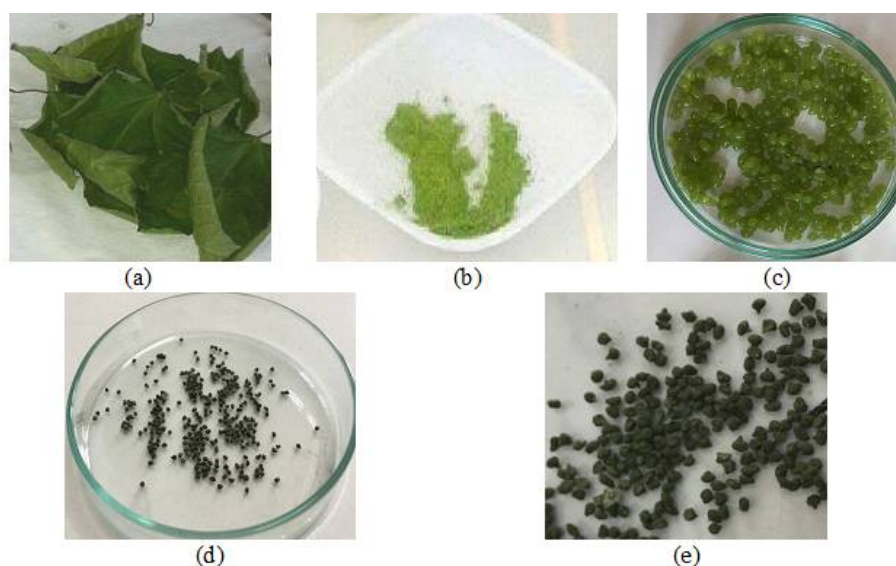

Figure 1. Dried (a) and powdered fig leaves (b), the as-prepared and dried (c, d, e) biocomposite.

3.1.1. FT-IR Analysis

F. carica-zeolite-alginate biocomposite was analyzed using a Fourier transform infrared spectrometer as shown in Figure 2. The absorption peak at 3375 cm-1and 3245 cm-1indicated the presence of both free and hydrogen-bonded -OH groups on the surface of the biocomposite. The other peaks observed at 1602, 1077, and 940 cm-1 may be due to C-C, C-O, and C-N stretching, respectively [12]. The peak at 821 cm-1 indicates the presence of -OH bending due to β-glycosidic linkage. The appearance of smaller peaks at 1314 and 1008 cm^{-1} may be attributed to -CH and to aromatic CH2 bending which originates probably from the lignin content of the fig leaves [13,14]. The hydrogel displays absorbance peaks of COOH at 1429 cm-1 [15]. The peaks located at 1112 and 1147 cm^{-1} can be assigned to stretching vibration of C-O-C bond of carbohydrate as polysaccharide which is attributed to the alginic acid [16]. It was supposed that immobilization of zeolite and fig leaves into the alginate beads reduced the binding efficiency of the active sites of alginate, which was resulted in the physical adsorption of lead in this study.
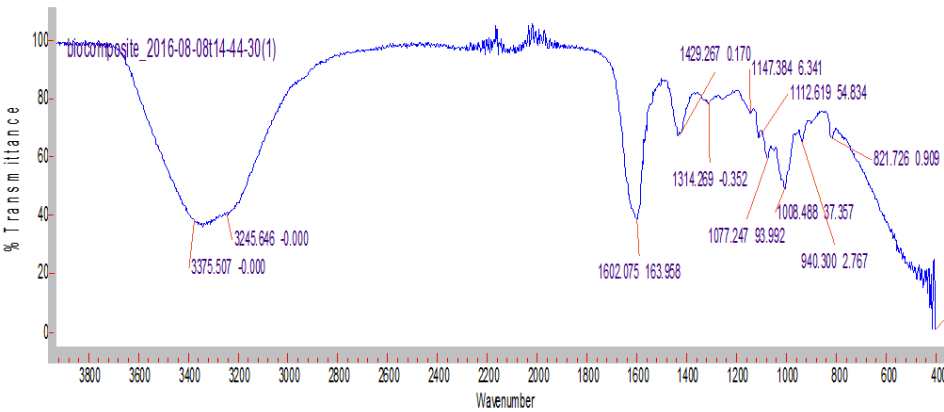
Figure 2. The Fourier Transform Infrared Spectroscopy spectra of biocomposite.

3.1.2. SEM Analysis

The microscopic images obtained by a scanning electron microscope clearly depicted the surface topography and internal architecture of the sorbent (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 simultaneous physical and chemical cross-linking in the biocomposite structure which was supported by FTIR findings and presumably affected the adsorption process.
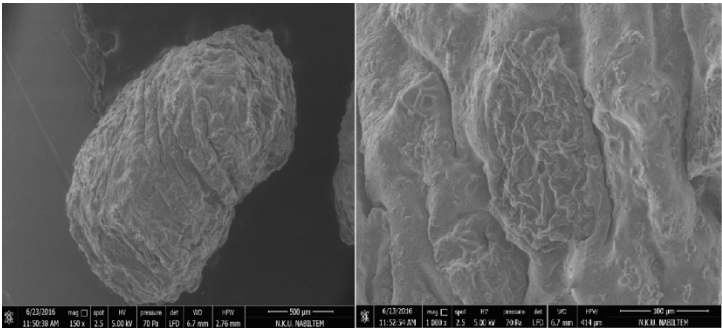

Figure 3. SEM micrographs of the prepared biocomposite.

3.2. Studies on optimum removal conditions

In order to compare the efficiency of the prepared biocomposite, the adsorption of lead ions were performed using separately F. carica L leaves powder, zeolite and alginate. The batch adsorption experiments were investigated under the conditions of 0.1 g of sorbent, 25 mL and 100mg/L of lead solution at pH 4, 25°C for 2 h at 200 rpm agitation speed. The obtained results show that adsorption capacities of F. carica L leaves powder, zeolite and alginate were 24%, 18% and 12%, respectively. However, at the same conditions maximum uptake of lead ions by the biocomposite was 40%.

3.2.1. 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 adsorption of Pb(II) ions onto biocomposite, the batch adsorption studies at different pH values were carried out. Experiments were investigated under the conditions

191 of 0.1g of sorbent, 25 mL and 10 mg/L of lead solution at 25 °C for 2h at 200 rpm agitation speed.
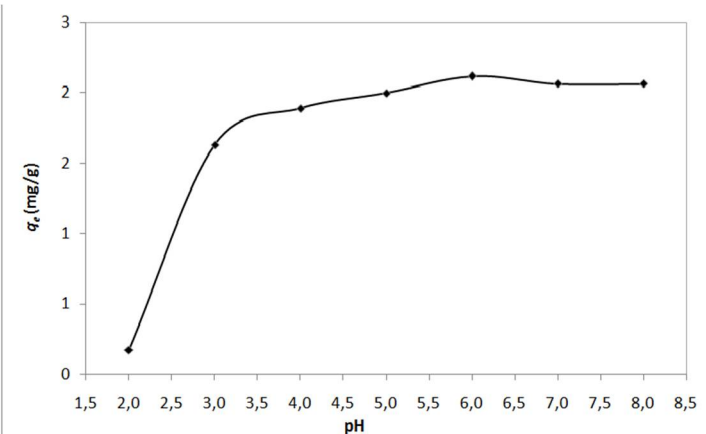192 Figure 4 shows that lead removal changes in a pH range of 2–8.

193

194   **Figure 4.** The adsorbed lead efficiency as a function of pH.

195   As can be seen from the Figure 4, the maximum adsorption of Pb(II) ions on the sorbent was
196 observed at pH 6.00 with 85%.After this pH a slight decrease in the adsorption process was
197 determined. At low pH, competition for metal binding sites between metal ions and hydrogen (H+)
198 ions has been established so that Pb removal showed a lower metal uptake due to the predominance
199 of hydrogen ions [17]. As the pH increases, this competitive effect is minimized and the sorbent
200 surface became deprotonated and negatively charged, which resulted in increasing binding of Pb.
201 Based on these facts, it can be admitted that the optimum pH value for Pb adsorption by
202 biocomposite was at pH 6 (Figure 4). Thus, the further experiments were performed at this pH.

203 3.2.2. The effect of initial Pb(II) concentration

204   The adsorption of Pb(II) was studied as a function of initial Pb(II)concentration. Adsorption
205 efficiencies of the biocomposite as a function of the initial concentration of lead between 5 and 200
206 mg/L were presented in Figure 5. The adsorption experiments were carried out under the conditions
207 of pH 6.0, 0.1 g of sorbent, 25 mL of lead solution, 25 °C temperature,2 h of contact time at 200 rpm
208 agitation speed.

209

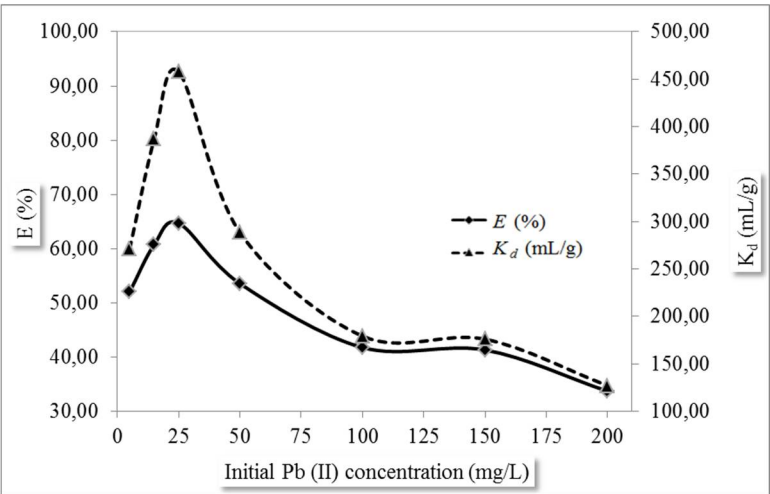210   **Figure 5.** The adsorbed lead efficiency as a function of initial Pb(II) concentration.

211   As seen in Figure 5, the Pb(II) sorption increased from 52.0 to 64.7% with an increase of the
212 initial lead concentration in solution from 5 to 25 mg/L and then decreased to 33.70% at200mg/L of
213 lead concentration. As noticed the adsorption efficiency decreases by increasing Pb(II) concentration

214 in solution. The biocomposite has a maximum lead sorption at 25mg/L initial lead concentration.
215 With the increase of metal ion concentration, the binding sites on the surface of the biosorbent
216 become saturated [18] and, hence, are no longer capable to remove Pb ions from media.

217 3.2.3. Effect of contact time

218 The contact time between the metal ions and biocomposite has great importance for designing
219 adsorption processes. The effect of contact time on the lead adsorption in the range of 30-720 min
220 was investigated with 25 mL and 100 mg/L of lead solution, 0.1 g of the sorbent at pH 6.0, 25 °C at
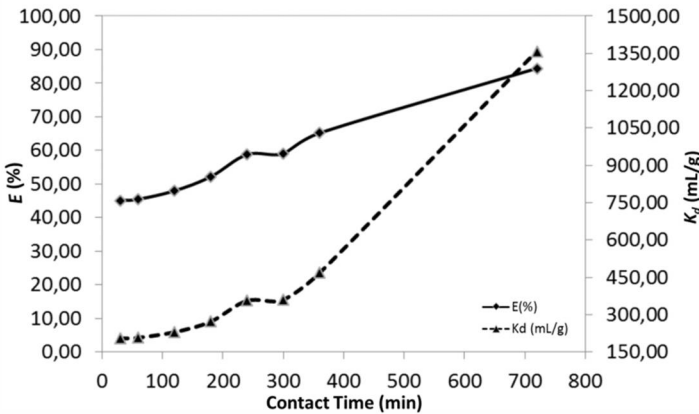221 200 rpm agitation speed. Figure 6 shows adsorbed lead efficiency as a function of contact time.

222

223 **Figure 6.** The adsorbed lead efficiency as a function of contact time.

224 As clearly seen from Figure 6, high removal percentage of lead is obtained even at the
225 beginning of the sorption. The adsorption efficiency increases rapidly over 65% at the first 360 min.
226 After 720 minutes, nearly 85% of lead ions have been removed from the solution. As the contact time
227 increased the active sites on the sorbent were filled.

228 3.2.4. Effect of temperature and thermodynamic studies

229 The effect of temperature on the adsorption of Pb(II) was studied varying 5 different
230 temperature from 288.15 to 328.15 K while the other parameters were kept constant (0.1g of
231 biocomposite in 25 mL and 50 mg/L of standard lead solution at pH 6.0 and 2 h of contact time at
232 200rpm agitation speed).The influence of different temperatures on adsorption of lead ions on the
233 biocomposite was examined and it was appeared to be temperature dependent over the temperature
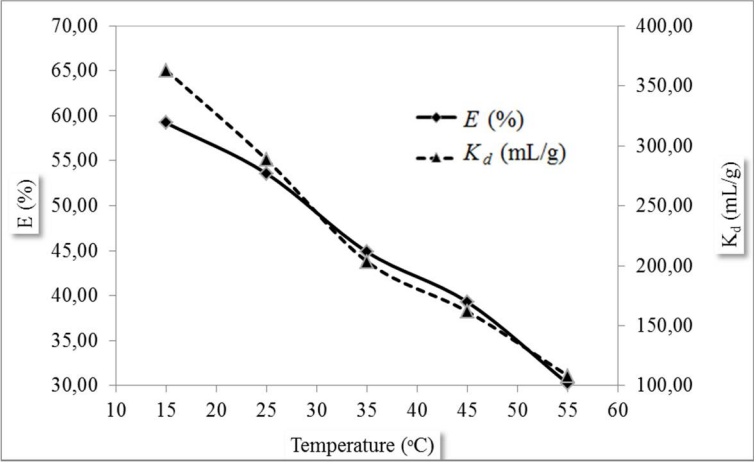234 range tested as shown in Figure 7. According to results, adsorption of lead ions was exothermic in
235 nature.

236

237   **Figure 7.** The adsorbed lead efficiency as a function of temperature.

238   Thermodynamic parameters (enthalpy, $\Delta H°$, entropy, $\Delta S°$, Gibbs energy change, $\Delta G°$) were
239   calculated by using the following equation:
240

241
$$lnK_{\mathrm{d}} = \left(\frac{\Delta S^{\mathrm{o}}_{\mathrm{ads}}}{R}\right) - \left(\frac{\Delta H^{\mathrm{o}}_{\mathrm{ads}}}{RT}\right) \qquad (7)$$

242   where K_{d} is distribution coefficient, R is the gas constant (8.314 J/molK), T is temperature in
243   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
244   1/T is created and the values of enthalpy and entropy were obtained from the slope and intercept of
245   the plot (Figure 8). The following well-known equation was used to calculate Gibbs free energy:
246

247
$$\Delta G = \Delta H - T\Delta S \qquad (8)$$
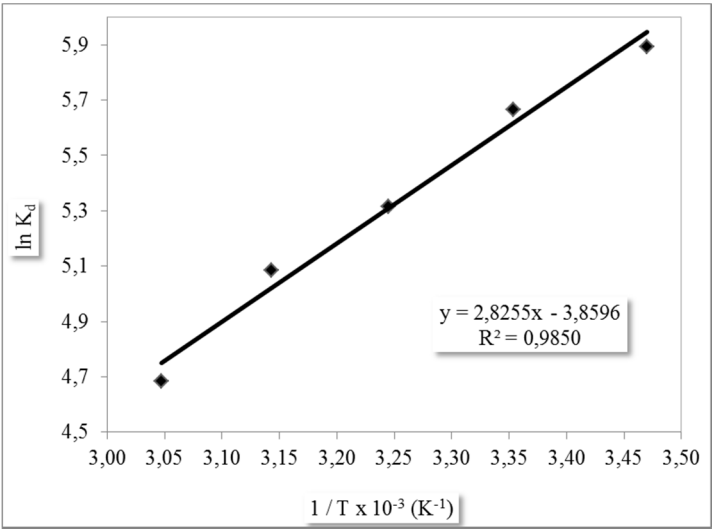
248

249

250   **Figure 8.** Influence of temperature on the thermodynamic behaviour of biosorption of Pb(II)on
251   biocomposite.

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

258   **Table 1.** Thermodynamic parameters for the adsorption of Pb(II).

$\Delta H°$	$\Delta S°$		$\Delta G°$ (kJ/mol)				
(kJ/mol)	(J/molK)	R²	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

259   *3.3. Adsorption Isotherms*

260   To acquire more insight into the adsorption of lead on to alginate-zeolite-F.carica L.
261   biocomposite, the results of equilibrium batch sorption experiments were evaluated with isotherm
262   models. The adsorption of lead on to biocomposite is a mass transfer operation that can be described
263   mathematically. The equilibrium is established between the concentration of the metal ions

264   dissolved in aqueous phase and that bound to the adsorbent [19, 20]. In order to analyze this process,
265   the experimental data have been subjected to different sorption isotherms namely Freundlich,
266   Langmuir and Dubinin–Radushkhevich models. Adsorption equilibrium in the concentration range
267   of 5–200 mg/L was studied with 100 mg of alginate-zeolite-F. carica L. biocomposite at 25°C, pH 6.0
268   and 120 min contact time. The constants and correlation coefficients (R2) of isotherm models have
269   been calculated from the plots for adsorption of lead on the biocomposite and the results are given in
270   Table 2.

271   **Table 2.** Constants of isotherm models for lead adsorption onto biocomposite.

Isotherm models	Parameters	
Langmuir	Q_0(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)	$2,97 \times 10^{-8}$
	E (kJ/mol)	4,10
	R^2	0.9817

272   3.3.1. Langmuir Isotherm

273   The equilibrium data for Pb(II) ions over the concentration range from 5 to 200 mg/L at 298.15 K
274   has been correlated with the Langmuir isotherm (Figure 9). Q_0 and b_L were calculated from the slope
275   and intercept of linear plots of Ce/qe versus Ce. Considering the comparative magnitudes of
276   correlation coefficients together with the isotherm constants suggests that the Langmuir isotherm
277   does not provide a particularly good model for the adsorption of lead. Thus, the behavior of lead
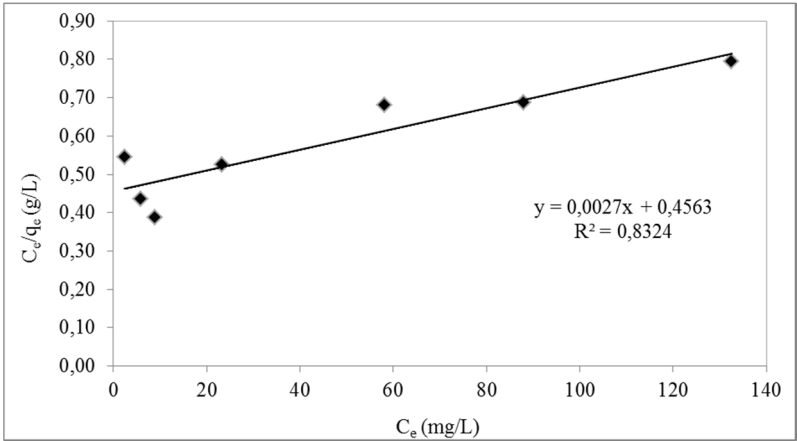278   adsorption onto biocomposite does not follow much to the Langmuir isotherm.

279

280   **Figure 9.** Linear isotherm model of Langmuir for lead biosorption on alginate-zeolite-Ficus carica L.
281   biocomposite.

282   3.3.2. Freundlich Isotherm

283   Linear plot of logqe versus logCe shows the applicability of Freundlich isotherm for lead
284   adsorption onto biocomposite (Figure 10). According to the correlation coefficients, the adsorption
285   process could be well described by Freundlich equation. The values of n are bigger than 1, reflecting
286   the beneficial adsorption. The numerical value of 1/n <1 indicates that sorption capacity is only
287   slightly suppressed at lower equilibrium concentration and suggests multiple binding sites, with the
288   highest strength sites binding the sorbate first. This isotherm predicts saturation of the sorbent by
289   the sorbate thus infinite surface coverage is predicted mathematically, indicating a multilayer
290   sorption of the surface [21]. The value of KF, which signify the sorption capacity, is calculated as 2.68
291   mg/g. Although the adsorption process can be described well by Freundlich equation according to
292   the correlation coefficient, the obtained result was observed to be incompatible with the measured
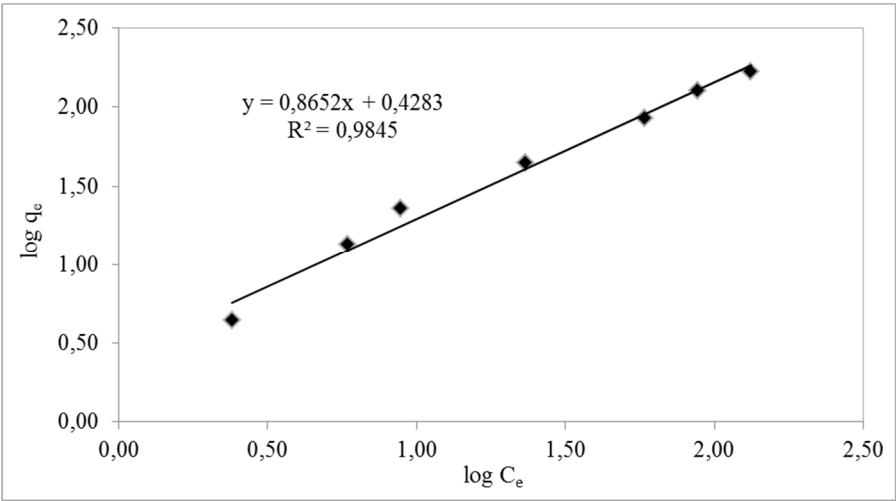293   adsorption capacity obtained by experiments.

294

295   **Figure 10.** Linear isotherm model of Freundlich for lead biosorption on alginate-zeolite-Ficus carica
296   L. biocomposite.

297   3.3.3. Dubinin-Radushkevich-Kaganer (DRK) isotherm

298   The plot of ln Cads against ε^2 is a straight line as shown in Figure 11. β and Xm can be obtained
299   from the slope and intercept, respectively. The calculated constants of Dubinin–Radushkevich
300   isotherm and mean free energies are given in Table 2. The adsorption capacity (Xm) of the D–R
301   model is 150.3 mg/g for lead ions. It is expected for this amount to be very close to the measured
302   adsorption capacity that was obtained by adsorption experiments. The magnitude of E is used to
303   estimate the reaction mechanism of adsorption process. If value of E is between 1 and 8 kJ/mol, it
304   indicates a physical adsorption. If value of E is higher than 8 kJ/mol, the adsorption process is of a
305   chemical nature. Hence, the value of E, 4.10 kJ/mol shows that the process is in the range of physical
306   adsorption.
307   Thus, the fact that the lead equilibrium data fits well within both Freundlich and DRK isotherm
308   models suggests that Pb adsorption onto biocomposite is of a heterogeneous nature. The
309   heterogeneous structure of the prepared biocomposite was also accomplished by SEM images.
310   Besides, the good fit of the DRK isotherm, with R^2 value greater than 0.9, suggests that this isotherm
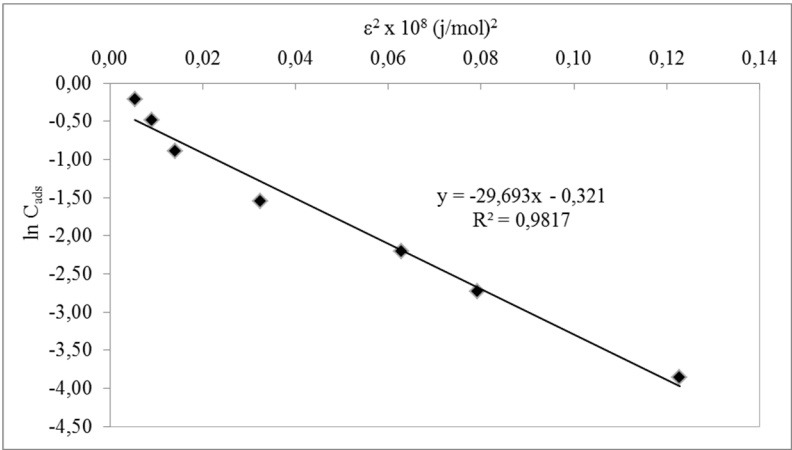311   could be more appropriate under industrial conditions [22].
312

313

314 **Figure 11.** Linear isotherm model of Dubinin–Radushkevich (D–R) for lead biosorption on
315 alginate-zeolite-Ficus carica L. biocomposite.

316 *3.4. Comparison of alginate-zeolite-F.carica L. biocomposite with other biosorbents*

317   Various studies have been performed on the adsorption of lead in literature for recent years. A
318 comparison of the lead metal uptake capacities of this study with those of other biosorbents reported
319 in the literature is given in Table 3. Although a direct comparison of the results of our study with
320 other reported biosorbents is difficult due to the varying experimental conditions employed in those
321 studies, in general, alginate-zeolite-F.carica L. biocomposite exhibited reasonable adsorption
322 capacity in comparison with those biosorbents.

323   **Table 3.** Comparison of lead uptake capacities (mg/g) of various biosorbents.

Biosorbent	Maximum uptake (mg/g)	References
Olive stone waste	9.30	[23]
Sulfured orange peel (MOP)	164.0	[24]
Cinnamomum camphora leaves	73.15	[25]
Modified lentil husk	81.43	[26]
Australian marine algae	322	[27]
Tea waste	65.0	[28]
Green algae	140.84	[29]
Alginate-zeolite-F. carica L. biocomposite	150.31	Present study

324

325   The last few decades, development of new low cost biosorbents that have metal binding
326 capacities and modification of the performance of existing ones has been intensified. Plants have
327 been known by their heavy metal accumulation properties and have recognized as bioindicators.
328 The study was performed under heavy metal accumulation level of F. carica bark and leaves [4]. The
329 removal efficiency of 31.02% was reached when raw F. carica leaves were used for the removal of
330 Co(II) and it was found that the treatment of the leaves with MgCl2 caused an increase in the
331 removal efficiency (57.15%) [18]. F. carica bastfiber was used for the adsorption of Cr(VI) and
332 maximum adsorption capacity was found as 19.68 mg/g [30]. Sharma et al. (2013) chemically
333 modified the F. carica bastfiber with acrylic acid and found 56% of adsorption of Cr(VI) for this
334 sorbent. Sasikala and Muthuraman (2015) used F. carica seeds for the adsorption of Cr(III) and found
335 the average percentage of adsorption as 94.6% that indicated the occurrence of a strong interaction
336 between the metal and adsorbent [31].

337   To the best of our knowledge, there is no study performed on the adsorption of lead ions on the
338   biocomposite containing F. carica L. leaf powder. The use of F. carica L. leaf powder in combination
339   with zeolite in the alginate beads lowers the amount of alginate necessary for adsorption, resulting
340   in lower cost. Moreover, the biodegradability of F. carica can contribute to a hale and hearty
341   ecosystem and their low cost and reasonable performance can fulfill the economic interest of various
342   industries.

4. Conclusions

344   Natural adsorbents are basically biodegradable that consists mainly of degradable organic
345   matter. The prepared biocomposite in this study was consisted of natural materials such as fig
346   leaves, alginate and zeolite. The adsorption process was lead ion concentration and pH dependent.
347   The maximum adsorption of Pb(II) ions on the biocomposite was observed 85% at pH 6.0 with
348   25mg/L initial Pb(II) concentration. This pH is appropriate for the treatment of wastewater where
349   Pb(II) concentration can be found in the diluted form. The negative value of enthalpy change ΔH
350   (-23.491kJ/mol K), shows that the adsorption of lead is exothermic process. The reaction is
351   spontaneous and more favorable at lower temperatures. The equilibrium data for biocomposite were
352   fitted well with the Freundlich and D-R isotherm models, suggesting that the multilayer adsorption
353   of Pb(II) ion occurred on the heterogeneous surface of the beads. Thetheoretical value of the sorption
354   capacity (X_m) is founded as 150.3 mg/g. The mean energy of adsorption calculated as 4.10 kJ/mol
355   shows that the process is in the range of physical adsorption. The results of present study have
356   suggested that the prepared biocomposite is suitable for the removal of Pb(II) ions from aqueous
357   solutions. The prepared biocomposite can be considered as a new approach to improve the quality of
358   the treated effluent and to clean up a polluted aqueous ecosystem.

359   **Author Contributions:** C. Gok and M. Kaygusuz conceived and designed the experiments; performed the
360   experiments; analyzed the data and wrote the paper. Both author checked the final paper.

364   **Conflicts of Interest:** The authors declare no conflict of interest.
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References

367   1.   Isaac R.A.; GilL.; CoopermanA.N.;HulmeK.; EddyB.; RuizM.; JacobsonK.; LarsonC.;PancorboO.C.
368   Corrosion in drinking water distribution systems: A major contributor of copper and lead to wastewaters
369   and effluents, Environ. Sci. Tech. 1997, 31: 3198–3203.
370   2.   Aslan A.; Üzüm (Işık) N.O. Determining the heavy metal contents of natural and artificial upholstery
371   leathers, Tekstil ve Konfeksiyon 2015, 25 (1): 33-37.
372   3.   Mondal M.K. Removal of Pb(II) ions from aqueous solution using activated tea waste: Adsorption on a
373   fixed-bed column, J. Environ. Manag. 2009, 90 (11): 3266-3271.
374   4.   Ugurlu I.; Unver M.C.; DoganY. Determination and comparison of heavy metal accumulation level of
375   Ficus carica bark and leaf samples in Artvin, Turkey, Oxid. Commun. 2016, 39: 765–775.
376   5.   Aksoy U.; Can H.Z.; Hepaksoy S.; SahinN. Incir yetistiriciligi (Fig farming), Turkiye Tarımsal Arastırma
377   Projesi Yayinlari 2001, Izmir, Turkey. (in Turkish).
378   6.   Chmielewská E.; Sabová L.; Peterlik H.; Wu A. Batch-wise adsorption, SAXS and microscopic studies of
379   zeolite pelletized with biopolymeric alginate, Brazilian J. Chem. Eng. 2011, 28 (01): 63-71.
380   7.   Sarioglu M., Removal of ammonium from municipal wastewater using natural Turkish (Dogantepe)
381   zeolite, Separ.P urif. Technol. 2005, 41 , 1-11.
382   8.   Navarro A.E.; Musaev H.; Serrano K.; Masud M.E. Adsorption kinetics of cobalt (II) ions onto alginate
383   beads from aqueous solutions, J Earth SciClim Change 2014, 5(8): 223-228.
384   9.   Langmuir I. The Adsorption of gases on plane surfaces of glass, mica and platinum. J. Amer. Chem. Soc.
385   1918, 40 (9): 1361–1403.
386   10.   Freundlich H.(1906) Adsorption in solution, Zeitschrift Für Physikalische Chemie, 57: 384–410.

387 11. Dubinin M.M.; Zaverina E.D.; Radushkevich L.V. Sorption and structure of active carbons I. adsorption of
388   organic vapors, Zhurnal Fizicheskoi Khimii 1947, 21: 1351–62.

389 12. Boufi S.; Alila S. Modified cellulose fiber as a biosorbent for the organic pollutants. In: Kalia S, Averous L
390   (eds) Biopolymers: biomedical and environmental applications, 1st edn. Wiley, New Jersey, USA, 2011 ,
391   pp.483–524.

392 13. Sharma S.; Pathania D.; Singh P. Preparation, characterization and Cr(VI) adsorption behaviour study of
393   poly(acrylic acid) grafted Ficus carica bastfiber, Adv. Mat.Lett. 2013, 4(4): 271-276.

394 14. Hu J. Biosynthesis of SnO2 Nanoparticles by fig (*Ficus carica*) leaf extract for electrochemically determining
395   Hg(II) in water samples, Int. J. Electrochem. Sci 2015., 10: 10668 - 10676.

396 15. Bayomi M.; Choi Y.S.; Christodoulides K.; Fathi P.; Ghodasara A.; Knazik J.et al Zeolite-loaded
397   alginate-chitosan hydrogel beads as a topical hemostat, University of Maryland, College Park, MD , 2015,
398   20742-7011 (301): 314-1328.

399 16. Jena J.; Pradhan N.; Dash B.P.; Sukla L.B.; Panda P.K. Biosynthesis and characterization of silver
400   nanoparticles using microalga Chlorococcum humicola and its antibacterial activity, Int. J.Nanomat.
401   Biostructures 2013, 3(1): 1-8.

402 17. Kosa S.A.; Al-Zhrani G.; Salam M.A. Removal of heavy metals from aqueous solutions by multi-walled
403   carbon nanotubes modified with 8-hydroxyquinoline, Chem. Eng. J. 2012, 181-182: 159-168.

404 18. Dabbagh R.; Moghaddam Z.A.; Ghafourian H. Removal of cobalt(II) ion from water by adsorption using
405   intact and modified Ficus carica leaves as low-cost natural sorbent, Desalin. Water Treat. 2016, 57(42):
406   19890-19902.

407 19. Gok C. Neodymium and samarium recovery by magnetic nano-hydroxyapatite, J. Radioanal. Nucl. Chem.
408   2014, 301 (3): 641–51.

409 20. Bayramoglu G. Biosorption of heavy metal ions on immobilized white-rot fungus trametesversicolor, J.
410   Haz. Mat. 2003, 101 (3): 285–300.

411 21. Aytas S.; Yurtlu M.; Donat R. Adsorption characteristic of U(VI) ion onto thermally activated bentonite, J.
412   Haz. Mat. 2009, 172(2-3): 667–74.

413 22. Alfaro-Cuevas-Villanueva R.; Hidalgo-Vázquez A.R.; Cortés Penagos C.J.; Cortés-Martínez R.
414   Thermodynamic, Kinetic, and Equilibrium Parameters for the Removal of Lead and Cadmium from
415   Aqueous Solutions with Calcium Alginate Beads, The Scientific World Journal 2014, 2014:1-9.

416 23. Fiol N.; VillaescusaI.; Mart´ınez M.; Miralles N.; Poch J.; Serarols J. Sorption of Pb(II), Ni(II), Cu(II) and
417   Cd(II) from aqueous solution by olive stone waste, Sep. Purif. Tech. 2006, 50: 132–140.

418 24. Liang S.; Guo X.; Tian Q. Adsorption of Pb2+ and Zn2+ from aqueous solutions by sulfured orange peel,
419   Desalination 2011, 275: 212–216.

420 25. Chen H.; Zhao J.; Dai G.; Wu J.; Yan H. Adsorption characteristics of Pb(II) from aqueous solution onto a
421   natural biosorbent, fallen Cinnamomum camphora leaves, Desalination 2010, 262: 174–182.

422 26. Basu M.; Guha A.K.; Ray L. Biosorptive removal of lead by lentil husk, J. Environ. Chem. Eng. 2015, 3 (2):
423   1088–1095.

424 27.] Matheickal J.T.; Yu Q. Biosorption of lead(II) and copper(II) from aqueous solutions by pre-treated
425   biomass of Australian marine algae, Biores. Tech. 1999, 69: 223-229.

426 28. Amarasinghe B.M.W.P.K.; Williams R.A. Tea waste as a low-cost adsorbent for the removal of Cu and Pb
427   from wastewater. Chem. Engin. J. 2007, 132: 299–309.

428 29. Gupta V.K.; Rastogi A. Biosorption of lead from aqueous solutions by green algae Spirogyra species:
429   Kinetics and equilibrium studies, J. Haz. Mat. 2008, 152: 407–414.

430 30. Gupta V.K.; Pathania D.; Agarwal S.; Sharma S. Removal of Cr(VI) onto Ficus carica biosorbent from
431   water, Environ. Sci. Pollut. Res. 2013, 20: 2632–2644.

432 31. Sasikala S.; Muthuraman G. Studies on adsorption of chromium (VI) onto Ficus carica seed from
433   wastewater, Int. J. Recent Sci. Res. 2015, 6(3): 3100-3108.

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