Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2022.29021

278 (2022) 117–128
December

Nonlinear modelisation of Cd(II) and Pb(II) removal from aqueous solution by *Helichrysum arenarium*

Paweł Staroń*, Jarosław Chwastowski

Department of Engineering and Chemical Technology, Cracow University of Technology, 24 Warszawska St., 31-155 Cracow, Poland, Tel.: +48 12 628 20 92; Fax: +48 12 628 20 36; email: pawel.staron@pk.edu.pl (P. Staroń) http://orcid.org/0000-0003-0814-4116, Tel.: +48 12 628 21 17; email: jaroslaw.chwastowski@pk.edu.pl (J. Chwastowski)

Received 28 June 2022; Accepted 10 October 2022

ABSTRACT

The aim of the work was to establish the possibility of using dwarf everlast (*Helichrysum arenarium*) as a natural sorbent for the removal of cadmium and lead ions. The research carried out allowed to select nonlinear equilibrium and kinetic models. Additionally conducted experiments enabled to perform tests for metal ions recovery from the surface of the sorbent. The material had a sorption capacity equal to 80.1 mg/g for lead ions and 23.3 mg/g for cadmium ions. The Freundlich isotherm model has the best fit for the lead ion sorption, while cadmium sorption is best described by the Temkin, Freundlich and Langmuir isotherm models. The kinetic experiments showed that process is of chemical nature and that the course of sorption is in accordance with the Elovich model for both chosen elements. Desorption studies confirmed the possibility of recovery of cadmium and lead ions at a level of ~76% and ~85% using acetic acid, respectively.

Keywords: Kinetic; Sorption; Cadmium; Lead; Equilibrium; Adsorption

---

1. Introduction

The development of industry worldwide has negative consequences in the form of increased discharges of industrial waste (including those containing heavy metals) into rivers, lakes or other natural water reservoirs, from which it can then flow into underground waters or other drinking water resources. Unfortunately, water pollution, especially by heavy metals such as lead, cadmium, zinc, copper, nickel or chromium, is a serious and continuing problem. The struggle against environmental pollution by heavy metals is still ongoing at many levels, due to their high sustainability and their ability to accumulate in the environment and living organisms. The threat of heavy metals is associated with their effects on living organisms, including damage to the nervous system and internal organs, and the capability of causing cancer [1–5].

Cadmium is a naturally occurring heavy metal that appears at low concentrations. It is widespread in rocks, soil, water, plants and animals. Cadmium does not perform any significant biological function, but can be toxic to humans, animals, plants and soil in elevated quantities. Excessive human and animal intake of cadmium can cause many diseases, including renal tubular dysfunction and bone damage. Elevated amounts of cadmium in the soil may contribute to its permeation to the plants. Additionally, there is a possibility that with the rainfall it will penetrate surface waters and groundwater, polluting them [6].

Lead is a waste with extremely high negative effects on humans, plants and animals. The risk of exposure to lead is related to the fact that it is a substitute for calcium in bone tissues and it accumulates there. In humans, in smaller quantities, it causes vomiting, malaise, while in larger quantities it can cause anorexia, mental problems, damage to the spine, anaemia, and finally death. One of the ways

---

* Corresponding author.

1944-3994/1944-3986

lead penetrates into living organisms is drinking water consumption, which is why it is so important to control its condition and seek methods to remove this metal from sewage and industrial waste water in order to reduce the risk of lead penetration into drinking water [7].

There are many methods of removing heavy metals from water and wastewater, however, many researchers have pointed out sorption processes that are based on bonding metals to various natural and synthetic materials. One of the types of sorption is the biosorption process, that is, the use of material of biological origin as a sorbent. Biosorption is a fast and reversible reaction of heavy metals with biomass. Waste from the production of biomaterials is used as biosorbent. Widely used biomass is made of waste from the wood industry or waste from agricultural production. Additionally, dead and live biomass is used as biosorbents. Coconut fibre, peat or wool are used as a dead biomass, whereas live parts of plants and various types of microorganisms are used as living ones. Microorganisms such as bacteria, fungi and algae have been studied and successfully used as biosorbents to remove many pollutants from wastewater [5]. The process of biosorption consists of many mechanisms such as ion exchange, precipitation, sorption by physical forces, chelation, capillary concentration in internal and pillar capillaries and structural spaces of lignin and polysaccharide networks [8,9].

The aim of the study was to check the possibility of using the flower of the dwarf everlast (*Helichrysum arenarium*) as a biosorbent in the sorption process of cadmium and lead ions. The dwarf everlast belongs to the Asteraceae family. This species is widespread in Europe, especially in the countries of Central and Eastern Europe and are known in traditional medicine in the treatment of various pathologies. Flowers of the sand insects contain many compounds, such as flavonoids, which belong to the group of polyphenolic compounds, as well as hydrophobic compounds (chlorophyll, essential oils and tannins) [10]. The sorption process was carried out in a dynamic system. Obtained test results allowed to determine the maximum sorption capacity in relation to the ions tested and the mechanism of sorption process was determined using nonlinear equilibrium and kinetic models. The novelty of the work is connected with using a cheap and widespread biosorbent for removal of the heavy metals including lead and cadmium. Use of the novel sorbent as an alternative material for the removal of metal ions has been studied. The characterization of dwarf everlast before and after the sorption process have been determined by scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR) analysis.

2. Materials and methods

The study used dried flowers of the dwarf everlast (*Helichrysum arenarium*), purchased on the commercial market. Fig. 1 shows a photo of the tested material.

The preparation has been properly prepared prior to the actual work. For this purpose, the plant material was crushed in a grinder to homogenize, then washed several times with deionized water and dried at 60°C for 24 h. Next, the research material was transferred and stored in an airtight container.

All reagents involved in the study were characterized by high purity and came from Sigma-Aldrich. All solutions were prepared using deionized water.

2.1. Sorption process

The process of sorption of heavy metal ions was conducted in a dynamic bed system. To 50 cm^3 containers, 0.2 g of the tested material was weighed with the accuracy of 0.0001 g, then 40 cm^3 of the solution of individual element were added and mixed at a constant rate at room temperature for 60 min. After the process, the mixture was filtered. The filtrate was analyzed on atomic absorption spectrometer in acetylene-air flame (F-AAS). The amount of absorbed metals on the adsorbent investigated was calculated from Eq. (1):

$$q_t = \frac{\left(C_0 - C_t\right)V}{m} \tag{1}$$

where q_t – sorption capacity at given time (mg/g), C_0 – initial concentration (mg/dm^3), C_t – metal concentration in solution after time t (mg/dm^3), V – solution volume (dm^3), m – mass of the material (g).

In order to select the metal ions and the highest affinity to the sorbent, a series of tests were carried out. Model solutions of ions Pb(II), Cd(II), Co(II), Ni(II), Cr(VI), Zn(II) and Cu(II) with a concentration of 500 mg/dm^3 were used.

The obtained results are shown in Fig. 2.

From the graph showed above, one can see that lead ions have the highest affinity for the dwarf everlast flower. The sorption capacity for the remaining metals is significantly lower and is arranged in the following order: $Ni^{2+} < Co^{2+} < Cu^{2+} < Cr^{6+} < Zn^{2+} < Cd^{2+} < Pb^{2+}$. In the further part of the work, only lead and cadmium ions were studied.

2.2. Sorption studies

Lead sorption tests were performed at concentrations: 500; 750; 1,000; 1,250 and 1,500 mg/dm^3. In order to carry out the sorption of metal ions, 0.2 g of the material was weighed with an accuracy of 0.0001 g into containers of 50 cm^3 capacity. 40 cm^3 of starting solutions of various concentrations were added to the material and stirred at room

Fig. 1. Dried flowers of dwarf everlast (*Helichrysum arenarium*).

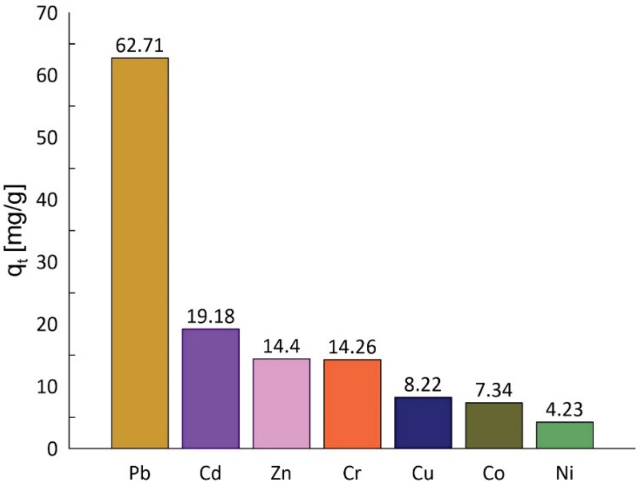

Fig. 2. Sorption capacity of *Helichrysum arenarium* for used metal ions.

temperature for a specified time. Then the mixture was separated and lead content in the filter on atomic absorption spectrometer (F-AAS) was determined. The contact times were: 0.5, 1, 3, 5, 8, 15, 30 and 60 min.

Analogously, cadmium adsorption tests were carried out from the solutions with concentrations: 300, 400, 500, 600 and 700 mg/dm^3.

Parameters of all conducted equilibrium and kinetic processes were:

- pH 4.5 for all used metal ion solutions,
- temperature was equal to 25°C.

2.3. Desorption

The desorption process is carried out in order to determine the possibility of regenerating the sorbent for its. Desorption also creates opportunities to recover lost metals in the production process.

Approximately 2 g of *Helichrysum arenarium* were weighed into the beaker and 400 cm^3 of solution containing 1,500 mg/dm^3 of lead was added and stirred for 60 min on a stirrer. The contents of the vessel were then separated on a filter. The filtrate was analysed for the presence of Pb(II) ions. Filtered sorbent was placed in a dryer and dried at 60°C for 24 h.

In the next stage, to 0.2 g of dried material containing metal ions, 40 cm^3 of desorbent was added and stirred for 60 min. Acetic acid – 0.1 mol/dm^3, sodium chloride – 0.1 mol/dm^3 and deionized water were used as eluents.

After the desorption process, the sorbent was separated from the solution by filtration. Eluates were tested for Pb(II) ions.

Cadmium desorption was examined in the same way. In this case the initial solution of Cd(II) had a concentration of 700 mg/dm^3.

Parameters of desorption have been carried out in the same manner as equilibrium/kinetic experiments (pH = 4.5, $T = 25°\text{C}$).

2.4. Statistical analysis of the fitted models

The estimation of parameters in equilibrium and kinetic models was made using the nonlinear regression method. Statistical analysis was performed in STATISTICA Statsoft® software (the 12th version). The determination coefficient (R^2) and the average relative error (ARE) were used to compare quality of the results [11,12]

$$R^2 = 1 - \frac{\sum_1^n \left(q_{\text{exp}} - q_{\text{pred}}\right)^2}{\sum_1^n \left(q_{\text{exp}} - \overline{q_{\text{exp}}}\right)^2} \tag{2}$$

$$\text{ARE} = \frac{100}{n} \sum_1^n \frac{\left|q_{\text{exp}} - q_{\text{pred}}\right|}{q_{\text{exp}}} \tag{3}$$

where n – number of experimental points, q_{exp} – experimental sorption capacity (mg/g), q_{pred} – predicted sorption capacity (mg/g), $\overline{q_{\text{exp}}}$ – the mean of experimental sorption capacity (mg/g).

2.5. Equilibrium studies

In general, the process of adsorption does not take place over the entire surface of the adsorbent, but in some places, called active centres. One or more layers of adsorbate molecules may form on the surface of the sorbent. This phenomenon continues until a state of thermodynamic equilibrium is established, which is described by the sorption isotherms. There are many models describing the adsorption equilibrium, but generally two are used: Langmuir, Freundlich. Temkin's and Dubinin–Radushkevich (D–R) models are also often used to determine the balance. It is particularly important to assign experimental data to a specific model of adsorption isotherms when conducting sorption studies. The interpretation of the obtained results enables to learn about the mechanism of the process and interactions between adsorbate and adsorbent. Table 1 shows the equations of applied equilibrium models.

2.6. Kinetic studies

The optimal time for adsorption is determined by the process kinetics. Based on the results obtained, it is possible to assess the sorption capacity of the tested material, as well as to learn its mechanism. Two kinetic models are most popular in adsorption processes: a pseudo-first-order model, also called Lagergren's model, and a pseudo-second-order model, invented by Ho [17]. In addition, the Elovich and Weber Morris models can also be used. These equations take into account the sorption capacity of adsorbents and are presented in Table 2. From the graphs, it is possible to determine the row of responses, the rate constant and the most appropriate response time. The most effective removal of metals from the solution occurs at the moment of establishing the balance of the adsorption process.

Table 1
Nonlinear equilibrium model equations

Isotherm models	Equations	References	Equations
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	[13]	(4)
Freundlich	$q_e = K_F C_e^{1/n}$	[14]	(5)
Temkin	$q_e = B \ln K_T C_e$	[15]	(6)
Dubinin–Radushkevich	$q_e = q_d \exp\left(-K_{\text{ad}} \varepsilon^2\right)$ $\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right)$	[16]	(7) (8)

Table 2
Nonlinear kinetic equations

Kinetic models	Equations	References	Equations
Pseudo-first-order	$q_t = q_1\left(1 - \exp\left(-k_1 t\right)\right)$	[18]	(9)
Pseudo-second-order	$q_t = \frac{t}{\left(1/k_2 q_2^2\right) + \left(t/q_2\right)}$	[19]	(10)
Elovich	$q_t = \frac{1}{\beta} \ln\left(1 + \alpha\beta t\right)$	[20]	(11)
Weber–Morris	$q_t = K_{\text{id}} \sqrt{t} + I$	[21]	(12)

3. Result and discussion

The surface of the dwarf everlast before and after the sorption process was examined using a scanning electron microscope (Hitachi TM-3000 equipped with an X-ray microanalyzer EDS) energy-dispersive X-ray spectroscopy. The obtained SEM-EDS micrographs are shown in Fig. 3A–C.

In the microphotography, fragments of material of different sizes are visible, which are characterized by high heterogeneity and high diversity of particles. Comparing the images before and after the sorption process, one can see that the structure of the material is deformed. The differences also occur in the elemental composition before and after the sorption process (Fig. 3D–F). The main elements present on the surface of the blanket are oxygen, carbon, potassium and calcium, which indicates the biological origin of the material. After the sorption process, the presence of cadmium (Fig. 3E) and lead (Fig. 3F) was additionally observed on the surface of the blanket, which indicates the process of bonding of these elements on the surface of the studied material.

The surface of the sand blanket was also examined using FTIR infrared spectroscopy on Nicolet iS5 with ATR iD7 from Thermo Scientific (Fig. 4). The analysis showed a difference in the chemical structure, the nature of the bonds and the interactions between the materials. Differences are observed in the frequencies and intensity of the bands, especially for material before sorption and material after Pb sorption. The most intense broad band in the range 2,960–3,500 cm^{-1} corresponds to the stretching vibrations of the hydroxyl groups –OH [22], 3,020 cm^{-1} corresponds to the C–H stretching region [23], peaks near 2,970 cm^{-1} are assigned to bending vibrations N–H [24], in the range 2,920–2,851 cm^{-1} asymmetrical vibrations CH_2 and tensile vibrations of groups C–H occur [25], peak at 2,361 and 2,150 cm^{-1} represents CO_2 and CO, which are present in the environment [26,27], tensile vibrations of carbonyl (–C=O) occur at 1,734 cm^{-1} [28], aliphatic C–H stretching in methyl and phenol alcohols are present at 1,366 cm^{-1} [29], for C–N binding of aliphatic amine compounds the area of 1,218–1,020 cm^{-1} is responsible, the strong band at 1,038–1,026 cm^{-1} corresponds to C–O stretching caused by glycosidic bonding, OH groups in sugars or C–O–C stretching vibrations in lignin or hemicellulose, δ C–H bonding of aromatic ring, S=O stretching, moreover, the relative intensity of the 1,033 cm^{-1} band increases markedly after the adsorption process [30–32], the vibrations in the N–H position are present in the band 895–655 cm^{-1}, within the band 600–400 cm^{-1} there are vibrations from CNC deformation [33].

3.1. Effect of time and initial concentration on metal ion sorption

To determine the time after which the sorption process reaches equilibrium, its effect on the sorption capacity of metals is examined. Initially, a rapid increase in ion concentration is observed on the surface of the sorbent. Over

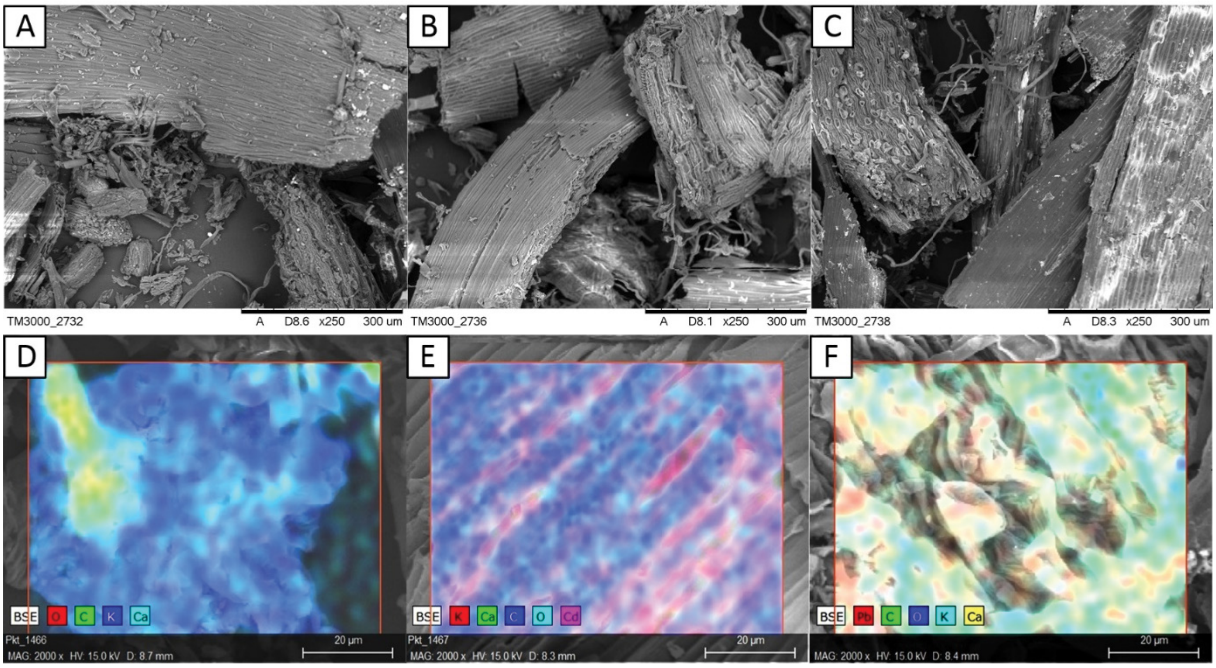

Fig. 3. Microphotography of a dwarf everlast 250×: (A) before sorption, (B) after sorption Cd, (C) after sorption Pb, SEM-EDS: (D) before sorption, (E) after sorption Cd, and (F) after sorption Pb.

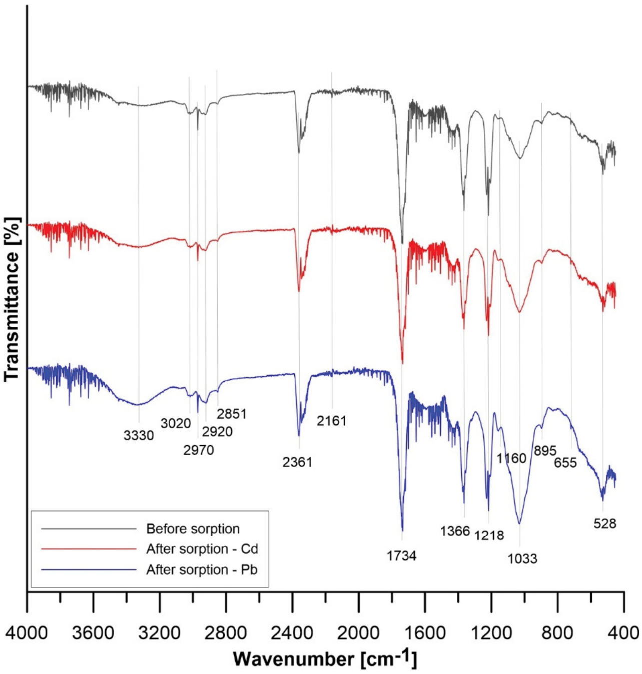

Fig. 4. Results of FTIR analysis for *Helichrysum arenarium* before and after sorption process.

time, the process slows down until constant values are obtained. From the results obtained it was established that the equilibrium state is reached after 60 min for both elements (Fig. 5). The highest instantaneous increase in sorption capacity is observed in the first 5 min of the process.

For a better understanding of the results, three-dimensional surface diagrams were made for graphical interpretation of the relationship between process variables (the experimental data were analysed using 12th version of STATISTICA Statsoft® software). It was confirmed that in the initial stage rapid sorption of both ions on the surface of the dwarf everlast was achieved due to the higher number of active sites available on the surface. A further increase in process time slowly increased the sorption capacity until equilibrium was achieved. The highest value of sorption capacity was indicated in red. The obtained three-dimensional graph is characterized by an elliptical shape, which indicates a significant interaction between the two factors. Additionally, it can be observed that the sorption curves of lead ions are characterized by a more vertical course than that of cadmium ions, which indicates a higher process speed in the first stage of sorption. The difference in the speed of the sorption process is related to an increase in the mass transfer force above the mass transfer resistance of the ions between the surface of the dwarf everlast and the metal ions, which results from the difference in the initial concentration between the metal ions (lead ions were 1.66–2.14 times higher than cadmium ions). The higher content of ions additionally increases the number of collisions between them and the active sites on the surface of the studied material, which is confirmed by a higher sorption rate for lead ions and an increase in sorption capacity of the sorbent in relation to the studied ions is observed together with an increase in the initial concentration [34]. Above 5 min a decrease in the sorption process is observed as a result of a decrease in the number of free active sites on the sorbent surface and, as a consequence, the equilibrium between metal ions and sorbent is established. In Fig. 5 showing the degree of removal of

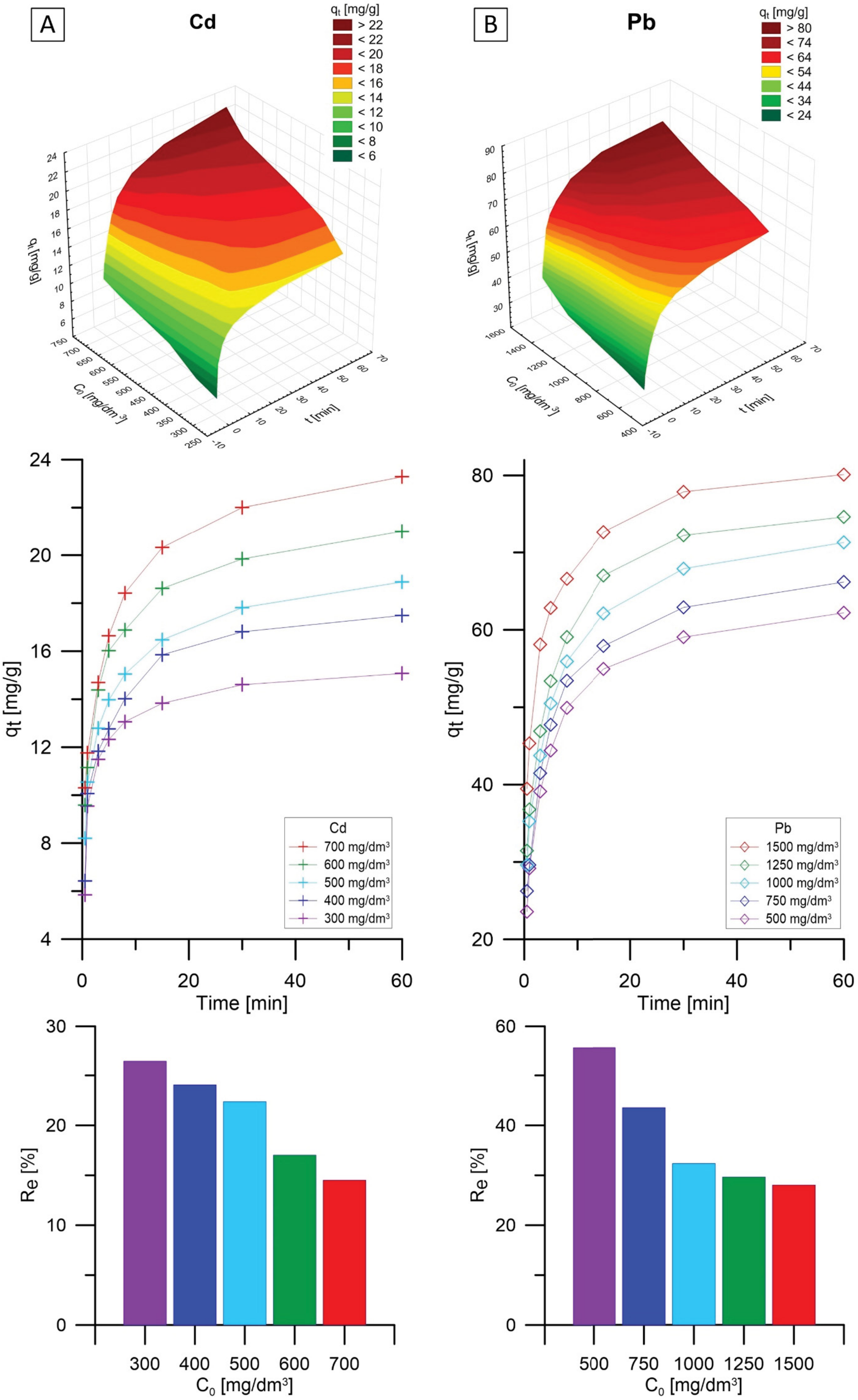

Fig. 5. 3-D surface plots of sorption capacity, time and ions concentration, sorption capacity in time depending on the initial concentration and the degree of metal removal from model solutions: (A) cadmium and (B) lead (pH = 4.5; $T = 25°C$).

metal ions Re, it can be seen that the degree of removal of metal ions decreases with increasing initial concentration. This is due to the number of active sites on the sorbent surface in relation to the total amount of ions in the solutions. The resulting number of collisions affects the degrees of removal, for cadmium ions we observe the highest difference between concentrations 500 and 600 mg/dm^3 (5.4 p.p.), for lead ions the difference between 500 and 750 mg/dm^3 is 12 p.p. a 750–1,000 mg/dm^3 11.2 p.p. For the remaining concentrations, a reduction in Re is observed below 3 p.p. on average. Maximum sorption capacities for Cd ions was equal to 23.3 mg/g and Pb ions equal to 80.1 mg/g. In literature one can find information about sorption capacities of other natural biosorbents against Cd ions like bamboo shoot (7.03 mg/g) [35], crab shell (3.43 mg/g) [36], oyster shell (29.5 mg/g) [37] and Pb ions like turmeric leaves (36.4 mg/g) [38], tomato waste (108 mg/g) [39], *Citrullus lanatus* peels (25.7 mg/g) [40].

3.2. Equilibrium studies

Balance and kinetic research is carried out towards understanding the nature of the process. On the basis of these studies it is possible to design, model and optimize processes introduced on a larger scale. In order to find out the mechanism by which the adsorption of elements takes place on the studied material, four isothermal models have been calculated for the obtained equilibrium states. The sorption isotherms of Langmuir, Freundlich, Temkin and Dubinin–Radushkevich were considered. On the basis of obtained data the isothermal parameters were calculated. Fig. 6 and Table 3 show the results obtained graphically and numerically respectively. The average relative error ARE and the correlation coefficient R^2 calculated on the basis of nonlinear regression allow concluding that the type of sorbed element influences the course of the sorption process. In case of lead ions, Freundlich's isotherm (ARE = 2%, $R^2 > 0.96$) was characterized by the highest matching parameters. The calculated parameter $1/n$ of 0.1734 (below 1) indicates that the material under study easily absorbs lead ions, which makes it possible to conclude that the dwarf everlast is a suitable sorbent for lead ions. Furthermore, on the basis of parameter $1/n$, it can be concluded that at lower equilibrium concentrations the sorption capacity is slightly suppressed. Freundlich's isotherm is a model of multilayer adsorption, which does not predict that sorbate saturates the surface of the material (it foresees infinite surface coverage) [41]. Additionally parameter $n = 5.77$ shows the favourable conditions of the sorption process ($n = 1–10$) [42]. For cadmium ions, it can be observed that the highest R^2 fit coefficients were found in Temkin's, Freundlich's and Langmuir's isotherms (above 0.96), while the average relative error ARE was 2.18% for Temkin's, 2.21% for Langmuir's and 2.37% for Freundlich's isotherms. From the results obtained we can conclude that all three isotherms describe the process of cadmium ion sorption on adwarf everlast in an improved way and the differences between the models are insignificant. Similarly as in the case of lead ions, sorption has a favourable course, which can be concluded from the n and $1/n$ parameters ($1/n < 1$ and $n = 2.57$).

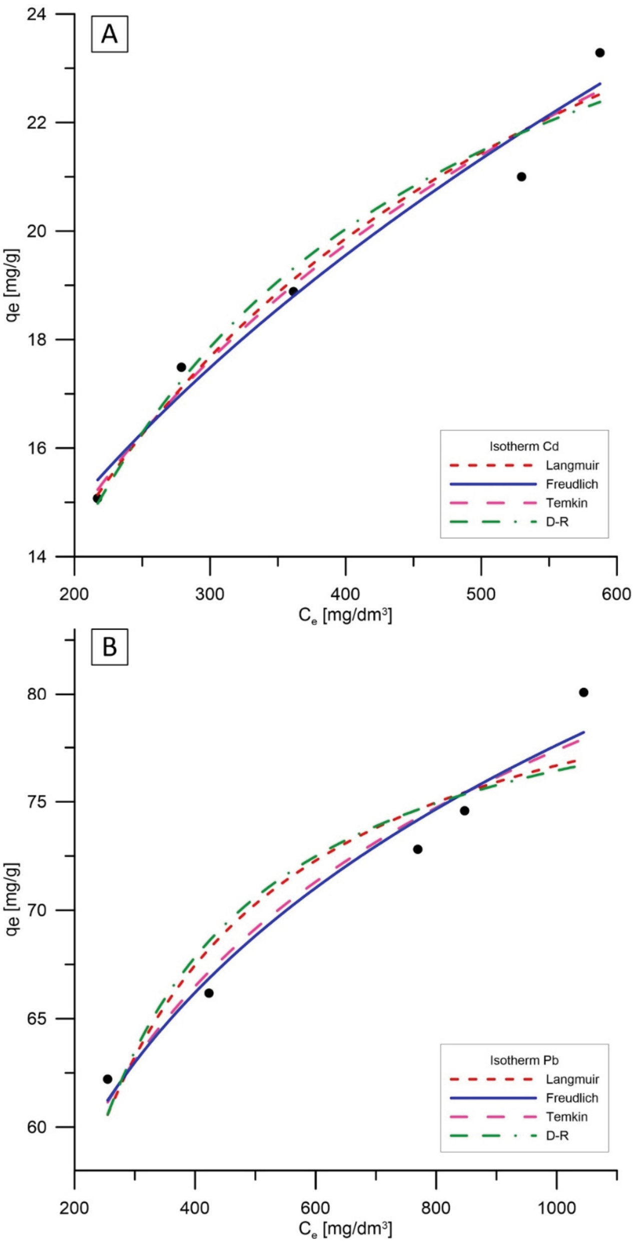

Fig. 6. Graphic representation of sorption isotherms for the process of ions adsorption: (A) Cd and (B) Pb (pH = 4.5; $T = 25°C$; $t = 60$ min).

Similar conclusions can be drawn from the separation coefficient R_L ($R_L = 1/1 + K_F C_o$), calculated from the Langmuir isotherm. The value of this coefficient for lead sorption ranged between 0.36–0.12 and 0.40–0.22 for cadmium. Therefore, it follows that the process of cadmium and lead sorption had favourable conditions for each concentration [16].

3.3. Kinetic studies

The rate of sorption can be influenced by many physicochemical factors. However, the greatest influence is exerted by interactions between the ion and the sorbent.

Table 3
Parameters of sorption isotherms models (pH = 4.5; T = 25°C; t = 60 min)

Isotherm model		Parameters			
		ARE (%)	R^2	q_m (mg/g)	K_L (dm^3/mg)
Langmuir	Cd	2.21	0.9630	31.524	0.0042576
	Pb	3.08	0.8967	84.352	0.0099872
		ARE (%)	R^2	K_F (mg$^{1-(1/n)}$ (dm^3)$^{1/n}$ g^{-1})	$1/n$
Freundlich	Cd	2.37	0.9660	1.89598	0.3895
	Pb	2.00	0.9625	23.42087	0.1734
		ARE (%)	R^2	K_T (dm^3/g)	B
Temkin	Cd	2.18	0.9660	0.0361935	7.389
	Pb	2.23	0.9514	0.6743728	11.879
		ARE (%)	R^2	K_{ad} (mol^2/kJ^2)	q_d (mg/g)
D–R	Cd	2.41	0.9569	0.05694855	28.333
	Pb	3.23	0.8807	0.03272589	82.778

Deposition of metal ions on the external surface of the tested material or their penetration into the pores may limit the process speed.

Observing the results of the sorption process of cadmium and lead, it can be seen that with the increase in the initial concentration, the ratio of the increase in the sorption capacity between the first and last measurement decreases. For cadmium ions, the increase in sorption capacity decreases from 2.58 times (300 mg/dm^3) to 2.26 times (700 mg/dm^3), while for lead ions, the decrease was 2.64 times (500 mg/dm^3) to 2.03 (1,500 mg/dm^3). The reduction in the sorption capacity increase ratio is related to the amount of ions in the solutions. In the beginning, there are fewer ions, as a result of which filling the free active spots on the sorbent surface is associated with less driving force through fewer active collisions between the ions and the sorbent. For higher concentrations, on the other hand, the amount of ions increases, resulting in more effective collisions between the ions and the sorbent causing a higher initial sorption capacity [34]. Additionally, it was observed that the sorption capacity for lead ions increased by 28.8% (between 500 and 1500 mg/dm^3), while for cadmium ions it increased by 54.4% (between 300 and 700 mg/dm^3), due to the fact that lead ions are much better sorbed on the surface of the dwarf everlast, thus a smaller increase in sorption capacity is observed. The results obtained were used to calculate the kinetics of adsorption of lead and cadmium ions on the *Helichrysum arenarium*. These data allowed to develop four kinetic models: pseudo-first-order, pseudo-second-order, Elovich and Weber–Morris models.

On the basis of the obtained results it was found that Elovich's model is the best fitting model (based on $R^2 > 0.95$ and ARE < 5.1) for cadmium and lead ions. Elovich's kinetic model was developed by Zeldowitsch [43], assuming that the real solid surface of the adsorbent is energetically heterogeneous and does not apply to interactions between adsorbed species. Elovich's α and β coefficients represent the initial adsorption rate and desorption coefficient. The α factor is also related to the extent of surface coverage and the energy of chemisorption activation. A higher value of α than β indicates a higher adsorption rate than desorption, which showed the superiority of the adsorption process [44]. The higher the initial ion concentrations, the greater the impact on the sorbate removal process the diffusion driving forces have, which in turn causes the lower initial concentration to be more conducive to chemical adsorption and intramolecular diffusion processes. Thus, for higher initial concentrations, the chemical activation energy is higher and there is more chemical adsorption, which tends to gradually increase the value of sorption capacity [45]. Additionally, comparing pseudo-first-order and pseudo-second-order models, it was found that cadmium and lead adsorption are best represented by a pseudo-second-order model. On this basis, it can be concluded that the sorption of cadmium and lead ions on the inflorescence of the dwarf everlast has a chemical character. The results obtained are shown in Fig. 7 and Table 4.

3.4. Desorption

The process of desorption of cadmium and lead ions from the surface of the dwarf everlast was carried out to determine the possibility of recovery of the tested ions from the sorbent. The results for selected eluents are presented in Table 5.

From the eluents used, the greatest ability to remove lead and cadmium ions from the surface of the sorbent was shown by acetic acid, respectively almost 85% and 75.5%. The reason for this is the fact that it belongs to the group of organic acids with chelating properties and as an organic acid it has a high ability to form various types of complexes. Additionally, it was observed that acetic acid removed more lead ions from the *Helichrysum arenarium* than cadmium. Sodium chloride solution, on the other hand, removed cadmium from the surface of the material at a level of ~63%, a much higher value compared to lead ~23%. During the desorption process with NaCl solution, Cd^{2+} or Pb^{2+} ions absorbed on the

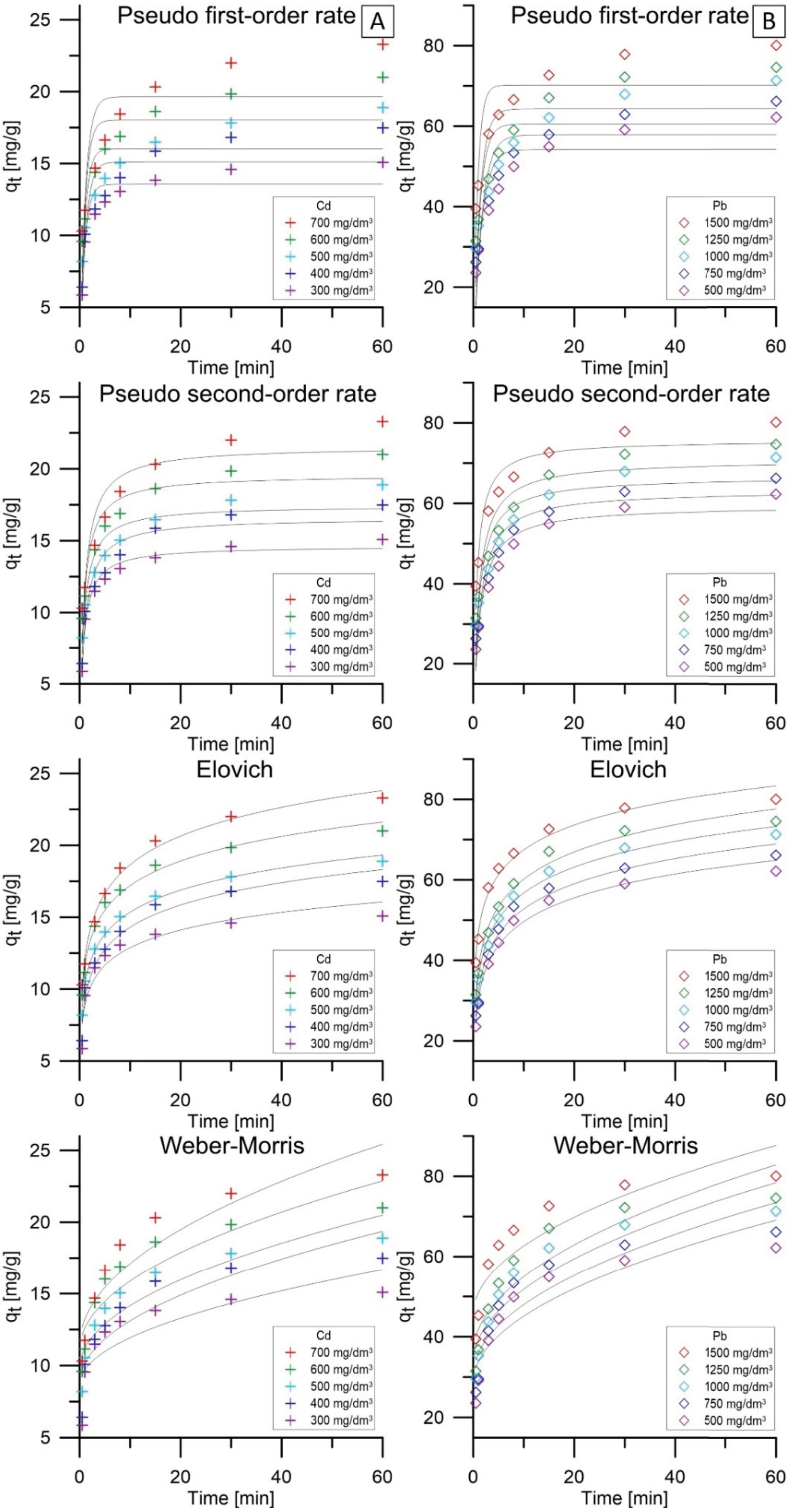

Fig. 7. Graphic representation of sorption kinetic models for the process of ions adsorption: (A) Cd and (B) Pb (pH = 4.5; T = 25°C).

Table 4
Parameters of sorption kinetic models for the sorption process Cd and Pb ions (pH = 4.5; T = 25°C)

Kinetic model	Cadmium ion concentration C_0 (mg/dm^3)				
	300	400	500	600	700
Pseudo-primary model					
q_1 (mg/g)	13.563	15.110	16.027	18.027	19.645
k_1 (min^{-1})	1.0990	0.9538	1.1103	1.0629	0.9471
R^2	0.8796	0.7721	0.7238	0.7297	0.6671
ARE (%)	6.67	11.54	11.02	11.73	13.69
Pseudo-secondary model					
q_2 (mg/g)	14.622	16.572	17.441	19.573	21.546
k_2 (min^{-1})	0.0993	0.0694	0.0787	0.0694	0.0537
R^2	0.9394	0.9261	0.9049	0.9119	0.8756
ARE (%)	4.09	6.93	7.10	6.55	8.58
Elovich's model					
β (g/mg)	0.5638	0.4462	0.4507	0.4050	0.3466
α (mg/g min)	252.8	132.0	224.1	261.3	184.7
R^2	0.9576	0.9635	0.9925	0.9901	0.9928
ARE (%)	7.96	5.11	2.05	2.17	1.98
Weber–Morris model					
I	8.6656	8.7853	9.7945	11.0496	11.3727
K_{id}	1.0329	1.3659	1.3811	1.5264	1.8143
R^2	0.6665	0.7803	0.8382	0.8246	0.8610
ARE (%)	14.31	12.59	9.75	10.35	9.47
Kinetic model	Lead ion concentration C_0 (mg/dm^3)				
	500	750	1,000	1,250	1,500
Pseudo-primary model					
q_1 (mg/g)	54.182	57.805	60.510	64.303	70.179
k_1 (min^{-1})	0.6499	0.6285	0.8135	0.7957	1.2101
R^2	0.7787	0.7731	0.6876	0.6994	0.7316
ARE (%)	14.25	14.02	14.63	14.67	11.00
Pseudo-secondary model					
q_2 (mg/g)	59.289	63.093	66.556	70.635	75.611
k_2 (min^{-1})	0.0149	0.0139	0.0153	0.0143	0.0211
R^2	0.9368	0.9300	0.8877	0.8952	0.9143
ARE (%)	7.57	7.44	9.21	8.97	6.12
Elovich's model					
β (g/mg)	0.1171	0.1104	0.1079	0.1020	0.1121
α (mg/g min)	283.9	305.4	422.3	452.6	1714.0
R^2	0.9867	0.9835	0.9918	0.9864	0.9840
ARE (%)	2.74	3.12	1.94	2.38	2.59
Weber–Morris model					
I	28.5444	30.3750	33.4719	35.6859	45.3822
K_{id}	5.2374	5.5636	5.8045	6.0894	5.4604
R^2	0.8181	0.8190	0.8571	0.8382	0.8018
ARE (%)	13.03	13.01	10.16	10.88	10.10

Table 5
Degree of ion removal from sorbent by eluents (pH = 4.5; T = 25°C; t = 60 min)

Eluents	Degree of desorption (%)	
	Cd	Pb
H_2O	4.98	12.03
NaCl	62.92	22.65
CH_3COOH	75.51	84.76

surface of the sorbent are replaced with Na^+ ions. The difference in desorption values results from the solubility of lead chloride, which is much lower than for cadmium chloride. As a result, the process of desorption of lead ions from the surface of the sorbent is difficult [46]. Due to the type of sorption (chemisorption) and thus the high energy needed to remove the sorbate from the sorbent, the water is able to desorb the ions examined to a negligible extent.

4. Conclusion

As a result of the research, it can be concluded that the objective of the research has been achieved. It was found that *Helichrysum arenarium* can be used as a sorbent to remove cadmium and lead ions from aqueous solutions. The SEM-EDS tests confirmed the presence of the tested ions on the sorbent surface after the sorption process. The material tested had a higher affinity for lead ions than for cadmium, the sorption capacity was 80.1 mg/g for Pb ions and 23.3 mg/g for Cd ions. The studies have shown that the sorption process of lead ions is performed according to Freundlich's isotherm (R^2 > 0.96, ARE = 2%), whereas for cadmium ions the process is described by Temkin's, Freundlich's and Langmuir's isotherms (R^2 > 0.96, ARE < 2.37). The calculated parameter $1/n$ for both elements below 1 indicates that the tested material easily absorbs the tested ions, which allows to conclude that *Helichrysum arenarium* is a suitable sorbent for cadmium and lead ions. The kinetic testing of the process allowed to select the model with the best fit. In both cases, the model with the highest fitting (R^2 > 0.95 and ARE < 5.1) was Elovich. Calculated parameters α than β showed higher adsorption rate than desorption. The studies on the recovery of cadmium and lead from the surface of the sorbent showed that the solution of acetic acid as an eluent was characterized by the highest degrees of ion recovery, which is related to its chelating properties and the ability to form complexes.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Compliance with ethical standards

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] T. Liu, Y. Lawluvy, Y. Shi, J.O. Ighalo, Y. He, Y. Zhang, P.-S. Yap, Adsorption of cadmium and lead from aqueous solution using modified biochar: a review, J. Environ. Chem. Eng., 10 (2022) 106502, doi: 10.1016/j.jece.2021.106502.

[2] J. Geng, Y. Yin, Q. Liang, Z. Zhu, H. Luo, Polyethyleneimine cross-linked graphene oxide for removing hazardous hexavalent chromium: adsorption performance and mechanism, Chem. Eng. J., 361 (2019) 1497–1510.

[3] M.A. Hashem, M. Hasan, M.A. Momen, S. Payel, M.S. Nur-A-Tomal, Water hyacinth biochar for trivalent chromium adsorption from tannery wastewater, Environ. Sustainability Indic., 5 (2020) 100022, doi: 10.1016/j.indic.2020.100022.

[4] Q. Shi, G.E. Sterbinsky, V. Prigiobbe, X. Meng, Mechanistic study of lead adsorption on activated carbon, Langmuir, 34 (2018) 13565–13573.

[5] P. Staroń, J. Chwastowski, Raphia-microorganism composite biosorbent for lead ion removal from aqueous solutions, Materials (Basel), 14 (2021) 7482, doi: doi: 10.3390/ma14237482.

[6] P. Loganathan, S. Vigneswaran, J. Kandasamy, R. Naidu, Cadmium sorption and desorption in soils: a review, Crit. Rev. Env. Sci. Technol., 42 (2012) 489–533.

[7] M. Irani, M. Amjadi, M.A. Mousavian, Comparative study of lead sorption onto natural perlite, dolomite and diatomite, Chem. Eng. J., 178 (2011) 317–323.

[8] J.A. Laszlo, F.R. Dintzis, Crop resides as lon-exchange materials treatment of soybean hull and sugar beet fiber (pulp) with epichlorohydrin to improve cation-exchange capacity and physical stability, J. Appl. Polym. Sci., 52 (1994) 531–538.

[9] N.A.A. Babarinde, J.O. Babalola, R.A. Sanni, Biosorption of lead ions from aqueous solution by maize leaf, Int. J. Phys. Sci., 1 (2006) 23–26.

[10] V.S. Grinev, A.A. Shirokov, N.A. Navolokin, N.V. Polukonova, M.N. Kurchatova, N.A. Durnova, A.B. Bucharskaya, G.N. Maslyakova, Polyphenolic compounds of a new biologically active extract from immortelle sandy flowers (*Helichrysum arenarium* (L) Moench), Russ. J. Bioorg. Chem., 42 (2016) 770–776.

[11] B.S. Marques, T.S. Frantz, T.R. Sant'Anna Cadaval Junior, L.A. de Almeida Pinto, G.L. Dotto, Adsorption of a textile dye onto piaçava fibers: kinetic, equilibrium, thermodynamics, and application in simulated effluents, Environ. Sci. Pollut. Res., 26 (2019) 28584–28592.

[12] J.L. Marques, S.F. Lütke, T.S. Frantz, J.B.S. Espinelli, R. Carapelli, L.A.A. Pinto, T.R.S. Cadaval, Removal of Al(III) and Fe(III) from binary system and industrial effluent using chitosan films, Int. J. Biol. Macromol., 120 (2018) 1667–1673.

[13] F.C. Wu, R.L. Tseng, R.S. Juang, A review and experimental verification of using chitosan and its derivatives as adsorbents for selected heavy metals, J. Environ. Manage., 91 (2010) 798–806.

[14] P. Baláž, A. Aláčová, J. Briančin, Sensitivity of Freundlich equation constant 1/*n* for zinc sorption on changes induced in calcite by mechanical activation, Chem. Eng. J., 114 (2005) 115–121.

[15] S.M. Mousa, N.S. Ammar, H.A. Ibrahim, Removal of lead ions using hydroxyapatite nano-material prepared from phosphogypsum waste, J. Saudi Chem. Soc., 20 (2016) 357–365.

[16] A.O. Dada, A.P. Olalekan, A.M. Olatunya, O. Dada, Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn^{2+} unto phosphoric acid modified rice husk, IOSR J. Appl. Chem., 3 (2012) 38–45.

[17] Y.S. Ho, G. McKay, Pseudo-second-order model for sorption processes, Process Biochem., 34 (1999) 451–465.

[18] C.W. Cheung, J.F. Porter, G. McKay, Sorption kinetics for the removal of copper and zinc from effluents using bone char, Sep. Purif. Technol., 19 (2000) 55–64.

[19] K.V. Kumar, Linear and non-linear regression analysis for the sorption kinetics of methylene blue onto activated carbon, J. Hazard. Mater., 137 (2006) 1538–1544.

[20] J. López-Luna, L.E. Ramírez-Montes, S. Martinez-Vargas, A.I. Martínez, O.F. Mijangos-Ricardez, M. del Carmen A. González-Chávez, R. Carrillo-González, F.A. Solís-Domínguez, M. del Carmen Cuevas-Díaz, V. Vázquez-Hip, Linear and nonlinear kinetic and isotherm adsorption models for arsenic removal by manganese ferrite nanoparticles, SN Appl. Sci., 1 (2019) 1–19.

[21] S. Svilović, D. Rušić, A. Bašić, Investigations of different kinetic models of copper ions sorption on zeolite 13X, Desalination, 259 (2010) 71–75.

[22] M.N. Prabhakar, A.U.R. Shah, K.C. Rao, J.-I. Song, Mechanical and thermal properties of epoxy composites reinforced with waste peanut shell powder as a bio-filler, Fibers Polym., 16 (2015) 1119–1124.

[23] L. Marcotte, G. Kegelaer, C. Sandt, J. Barbeau, M. Lafleur, An alternative infrared spectroscopy assay for the quantification of polysaccharides in bacterial samples, Anal. Biochem., 361 (2007) 7–14.

[24] M. Ahsan Habib, S.P. Maheswari, Electrochromism of polyaniline: an in situ FTIR study, J. Electrochem. Soc., 136 (1989) 1050, doi: 10.1149/1.2096782.

[25] D. Bhaduri, A. Saha, D. Desai, H.N. Meena, Restoration of carbon and microbial activity in salt-induced soil by application of peanut shell biochar during short-term incubation study, Chemosphere, 148 (2016) 86–98.

[26] V.P. Singh, R. Vaish, Adsorption of dyes onto candle soot: equilibrium, kinetics and thermodynamics, Eur. Phys. J. Plus, 133 (2018) 446, doi: 10.1140/epjp/i2018-12212-x.

[27] R.M.D. Soares, A.M.F. Lima, R.V.B. Oliveira, A.T.N. Pires, V. Soldi, Thermal degradation of biodegradable edible films based on xanthan and starches from different sources, Polym. Degrad. Stab., 90 (2005) 449–454.

[28] P. Manoj Kumar Reddy, S. Mahammadunnisa, B. Ramaraju, B. Sreedhar, C. Subrahmanyam, Low-cost adsorbents from bio-waste for the removal of dyes from aqueous solution, Environ. Sci. Pollut. Res., 20 (2013) 4111–4124.

[29] Ş. Taşar, F. Kaya, A. Özer, Biosorption of lead(II) ions from aqueous solution by peanut shells: equilibrium, thermodynamic and kinetic studies, J. Environ. Chem. Eng., 2 (2014) 1018–1026.

[30] M.A. Wahab, H. Boubakri, S. Jellali, N. Jedidi, Characterization of ammonium retention processes onto *Cactus* leaves fibers using FTIR, EDX and SEM analysis, J. Hazard. Mater., 241–242 (2012) 101–109.

[31] A. Cherdoud-Chihani, M. Mouzali, M.J.M. Abadie, Study of crosslinking acid copolymer/DGEBA systems by FTIR, J. Appl. Polym. Sci., 87 (2003) 2033–2051.

[32] O. Abbas, C. Rebufa, N. Dupuy, J. Kister, FTIR—multivariate curve resolution monitoring of photo-Fenton degradation of phenolic aqueous solutions: comparison with HPLC as a reference method, Talanta, 77 (2008) 200–209.

[33] S. Gunasekaran, R.K. Natarajan, V. Renganayaki, S. Natarajan, Vibrational spectra and thermodynamic analysis of metformin, Indian J. Pure Appl. Phys., 44 (2006) 495–500.

[34] F.A.A. Al-Rub, M. El-Naas, F. Benyahia, I. Ashour, Biosorption of nickel on blank alginate beads, free and immobilized algal cells, Process Biochem., 39 (2004) 1767–1773.

[35] H.N. Tran, H.P. Chao, Adsorption and desorption of potentially toxic metals on modified biosorbents through new green grafting process, Environ. Sci. Pollut. Res., 25 (2018) 12808–12820.

[36] C. Zhou, X. Gong, W. Zhang, J. Han, R. Guo, A. Zhu, Uptake of Cd(II) onto raw crab shells: isotherm, kinetic, adsorption properties and mechanisms, Water Environ. Res., 89 (2017) 817–826.

[37] D. Alidoust, M. Kawahigashi, S. Yoshizawa, H. Sumida, M. Watanabe, Mechanism of cadmium biosorption from aqueous solutions using calcined oyster shells, J. Environ. Manage., 150 (2015) 103–110.

[38] J.B. Dulla, B. Sumalatha, V.N. Alugunulla, T. Venkateswarulu, Ultrasonic treated dried turmeric leaves powder as biosorbent for enhanced removal of lead from aqueous solutions, Int. J. Environ. Anal. Chem., (2022), doi: 10.1080/03067319.2022.2089566.

[39] E. Heraldy, W.W. Lestari, D. Permatasari, D.D. Arimurti, Biosorbent from tomato waste and apple juice residue for lead removal, J. Environ. Chem. Eng., 6 (2018) 1201–1208.

[40] S. Latif, R. Rehman, M. Imran, M.S. Hussain, S. Iqbal, L. Mitu, Removal of Cadmium(II) and lead(II) from water by chemically treated citrullus lanatus peels as biosorbent in cost effective way, Rev. Chim., 71 (2020) 182–192.

[41] T.-H. Mu, H.-N. Sun, Polyphenols in Plants, Sweet Potato Leaf Polyphenols: Preparation, Individual Phenolic Compound Composition and Antioxidant Activity, Elsevier, 2019, pp. 365–380.

[42] E. Erdem, N. Karapinar, R. Donat, The removal of heavy metal cations by natural zeolites, J. Colloid Interface Sci., 280 (2004) 309–314.

[43] F.T. Akinhanmi, A.I. Adeogun, A. Adegbuyi, Removal of Cu^{2+} from aqueous solution by adsorption onto quail eggshell: kinetic and isothermal studies, J. Environ. Biotechnol. Res., 5 (2016) 1–9.

[44] T.A. Khan, S.A. Chaudhry, I. Ali, Equilibrium uptake, isotherm and kinetic studies of Cd(II) adsorption onto iron oxide activated red mud from aqueous solution, J. Mol. Liq., 202 (2015) 165–175.

[45] Z. Huang, S. Liu, B. Zhang, L. Xu, X. Hu, Equilibrium and kinetics studies on the absorption of Cu(II) from the aqueous phase using a β-cyclodextrin-based adsorbent, Carbohydr. Polym., 88 (2012) 609–617.

[46] K. Kawai, A. Hayashi, H. Kikuchi, S. Yokoyama, Desorption properties of heavy metals from cement hydrates in various chloride solutions, Constr. Build. Mater., 67 (2014) 55–60.