CADMIUM AND LEAD IONS COMPETITIVE ADSORPTION ONTO CALCIUM ALGINATE PREPARED BY TRADITIONAL AND GREEN METHODS

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Calcium alginate (CaAlg) beads prepared by conventional, ultrasound and microwave-assisted synthesis as green methods have been applied to remove Pb(II) and Cd(II) from binary aqueous solutions. Mathematical modelling of the competitive adsorption process of Pb(II) and Cd(II) ions from binary using linear modified Langmuir isotherm equation was realized. The obtained results showed that both metal ions have an inhibitory effect in the process of removal from binary solutions. Combination of microwave and ultrasound determines the increase of the adsorption capacity of CaAlg. These results illustrate potential application of the CaAlg prepared by green methods in batch remediation of cadmium and lead ions polluted effluents.

Keywords: calcium alginate beads, ultrasound-assisted synthesis, microwave-assisted synthesis, heavy metal competitive removal

1. Introduction

Pb(II) and Cd(II) ions are found in numerous industrial wastewater, such as those in the industries: inorganic chemistry (pigments), organic chemistry (petrochemical), electronics industry (battery manufacturing), steel industry, metallurgy galvanizing, mining, production and application of fertilizers and pesticides [1]. In industrial waters from the metallurgical industry (from

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galvanizing baths), from the mining industry, batteries, pesticides, fertilizers and dyes, Pb(II) ions are found mixed with Cd(II) ions, but also other metallic ions. The concentration of Pb(II) and Cd(II) ions in these wastes varies from a few ppm to a few hundred ppm. Due to the negative effects they produce, Pb(II) and Cd(II) ions are included in the category of priority hazardous substances [2].

The conventional remediation technologies used to remediate heavy metal ions are: chemical precipitation, coagulation, flocculation, ion exchange, electrocoagulation, solvent extraction membrane processes [3]. The high costs, the fact that large volumes of sludge are produced, the losses of solvents, they require the use of chemicals and cannot be applied for the treatment of wastewater with a low content of metal ions represent some of the disadvantages of conventional methods [4]. Furthermore, electrocoagulation requires replacement of electrodes and ordinary maintenance [5].

Adsorption represents one of the most relevant conventional processes to remove contaminants from synthetic solutions and industrial effluents [6]. This technology has as main advantages: high removal efficiency, low cost, ease of implementation, excellent flexibility in design and operation, the ability to use many natural and synthetic materials, and waste from various industrial and agricultural processes as adsorbents [7]. In addition, under certain conditions, the removal of contaminants can be performed with a yield of 100%, and the regenerated adsorbents can be reused in several cycles of adsorption [6].

Biosorption and bioremediation are unconventional treatment technologies applied for clean-up of heavy metal ions polluted effluents [8]. These technologies are more advantageous than conventional technologies, being low cost and can be applied to remove low contamination with heavy metal ions. Cd(II) and Pb(II) polluted effluents remediation has been examined by the use of bacteria [9-11], fungi [12, 13], algae [14, 15], yeast [16], agricultural waste [17, 18] and biopolymers [19, 20]. Biopolymers are naturally extracted materials from ecosystem characterized by biodegradability and higher economic value being applied to remove heavy metal ions and other contaminants from synthetic and industrial effluents [21].

Among biopolymers, alginates are defined by high bio-compatibility, bio-degradability, and renewability, the presence of plentiful hydroxyl and carboxyl groups. These characteristics are responsible for high adsorption affinity for heavy metal ions and for its uses in remediation of aqueous polluted effluents [22]. Sodium alginate (NaAlg) presents low mechanical strength, low stability, and relative low heat resistance. These disadvantages lead to the development of new strategies to physical and/or chemical modification of its to enhance the uses in heavy metal adsorption [23]. Calcium cross-linked alginate has relatively poor adsorption capacity on monovalent ions, but it has a good selectivity and adsorption

performance on divalent ions [22]. Unlike sodium alginate, calcium alginate can be used to remove metal ions from wastewater both in column and batch systems [24].

The simplest method of modifying NaAlg is to convert it to calcium alginate. The method of dripping NaAlg into one reactor containing calcium chloride solution is called external gelation or "diffusion method" [25]. In this method, the calcium cations diffuse from the continuous phase to the interior of the alginate droplets. By this, they form a gelled alginate matrix, from the outside migrating to the center of the alginate droplet [25]. The time needed for crosslinking and particle hardening varies between 3 and 24 h [26]. To reduce this time and consequently to reduce energy consumption, green technologies such as ultrasound (US) and microwave (MW) can be applied [24].

Ultrasound (US) technology intensifies the processes, enhances the mass transfer through cavitation phenomena [27], reduces the energy consumption, changes the structure and functional properties of materials [28]. These are the avantages why it is considered a green technology. In our previous study, an ultrasonic bath and an ultrasonic clamp-on device have been used to prepare CaAlg beads [22]. The maximum Pb(II) exchange capacity of CaAlg prepared in US of 355 mg/g is 11% greater than the exchange capacity of the CaAlg beads conventionally prepared [22].

MW irradiation as one of the most efficient, inexpensive, nonconventional and environmentally friendly heating methods is widely examined in the materials synthesis [29].

Thus, the goal of this study was to use CaAlg beads previously prepared using traditional, US and MW alone or combined in a hybrid device in batch systems to remediate polluted waters with Cd(II) and Pb(II). Competitive Cd(II) and Pb(II) adsorption modelling has been applied to demonstrate the inhibitory effect of the competitive pollutant.

2. Materials and Methods

2.1. Chemicals

Calcium chloride and sodium alginate (medium viscosity) were purchased from Sigma Aldrich Corporation, USA. $Pb(NO_3)_2$ and $Cd(NO_3)_2{\cdot}4H_2O$ were obtained from Merck, Germany. 1000 mg/L $Cd(NO3)_2$ and 1000 mg/L $Pb(NO_3)_2$ stock solutions have been diluted with deionized water to prepare monocomponent and binary solutions of Cd(II) and Pb(II). All the chemicals were used without any further purification.

2.2. Equipment

The concentration of Cd(II) and Pb(II) ions in initial and treated water was performed using an AAnalyst 400 Atomic Absorption Spectrometer from Perkin Elmer (USA).

2.3. CaAlg preparation methods

The preparation protocols are described in detail in our previous work [30]. Six types of CaAlg samples have been prepared and characterized. The process of the CaAlg preparing cand be divided in two phases: the first stage in considered the external gelation and the second stage is external gelation or hardening stage. The differences between the six samples are derived from the preparation stage. In function of these observations, the CaAlg samples have been abbreviated as follows:

- CaAlg-C-C (meaning that both internal and external gelation phase have been realized in conventional mode),
- CaAlg-C-US (is the sample that the internal gelation has been realized in conventional mode and the external gelation phase in US),
- CaAlg-C-MW (is the sample that the internal gelation has been realized in conventional mode and the external gelation phase in MW),
- CaAlg-MW-C (is the sample that the internal gelation has been realized in MW and the external gelation phase in conventional mode),
- CaAlg-MW-US (is the sample that the internal gelation has been realized in MW and the external gelation phase in US),
- CaAlg-MW-MW (is the sample that both internal gelation and the external gelation phase have been performed in MW) [30].

2.4. Adsorption experiments

Experiments were carried out in batch system regarding the removal of Cd(II) and Pb(II) ions from monocomponent and binary aqueous solutions. Tests were performed at room temperature and optimum conditions (previously determined) using a GFL 3015 shaking system at 150 rpm.

The removal capacity of Cd(II)/Pb(II) ions at various time intervals and at various pH values was calculated using the equation below, (1):

$$Q_t = \frac{(C_0 - C_t) \cdot V}{m} \quad (1)$$

where: Q_t represents the removal capacity, expressed by the amount of Cd(II)/Pb(II) ions retained per unit mass of CaAlg (mg/g); C_0 is the initial concentration of Cd(II)/Pb(II) ions in the solution (mg/L); C_t means the concentration of Cd(II)/Pb(II) ions at a certain time t (or at different pH values) (mg/L); V represents the volume of Cd(II)/Pb(II) ion solution (L); m defines the mass of CaAlg (g).

The affinity of any adsorbent towards heavy metal ions is determined by various factors which are classified into three categories:

(1) properties of heavy metal ions, e.g. ionic radius, radius of hydrated ions, enthalpy of hydration, electronegativity;

(2) adsorbent properties, e.g. specific surface area, porosity, types and number of functional groups;

(3) solution properties e.g. concentration, pH and occurrence of competing ions.

The modified Langmuir isotherm model can be used to characterize the competitive adsorption of pollutants (metal ions/other pollutants) from binary solutions. For this, the mathematical model presented by equation (2) can be applied [31]:

$$Q_{e,M1} = \frac{Q_{max,M1}K_{L,M1}C_{e,M1}}{1+K_{L,M1}C_{e,M1}+K_{L,M2}C_{e,M2}} \quad (2)$$

The linearized form of equation 2 is (for metal ion 1 (M1):

$$\frac{1}{Q_{e,M1}} = \frac{1}{Q_{max,M1}} + \frac{1}{Q_{max,M1}K_{L,M1}}\left[\frac{1}{C_{e,M1}} + \frac{K_{L,M2}C_{e,M2}}{C_{e,M1}}\right] \quad (3)$$

For metal ion 2 (M2) the linearized form of the Langmuir model is:

$$\frac{1}{Q_{e,M2}} = \frac{1}{Q_{max,M2}} + \frac{1}{Q_{max,M2}K_{L,M2}}\left[\frac{1}{C_{e,M2}} + \frac{K_{L,M1}C_{e,M1}}{C_{e,M2}}\right] \quad (4)$$

In these equations the parameters are defined as follows:

- $C_{e,M1}$, $C_{e,M2}$, $Q_{e,M1}$, and $Q_{e,M2}$ are the equilibrium concentrations and equilibrium retention/adsorption capacity of metal ions (1) (Pb(II)) and (2) (Cd(II) in binary solutions;
- $K_{L,M1}$ and $K_{L,M2}$ are the characteristic equilibrium constants for the adsorption of the respective metal ions from monocomponent solutions;
- $Q_{max,M1}$ and $Q_{max,M2}$ are the maximum adsorption capacities characteristic of calcium alginate for the metal ions tested from the binary solutions [31].

The ratio $\frac{Q_{max,binary}}{Q_{max,monocomponet}}$ provides information on the dynamics of the adsorption process of Pb(II) and Cd(II) ions from binary solutions. The two metal ions can have a synergistic effect when the value of the ratio $\frac{Q_{max,binary}}{Q_{max,monocomponet}}$ is > 1, and the effect of the mixture is stronger than the effect of the individual metal ions. If the ratio $\frac{Q_{max,binary}}{Q_{max,monocomponet}}$ is < 1, the two metal ions have an antagonistic effect, with the mixture having a weaker effect than the effect of the individual metal ions. If the ratio $\frac{Q_{max,binary}}{Q_{max,monocomponet}}$ has a value equal to 1, then the mixture has no influence on the adsorption process of metal ions from binary solutions [32].

All the adsorption tests were carried out in triplicate and the standard error was within 5%.

3. Results and discussion

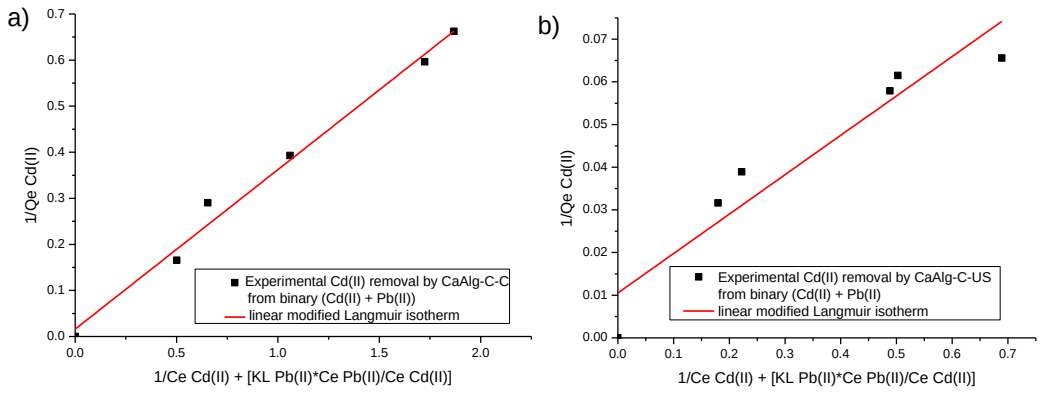
3.1. Competitive adsorption

Real wastewaters contain more than one metal ion. Hence, the remediation tests in multicomponent systems are essential to define the interference of competitive metal ions present in the solution [32]. Three types of interaction between the adsorbates–adsorbents have been reported in the literature. They are defined based on the ratio between maximum removal capacity in a bicomponent solution to monocomponent solution $\frac{Q_{max,binary}}{Q_{max,monocomponent}}$ [33].

Based on this ratio, the interaction can be non-interactive (if $\frac{Q_{max,binary}}{Q_{max,monocomponent}} = 1$), synergistic (if $\frac{Q_{max,binary}}{Q_{max,monocomponent}} > 1$) and antagonistic (if $\frac{Q_{max,binary}}{Q_{max,monocomponent}} < 1$) [33].

The simultaneous adsorption data of Cd(II) and Pb(II) on the CaAlg beads were simulated with multi-component linearized isotherm equations (Eqs. 3 and 4), which derived from the single-component Langmuir isotherm model.

The interaction between Cd(II) ions and Pb(II) ions in a binary system was evaluated by comparing the removal capacity in the binary system ($Q_{max,binary}$) to that in monocomponent system ($Q_{max,monocomponent}$). The results of the removal tests have been fitted with the modified Langmuir isotherm model (equations 3 and 4). The graphs used to establish the values of the parameters of the linear modified Langmuir isotherm equations are presented in Figs. 1 and 2. They are used to calculate the maximum removal capacity values for Cd(II) and Pb(II) ions and the $\frac{Q_{max,binary}}{Q_{max,monocomponent}}$ ratio values for the synthesized CaAlg samples (Table 1).



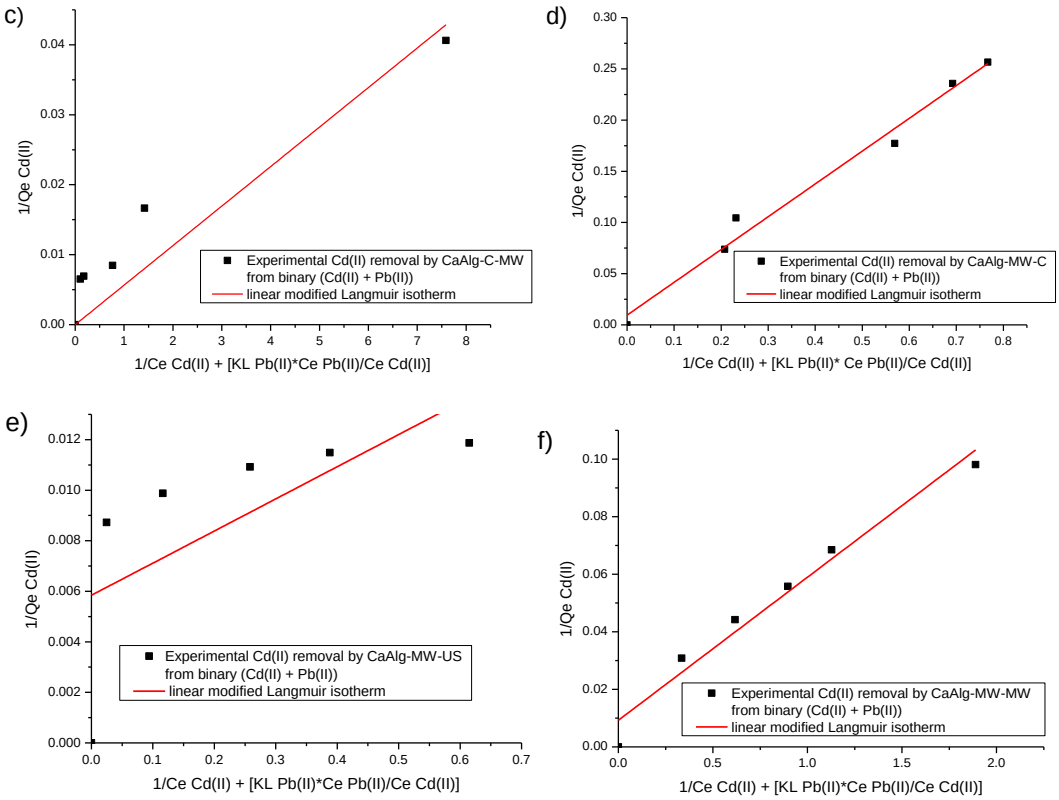
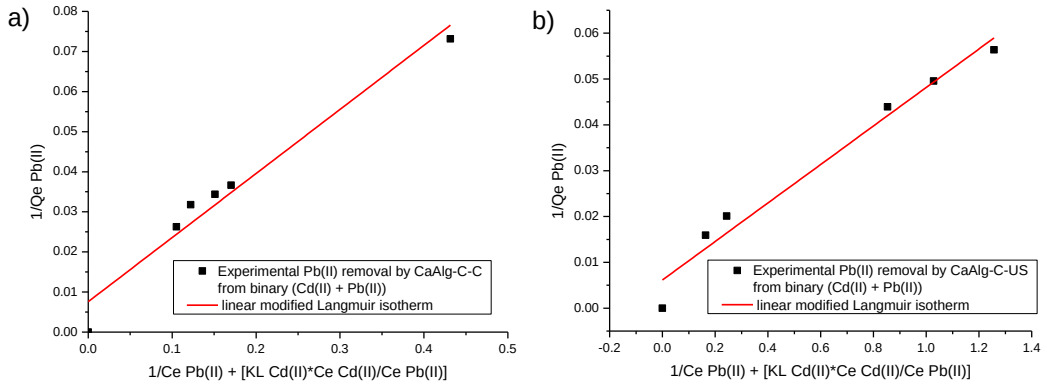


Fig. 1. Linear Langmuir isotherm plots for Cd(II) removal from binary Cd(II) + Pb(II) solutions by adsorption onto: a) CaAlg-C-C; b) CaAlg-C-US; c) CaAlg-C-MW; d) CaAlg-MW-C; e) CaAlg-MW-US; f) CaAlg-MW-MW.



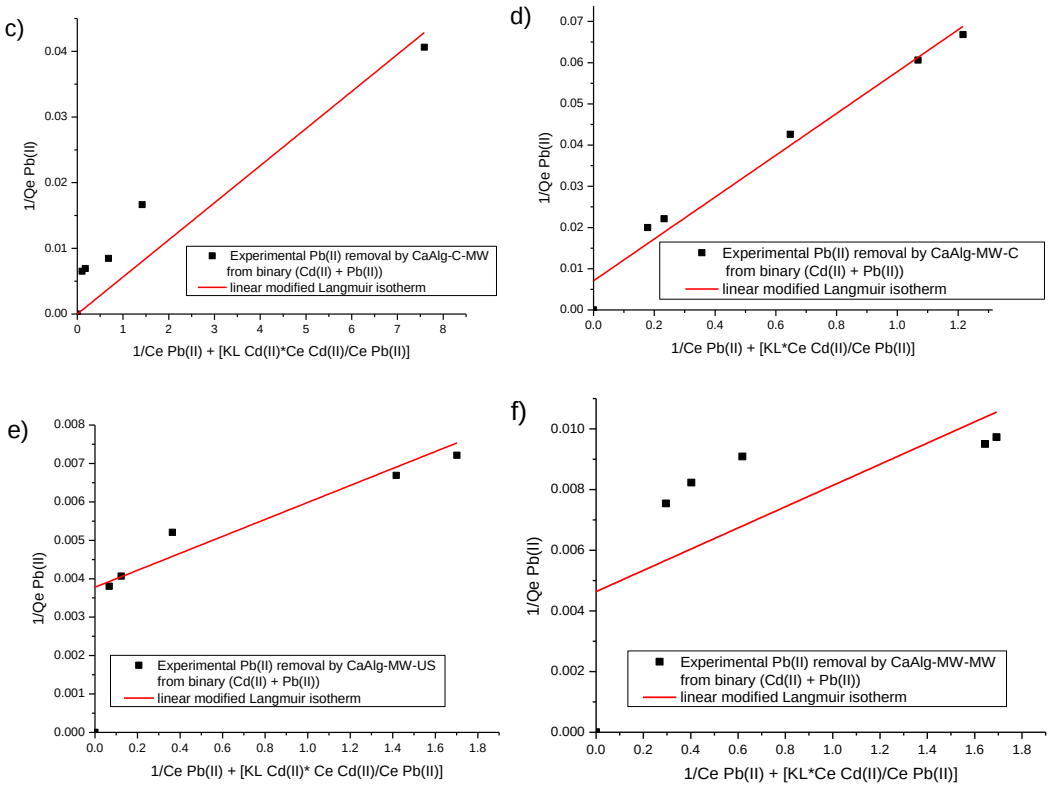


Fig. 2. Linear Langmuir isotherm plots for Pb(II) removal from binary Cd(II) + Pb(II) solutions by adsorption onto: a) CaAlg-C-C; b) CaAlg-C-US; c) CaAlg-C-MW; d) CaAlg-MW-C; e) CaAlg-MW-US; f) CaAlg-MW-MW.

Table 1

The maximum adsorption capacities of the calcium alginate samples prepared in absence and in presence of US and MW for monocomponent and binary solutions

Adsorbent	**Heavy metal ion**	**Q_{max} (monocomponent solution) (mg/g)**	**Q_{max} (binary solution) (mg/g)**	$\frac{Q_{max,binary}}{Q_{max,monocomponent}}$
CaAlg C-C	Pb(II)	201.7167	131.7523	0.6532
	Cd(II)	104.5969	62.0347	0.5931
CaAlg C-US	Pb(II)	217.9757	162.8664	0.7472
	Cd(II)	129.3702	95.0578	0.7348
CaAlg C-MW	Pb(II)	220.9995	176.9902	0.8008
	Cd(II)	135.6239	107.1502	0.7900
CaAlg MW-C	Pb(II)	215.2959	141.4427	0.6570
	Cd(II)	126.7300	104.9318	0.8280
CaAlg MW-MW	Pb(II)	308.2313	215.5172	0.6992
	Cd(II)	139.3718	108.2251	0.7765
CaAlg MW-US	Pb(II)	328.8655	264.5502	0.8044
	Cd(II)	195.4709	171.2328	0.8760

Based on our results, there is a decrease in the removal capacity for each of heavy metal ions from binary solution compared to their adsorption from the monocomponent solution. The ratio $\frac{Q_{max,binary}}{Q_{max,monocomponent}}$ is less than 1 for all CaAlg samples (Table 1). This result demonstrates the competition between Cd(II) and Pb(II) ions to occupy the free active sites of CaAlg. Consequently, the removal of heavy metal is hindered by the presence of the second heavy metal ion [32].

The adsorption capacity of primary metal ion decreases with the presence of the secondary metal ions in the binary metal mixed solutions. It was also observed that, the affinity of the CaAlg beads for Pb(II) ions is greater than that for Cd(II) ions.

It was also noticed that the removal of Cd(II) ions is more significantly controlled by the presence of the coexistent Pb(II) species for CaAlg samples for which the internal gelation has been performed in conventional mode, while the interference of Cd(II) in the sorption of Pb(II) is considerably less intense. For the samples for which the internal gelation has been performed in MW, the removal of Pb(II) ions is more significantly controlled by the presence of the coexistent Cd(II) species. These can be due to the surface morphology of the CaAlg samples that is influenced by the synthesis protocol.

3.2. Comparison of removal capacity of CaAlg beads with other adsorbents

The results obtained are presented and discussed in comparing to other previous research. The maximum removal capacity (Q_{max}) of alginate-based adsorbents for Cd(II) and Pb(II) is shown in Table 2.

Table 2

Comparison of Cd(II) and Pb(II) adsorption capacity for various alginate based adsorbents

Adsorbent	Cd(II) adsorption capacity (mg/g)	Pb(II) adsorption capacity (mg/g)	Reference
Phosphate-embedded calcium alginate beads	82.64	263.16	[34]
Titania-coated silica/alginate	16.73	26.89	[35]
Alginate/activated carbon/bentonite/Fe_2O_3	41.3	74.2	[36]
Graphene oxide-sodium alginate composite	139.62	887.21	[37]
NaAlg intercalated MgAl-layered double hydroxide	95.55	243.67	[38]
Calcium alginate beads	27.4	150.4	[39]
Water Pennywort Fixed on Alginate	11.48 10.23 (binary 1:1)	22.22 18.23 (binary 1:1)	[40]

	13.59 (binary 2:1) 7.86 (binary 1:2)	24.42 (binary 2:1) 10.23 (binary 1:2)	
CaAlg-C-C	104.60 62.03 (binary)	201.72 131.75 (binary)	This study
CaAlg-C-US	129.37 95.06 (binary)	217.98 162.87 (binary)	This study
CaAlg-C-MW	135.62 107.15(binary)	217.98 162.87 (binary)	This study
CaAlg-MW-C	126.73 104.93 (binary)	221 176.99 (binary)	This study
CaAlg-MW-MW	139.37 108.22 (binary)	308.23 215.52 (binary)	This study
CaAlg-MW-US	195.47 171.23 (binary)	328.87 264.55 (binary)	This study

Table 2 reveals that the CaAlg samples investigated in these experiments have higher removal capacities than other related adsorbents. The lower adsorption capacity of the prepared CaAlg beads compared to other alginate-based adsorbents can be explained by the fact that the alginate-based adsorbents were modified to increase their adsorption capacity. The results show that US and MW significantly improve the removal capacity of CaAlg beads.

4. Conclusions

CaAlg beads successfully prepared using green synthesis protocols. Ultrasound with different ultrasonic power (50% amplitude, 100% amplitude, 50W), microwave (21 W diffused power, 3-8 W reflected power, 13 W injected power into the system) and ultrasound synergized with microwave treatments were applied to remove Cd(II) and Pb(II) ions from single and binary solutions.

The combination of MW with US is effective to improve Cd(II) and Pb(II) removal capacity of CaAlg beads. Adsorption of Cd(II) and Pb(II) from binary solutions shows the antagonistic competitive effect. We can conclude that through our study we have demonstrated that these new green synthesis methods can be successfully applied to prepare adsorbents with improved removal capacity that can be used for wastewater treatment.

Acknowledgement

Financial support from the Competitiveness Operational Program 2014-2020, Action 1.1.3: Creating synergies with RDI actions of the EU's HORIZON 2020 framework program and other international RDI programs, MySMIS Code

108792, Acronym project "UPB4H", financed by contract: 250/11.05.2020 is gratefully acknowledged.

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