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TAGUCHI DESIGN-BASED ENHANCEMENT OF HEAVY METALS BIOREMOVAL BY AGROINDUSTRIAL WASTE BIOMASS FROM ARTICHOKE

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Abstract

The Taguchi method of designing experiments is based on a system of tabulated designs (arrays) that enables the maximum number of variables to be estimated in a neutral (orthogonal) balanced manner with a minimum number of experimental sets. Heavy metals remediation of aqueous streams is of special concern due to its highly toxic and persistent nature. Taguchi approach was used for enhanced bioadsorptive removal of Pb(II), Cu(II) and Cd(II) from aqueous solutions using agroindustrial waste biomass from globe artichoke as inexpensive sorbent. Sorbent biomass was characterized as to its chemical composition by infrared spectroscopy (FTIR), revealing the presence of hydroxyl, carboxyl, sulphonic and amine functional groups. Ranks of four factors (pH, temperature, sorbent dosage and initial metal concentration) at three levels each, in a L9 array were conducted, in batch sorption tests, for the individual metal ions of concern. The sorption capacity (q_e) values were transformed into an accurate signal-to-noise (*S/N*) ratio for a "higher is better" response. The best conditions for individual heavy metal sorption were determined reaching up to 86.2 $mg.g^{-1}$ for Pb, 35.8 $mg.g^{-1}$ for Cd and 24.4 $mg.g^{-1}$ for Cu. This paper also discusses the equilibria and kinetic aspects of the sorption process. Sorption isotherms were successfully described by the Sips model. In addition, the experimental data showed that the uptake kinetic profiles of the three metal ions closely fitted the pseudo-second order model. Conclusively, the agroindustrial waste biomass from globe artichoke represents a potentially viable sorbent for the bioremoval of Pb(II), Cu(II) and Cd(II) ions from aqueous systems.

Keywords: Agricultural waste; Low-cost sorbent; *Cynara scolymus* by-products; Lignocellulosic biomass; Taguchi methodology

1. Introduction

Water is a finite natural resource necessary for the sustenance of life and ecological systems and a key resource for social and economic development. The treatment of domestic and industrial wastewater is important in order to comply with the strict environmental regulations that are set by government entities. The main objective of wastewater treatment is generally to allow human and industrial effluents to be disposed of without danger to human health or unacceptable damage to the natural environment (UNESCO, 2015). Despite improvements in water-reuse, the incidence of water pollution has increased as a result of population growth and expanding economic activities, causing or exacerbating major environmental problems (Gupta and Suhas, 2009). In recent decades the issue of water contamination by organic and inorganic pollutants emitted from industrial and non-industrial activities has become a worldwide concern (Sizmur et al., 2017; Sousa et al., 2018).

Heavy metals are among the most common pollutants found in wastewater (Fu and Wang, 2011; He and Chen, 2014; Rosique et al., 2016). The main sources of heavy metals contamination in aquatic ecosystems include landfill leaches, mining wastes, urban runoff and industrial and municipal wastewaters (Gautam et al., 2014). Current wastewater treatment technologies to remove heavy metals are energy intensive, costly, and require the safe disposal of toxic sludges (Shannon et al., 2008; Barakat, 2011). These limitations of the current available technologies have led to a demand for an efficient, cost-effective and selective treatment. In this respect, the versatility and wide applicability of sorption processes for heavy metals removal is well established (Gavrilescu, 2004; Ngah and Hanafiah, 2008; Burakov et al., 2018), and in recent years, an extensive range of low-cost adsorbents, with high removal capacity, have been investigated to achieve an economically viable treatment of metal-contaminated wastewaters (Kurniawan et al., 2006; Nguyen et al., 2013; Rosales et al., 2017). The concept of bioadsorptive removal is based on the use of materials of biological origin, characterized by the presence of reactive groups similar to those found in common chelating or ion-exchange resins. Within this field, there is a great deal of research being carried out into using lignocellulosic biomass from agrowastes and by-products as an environmentally friendly alternative sorbent in heavy metal pollution remediation (Garcia-Reyes and Rangel-Mendez, 2009; Nguyen et al., 2013; Salman et al., 2015). The metal-sequestering properties of agrowaste biomass provide a basis for a new approach to the bioremoval of heavy metals when they occur in low concentrations. Consequently, sorbents derived from abundant renewable resources, agroindustrial by-products or waste plant material, are considered among the most viable novel alternatives for heavy metals sorption.

Globe artichoke (*Cynara scolymus* L.) is an herbaceous perennial plant, originating from the Mediterranean Basin, which is grown throughout the world. It is widely cultivated for its large immature inflorescences, with edible fleshy leaves (bracts) and receptacle, which represent an important component of the Mediterranean diet, being a rich source of bioactive phenolic compounds, and also inulin, dietary fibre and minerals (Orlovskaya et al., 2007; Pandino et al., 2013). The edible parts of the artichoke plants are the large immature flowers (more formally referred to as capitula), harvested in the early stages of their development, which represent about the 30–40% of its fresh weight, depending on the variety and the harvesting time. Since only the central portion of the capitula is consumed, the ratio of edible fraction/total biomass produced by the plant is very low, being less than 15–20% of total plant biomass (Lattanzio, et al., 2009). Hence, the industrial processing of this plant generates large quantities of leafy lignocellulosic waste, which could be efficiently and sustainably valorized as sorbent in the removal of heavy metals. Metal ion binding to lignocellulosic sorbents is thought to occur through chemical functional groups such as phenolic, amino, alcohol, aldehyde, ketone or carboxyl groups (Shin and Rowell, 2005), which have the ability to bind heavy metals to varying extents through the donation of an electron pair to form complexes with the metal ions in solution (Pagnanelli et al., 2003). As a lignocellulosic biomass, this by-product has a great potential to be used as alternative low-cost sorbent, although it has yet to be systematically assessed.

Among the most abundant metal ions found in industrial wastewaters are Cu(II), Cd(II) and Pb(II) (Benettayeb et al., 2017). Taguchi (design of experiments) approach of orthogonal array experimental design was used for multivariate optimization of the sorption process. This methodology, not only contributes to a considerable saving in items and costs, but also leads to more fully developed processes by providing systematic, simple and efficient methodology for the optimization of the near optimum design parameters with only a few well defined experimental sets (Taguchi, 1990). Taguchi method uses a special design of orthogonal arrays which distribute the variables in a balanced manner to study the entire parameter space with a small number of experiments. The values obtained in the experimental results are transformed into a signal–to–noise ratio (*S/N*). In Taguchi method, the term 'signal' represents the desirable value (mean) for the output characteristic and term 'noise' represents the undesirable value (standard deviation) for the output characteristic. Therefore, the *S/N* ratio is the ratio of the mean and the standard deviation. Here, it is suggested that the optimal level of process parameters is the level with the highest *S/N* ratio.

According to our knowledge this is the first study on the utilization of agrowaste from globe artichoke as efficient and cost-effective sorbent of heavy metals in aqueous solution. Thus, the main objective of this investigation is to apply the Taguchi design approach to identify effective parameters for enhancing Pb(II), Cu(II) and Cd(II) bioadsorptive removal using as sorbent lignocellulosic biomass from globe artichoke agrowaste, with the aim of valorizing this agricultural by-product. Furthermore, isotherm modeling and kinetic studies are comprehensively investigated.

2. Materials and methods

2.1. Preparation and characterization of sorbent

Agrowaste biomass from globe artichoke (*Cynara scolymus* L.) grown in the Region of Murcia, a typical area for the cultivation of this plant in south-eastern Spain, was used. The starting materials, mainly composed of external bracts and stems, were dried at 70 ºC for 24 h before being milled and passed through a sieve of a number 18 mesh (1 mm) to obtain artichoke by-products powder. A CHNS/O Analyzer 628 Series of Leco Corporation (St. Joseph, Michigan), was used. Fourier transform infrared (FTIR) spectroscopy in the 4000−400 cm^{-1} region was used to investigate the functional groups present in the sorbent biomass.

2.2. Taguchi orthogonal array and experimental parameters

Taguchi method enables the effect of factors on the response to be ascertained and identifies the optimal experimental conditions with the least variability. This study considers four controllable factors (pH, temperature, sorbent dosage and initial metal concentration) at three levels (Table 1). To perform the Taguchi approach nine different experiments, using L9 orthogonal array, were run for each metal ion investigated.

Table 1.

Controllable factors and their levels

Factor	Description	Level 1	Level 2	Level 3
A	pH	3.0	4.0	5.0
B	Temperature (ºC)	20	30	40
C	Sorbent dosage ($g \cdot L^{-1}$)	0.5	1.0	2.0
D	Initial metal concentration ($mg \cdot L^{-1}$)	10	30	50

According to the Taguchi approach, the *S/N* ratio is analyzed to assess the experimental results. Usually, three types of *S/N* ratio analysis are possible: (1) lower is better (LB), (2) nominal is best (NB), and (3) higher is better (HB) (Zolfaghari et al., 2011). Because the target of this investigation is to achieve the greatest possible removal of pollutants, the optimal level of the process parameters is the level with the highest *S/N* ratio, which is given by Eq. (1):

$$S/N = -10\ \log_{10}\left[\frac{1}{n}\sum_{i=1}^{n}\left(\frac{1}{y_i}\right)^2\right] \quad (1)$$

where n is the number of repetitions under the same experimental conditions, and y represents the results of measurements. An analysis of variance (ANOVA) was used to determine the effect of factors on the sorption capacities (Hsieh et al., 2005). Minitab 17 software was used in the Taguchi approach.

2.3. Sorption tests

Stock metal solutions (1000 mg.L^{-1}) of Cu(II), Cd(II) and Pb(II) were prepared by dissolving metal salts ($Cu(NO_3)_2 \cdot 3H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Pb(NO_3)_2$) in Milli Q water. The stock solutions were diluted to a given metal concentration with Milli Q water prior to experiments. The pH was adjusted to target values using NaOH and/or HCl (0.1 M) solutions. The batch sorption experiments were carried out by shaking 100 mL of metal solution at a fixed concentration (C_0) and a known amount of sorbent in a reciprocal shaker (150 rpm, 24 h). The solutions were then filtered and the residual metal concentration in the solution (C_e) was quantified using an Agilent 720/725 inductively coupled plasma (ICP-OES) system.

The amounts of metal (Pb, Cu or Cd) adsorbed at equilibrium (q_e), also known as metal removal efficiency and evaluated as mg metal / g dry biomass, were determined by the mass balance equation (Eq. (2)) on the basis of the metal concentration values in the solution at the beginning (C_0), and at the end of the test (C_e):

$$q_e \ (mg \cdot g^{-1}) = \frac{(C_0 - C_e) \cdot V}{m} \tag{2}$$

where V is the solution volume (L) and m the sorbent dry weight (g). Table 2 gives more details of the experimental results.

2.4. Modeling of uptake kinetics and sorption isotherms

To assess the speed of these processes and the sorption mechanisms involved, the chemical reactions and the mass transfer balances should be considered. In this context, it is known that sorption kinetics strongly depend on the physicochemical characteristics of the sorbent biomass, which also influences the sorption mechanism. Pseudo-first order (Eq. (3)), pseudo-second order (Eq. (4)), and intra-particle diffusion model (Eq. (5)) are the most frequently used kinetic models to explain the sorption processes (Ho and McKay, 1998).

$$\frac{dq_t}{dt} = k_1 \cdot (q_e - q_t) \tag{3}$$

$$\frac{dq_t}{dt} = k_2 \cdot \left(q_e - q_t\right)^2 \tag{4}$$

$$q_t = k_i \cdot t^{1/2} + a \tag{5}$$

where q_e and q_t (mg.g^{-1}) are the metal uptake at equilibrium and at time t, respectively; k_1 is the pseudo-first order constant (h^{-1}); k_2 is the pseudo-second order constant (g.mg^{-1}.h^{-1}); k_i is the diffusion rate constant (mg.g^{-1}.h$^{-1/2}$), and a is a constant (mg.g^{-1}).

Equally important is the study of the equilibrium data to develop mathematical models to achieve the quantitative description of the sorption results. Two-parameter models are often used to describe the sorption isotherm, because, though quite simple, they can be easily modeled. With three-parameters models the mathematical fit is obviously improved while introducing a new parameter in the model (Benettayeb et al., 2017). Experimental data were fitted to the Langmuir (two-parameters), Freundlich (two-parameters) and Sips (three-parameters) equations to model the sorption isotherms.

The Langmuir isotherm considers sorption as a chemical phenomenon and assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites in the biomass. Basically the Langmuir isotherm equation can be expressed as:

$$q_e = \frac{q_{\max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \tag{6}$$

where q_{max} (mg.g^{-1}) is the maximum metal uptake and K_L (L.mg^{-1}) the Langmuir equilibrium constant which were calculated by a non-linear regression correlation method.

Freundlich isotherm model is applied to sorption on heterogeneous surfaces or surfaces supporting sites of different affinities. This model suggests that binding strength diminishes as the site occupation increases, so the stronger binding sites are occupied first (Vijayaraghavan et al., 2006). This isotherm can be represented by the empirical equation:

$$q_e = K_F \cdot C_e^{1/n} \tag{7}$$

where K_F ($\mathrm{mg}^{\frac{n-1}{n}}.\mathrm{g}^{-1}.\mathrm{L}^{1/n}$) is the Freundlich constant associated to sorption intensity and n the Freundlich exponent representing sorption ability.

Sips isotherm model is a three-parameter isotherm, that results from the combination of the Lagmuir and Freundlich models to circumvent the limitations of both (Foo and Hameed, 2010). It can be expressed as:

$$q_e = \frac{K_S \cdot C_e^{\beta_S}}{1 + a_S \cdot C_e^{\beta_S}} \quad (8)$$

Where K_S ($\mathrm{mg}^{1-\beta}.\mathrm{g}^{-1}.\mathrm{L}^{\beta}$) and a_s ($\mathrm{L.mg}^{-1})^{\beta}$ are the Sips isotherm constants, and β_S is the Sips isotherm exponent.

3. Results and discussion

3.1. Sorbent analysis

The elemental analysis of the sorbent biomass (Table 2) revealed a significant amount of oxygen (48 %), which indicates the important presence of oxygen-functional groups (O−H, C−O, C=O). The level of nitrogen points to the existence of functional groups with C−N and N−H bonds, while the presence of sulfur would confirm the C−S bonds in the biomass.

Table 2.

Elemental analysis (mean ± SD; n=3) of agrowaste biomass from globe artichoke

Element	**%**
C	42.3 ± 0.5
O	48.1 ± 0.7
H	6.2 ± 0.5
N	3.0 ± 0.3
S	0.3 ± 0.1

3.2. Optimization using Taguchi approach

Table 3 shows the individual metal removal efficiencies (q_e) measured for Pb(II), Cu(II) and Cd(II), in each of the experiments carried out.

Table 3.

L9 orthogonal array for each one of the metals investigated and results obtained for metal removal efficiency (q_e) and signal-to-noise (S/N) ratio (mean ± SD; n=3).

RUN	pH	Temp (ºC)	Sorbent dosage ($g.L^{-1}$)	[Pb(II)] ($mg.L^{-1}$)	q_e ($mg.g^{-1}$)	S/N ratio
1	3	20	0.5	10	19.6 ± 0.2	25.8 ± 0.3
2	3	30	1	30	30.5 ± 0.1	29.7 ± 0.2
3	3	40	2	50	25.1 ± 0.1	28.0 ± 0.2
4	4	20	1	50	44.4 ± 0.3	32.9 ± 0.4
5	4	30	2	10	4.3 ± 0.1	12.7 ± 0.2
6	4	40	0.5	30	54.0 ± 0.3	34.6 ± 0.4
7	5	20	2	30	11.7 ± 0.2	21.4 ± 0.3
8	5	30	0.5	50	85.5 ± 0.2	38.7 ± 0.4
9	5	40	1	10	7.7 ± 0.1	17.8 ± 0.2

RUN	pH	Temp (ºC)	Sorbent dosage ($g.L^{-1}$)	[Cu(II)] ($mg.L^{-1}$)	q_e ($mg.g^{-1}$)	S/N ratio
1	3	20	0.5	10	5.2 ± 0.1	14.3 ± 0.1
2	3	30	1	30	19.3 ± 0.6	25.7 ± 0.7
3	3	40	2	50	6.0 ± 0.2	15.5 ± 0.3
4	4	20	1	50	19.6 ± 0.4	25.8 ± 0.5
5	4	30	2	10	3.6 ± 0.5	11.1 ± 0.6
6	4	40	0.5	30	19.0 ± 0.8	25.6 ± 0.9
7	5	20	2	30	10.9 ± 0.2	20.7 ± 0.4
8	5	30	0.5	50	26.4 ± 0.4	28.4 ± 0.5
9	5	40	1	10	7.5 ± 0.4	17.4 ± 0.5

RUN	pH	Temp (ºC)	Sorbent dosage ($g.L^{-1}$)	[Cd(II)] ($mg.L^{-1}$)	q_e ($mg.g^{-1}$)	S/N ratio
1	3	20	0.5	10	3.4 ± 0.1	10.8 ± 0.2
2	3	30	1	30	20.3 ± 0.3	26.1 ± 0.4
3	3	40	2	50	9.4 ± 0.3	19.5 ± 0.4
4	4	20	1	50	17.9 ± 0.3	25.1 ± 0.4
5	4	30	2	10	5.4 ± 0.2	14.6 ± 0.3
6	4	40	0.5	30	3.2 ± 0.1	10.0 ± 0.1
7	5	20	2	30	10.4 ± 0.1	20.3 ± 0.2
8	5	30	0.5	50	35.1 ± 0.2	30.9 ± 0.3
9	5	40	1	10	6.3 ± 0.2	16.2 ± 0.3

Each trial condition was repeated three times. It can be appreciated that the highest sorption efficiency is shown with Pb(II) (85.7 mg.g^{-1}), followed by Cd(II) (35.3 mg.g^{-1}) and Cu(II) (26.8 mg.g^{-1}). Note that the removal efficiency is strongly influenced by both the nature of the metal ion, and the parametric conditions. The *S/N* ratio for each factor at levels 1, 2, and 3, along with total increments (delta values) and ranks are given in Table 4. The delta value measures the size of the effect by taking the difference between the highest and lowest characteristic average for a factor, and indicates the relative influence of the effect. The higher the difference, the more intense the influence (Srivastava et al., 2007). The rank value enables direct identification of the factors with the largest effect.

Table 4.

Average of the response characteristic at each level of the factor for signal-to-noise (*S/N*) ratios (larger is better).

Level	pH	Temp.	Sorbent Dosage	[Pb(II)]
L1	25.9	26.7	33.0	18.8
L2	26.8	27.0	26.8	28.6
L3	27.8	26.8	20.7	33.2
Delta	1.9	0.3	12.3	14.4
Rank	3	4	2	1

Level	pH	Temp.	Sorbent Dosage	[Cu(II)]
L1	18.5	20.3	22.8	14.3
L2	20.8	21.7	23.0	24.0
L3	22.2	19.5	15.8	23.2
Delta	3.7	2.2	7.2	9.7
Rank	3	4	2	1

Level	pH	Temp.	Sorbent Dosage	[Cd(II)]
L1	18.8	18.7	17.2	13.8
L2	16.6	23.9	22.4	18.8
L3	22.4	15.2	18.1	25.2
Delta	5.8	8.7	5.2	11.4
Rank	3	2	4	1

The largest factor affecting the *S/N* ratio was the initial metal concentration in all cases (Pb, Cu and Cd). For Pb and Cu, the initial metal concentration was followed by the sorbent dosage, the pH and finally, the temperature. For Cd, however, temperature turned out to be the second most influencing factor, followed by the pH and sorbent dosage.

The response curves for the individual effects of the metal adsorption parameters on the sorption capacities (q_e) and respective *S/N* ratios are shown in Fig. 1, which is a pictorial representation of the general trend of the influence of the factors. The variation in the response characteristic with the change in levels of a parameter can easily be visualized from these curves.

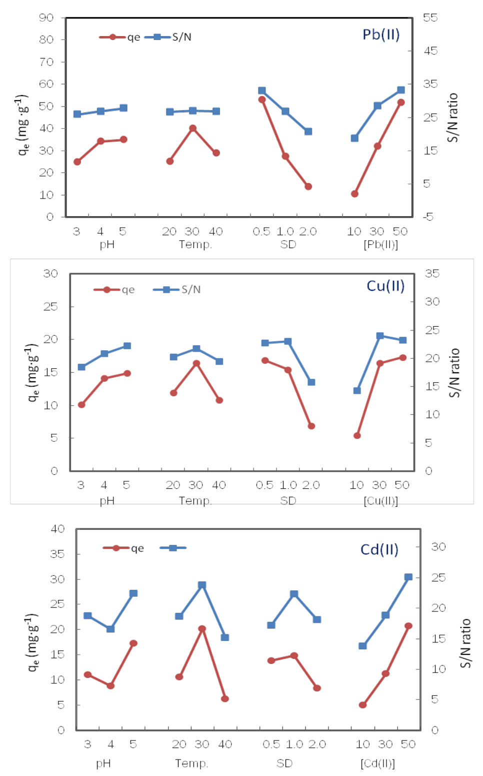

Fig. 1. Effect of factors on q_e and *S/N* ratio for metal ion adsorption.

The removal of metal ions was highly affected by the initial concentration of the solution since the transport from the bulk solution to the surface sorbent is governed by the metal concentration difference between the sorbent and the solution as the driving force (Sahmoune et al., 2011; Kumar et al., 2011). The *S/N* ratio of the Pb(II) and Cd(II) uptake by artichoke biomass (Fig. 3) increased as the initial concentration of these metal ions increased from 10 to 50 mg.L^{-1}. In contrast to these results, the removal efficiency of Cu(II) uptake by artichoke biomass increased from 10 to 30 mg.L^{-1}, but it showed a smooth decrease between 30 and 50 mg.L^{-1}. In general, it is accepted that an increased sorption performance is related to a more favourable transport of the metal ion at higher concentrations. Due to this improved transport, the ions in the solution can migrate more easily to the active sites on the biomass. However, when the initial concentration becomes too high, the active sites are saturated more quickly which results in preventing further ion uptake (Singha and Guleria, 2014; Zhu et al., 2015).

The sorbent dosage plays an important role on the adsorption process, and to enhance the sorption capacity, the optimum sorbent dosage must be determined. The number of active sites available and surface area depends on the sorbent dosage, and so the uptake of metal ions increases with increasing amounts of sorbent (Kumar et al., 2011). On the other hand, because the overlapping of adsorption sites decreases the total surface area, and the adsorption capacity has been reported to decrease with increasing sorbent dosage (Boota et al., 2009). The effect of sorbent dosage on the *S/N* ratio in the removal of Pb(II) pointed to a decrease in the response curve as the dosage increased from 0.5 to 2.0 g.L^{-1}. In the case of Cu(II) and Cd(II) removal, maximum adsorption, according to the response curve, was attained at the sorbent dosage of 1.0 g.L^{-1}.

The pH value of the solution has a marked influence on the solution chemistry of heavy metals and in the site dissociation of the sorbent surface (Castro et al., 2017). The adsorption of metal ions onto hydrous sorbent is described as a chemical coordinated and electrostatic process involving specific interactions at the solid–solution interface. The pH governs the speciation and solubility of the metal ion, which, in turn, affects the binding mechanism, although it can also induce precipitation phenomena. At low pH values, the sites of interaction of the lignocellulosic agrowaste sorbent from artichoke are fully protonated and, consequently, restrict the approach of metal ions as a result of repulsive forces. As the solution pH increases, the metal uptake is greater because of the level of protonation of these sites of interaction decreases and they become negatively charged. The adsorption of metal ions is easier when the sorbent sites are negatively charged because of electrostatic attraction (Zolfaghari et al., 2011; Mendoza-Castillo et al., 2015). The *S/N* ratio revealed that pH has a strong effect on Cu(II) and Cd(II) adsorption, with an optimum pH of 5.0. In the case of Pb(II) adsorption, the pH effect was lighter, showing a moderate influence on the sorption capacity.

Temperature affects the solubility of metal ions and their diffusion rate. According to the surface functional groups of the sorbent biomass, temperature has a certain impact on the sorption capacity. Fig. 3 shows that a temperature increase from 20 to 30 ºC leads to an increase in the *S/N* ratio, but when the temperature increases to 40 ºC the removal capacity decreases in all cases investigated. A common conclusion of many studies is that temperature has a limited effect, and only in a certain temperature range (Nguyen et al., 2013), which is why room temperature is most commonly used in most heavy metal bioremoval experiments.

The percentage contribution of each of the four factors considered for the sorption efficiency as the desired response characteristic is shown in Fig. 2. The initial metal concentration was the most significant factor in the adsorption of the three metal ions considered, ranging from 43.4 % for Cd(II) to 49.3 % for Cu(II).

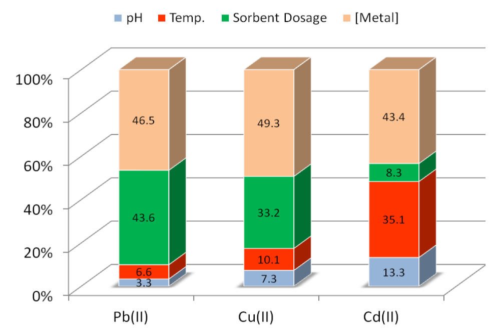

Fig. 2. Percentage of contribution of factors in the sorption efficiency.

The analysis of experimental results based on *S/N* ratios provides the optimal factor levels for the highest *S/N* response. Table 5 shows information on the optimal level of each factor after checking the response curves (Fig. 1) of sorption efficiency and *S/N* ratio for metal adsorption onto globe artichoke biomass. The suggested conditions for the optimal removal efficiency of Pb(II), with a predicted q_e of 85.6 mg.g^{-1}, were: factor A (pH) at level 3 (5.0), factor B (temperature) at level 2 (30 ºC), factor C (sorbent dosage) at level 1 (0.5 g.L^{-1}) and factor D (initial Pb(II) concentration) at level 3 (50 mg.L^{-1}). For optimal Cu(II) adsorption with agrowaste biomass from artichoke the suggested conditions were: factor A (pH) at level 3 (5.0), factor B (temperature) at level 2 (30 ºC), factor C (sorbent dosage) at level 2 (1.0 g.L^{-1}) and factor D (initial Cu(II) concentration) at level 2 (30 mg.L^{-1}), with a predicted q_e of 24.1 mg.g^{-1}. The suggested optimal operating conditions for Cd(II) adsorption were: factor A (pH) at level 3 (5.0), factor B (temperature) at level 2 (30 ºC), factor C (sorbent dosage) at level 2 (1.0 g.L^{-1}) and factor D (initial Cu(II) concentration) at level 3 (50 mg.L^{-1}), with a predicted q_e of 36.0 mg.g^{-1}. The sorption efficiencies in experiments performed under the suggested optimal operating conditions (Table 5) showed negligible differences from their predicted values.

Table 5.

Predicted optimal q_e values and results (mean ± SD, n=3) of confirmation experiments.

Metal ion	Optimal Level of Parameters	*S/N*	q_e predicted ($mg.g^{-1}$)	q_e experimental ($mg.g^{-1}$)
Pb(II)	A3 B2 C1 D3	38.8	85.6	86.2 ± 0.6
Cu(II)	A3 B2 C2 D2	29.4	24.1	24.4 ± 0.4
Cd(II)	A3 B2 C2 D3	36.1	36.0	35.8 ± 0.4

Fourier−transform infrared spectroscopy (FTIR) was used for the qualitative analysis of the main functional groups involved in metal binding. Fig. 3 shows the FTIR spectra of the artichoke biomass before and after the sorption process. The spectra exhibit a broad and intense band around 3280 cm^{-1} corresponding to the stretching vibration of the O−H and N−H groups. After interaction with the metal ions, this band shifted to 3320 cm^{-1}. A band around 1600 cm^{-1} was registered, which is characteristic of the stretching vibrations of carboxylic groups, and was moved to 1640 cm^{-1} after the sorption process. These results are in line with previously reported works that establish that both hydroxyl and, mostly, carboxylic groups play a crucial role in the binding process of metal ions on lignocellulosic substrates (Zhong et al. 2012; Basu et al., 2015). A band was also observed around 1240 cm^{-1}, it was was assigned to the stretching vibration of the C−S bound, which is characteristic of sulphonic acid. This suggests that sulfonate groups would also be involved in the sorption process.

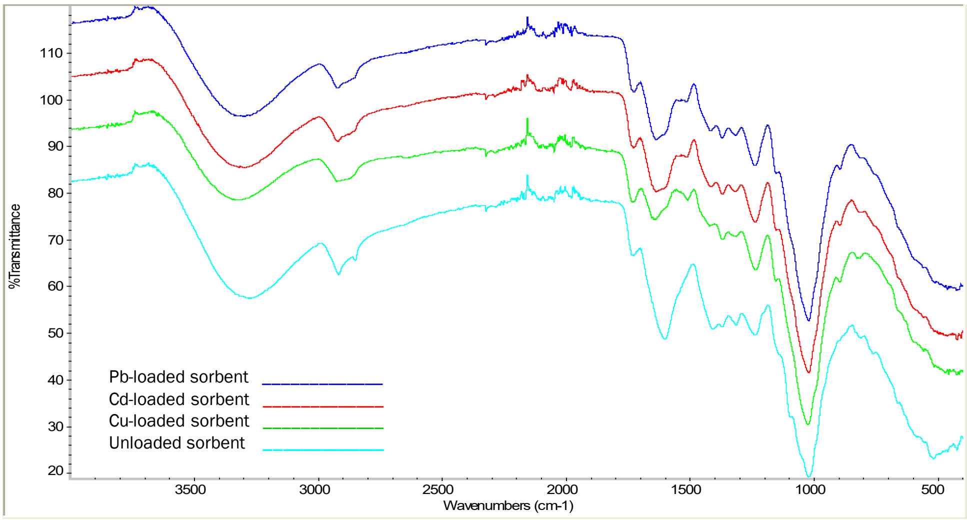

Fig. 3. FTIR spectra of the sorbent biomass before and after metal sorption

3.3. Sorption isotherms

Isotherm models are essential for establishing the most appropriate sorption equilibrium behavior, which is indispensable for the reliable prediction of sorption parameters and a quantitative comparison of novel sorbent behavior for different experimental conditions. This modeling is critical to obtain information about sorption mechanism, expression of the surface properties and sorbent capacity (Wasewar et al., 2008). Sorption isotherms describe the equilibrium distribution of the metal ions between the solid (sorbent biomass) and liquid phases: sorption capacity is plotted *vs.* the residual metal concentration in the liquid phase.

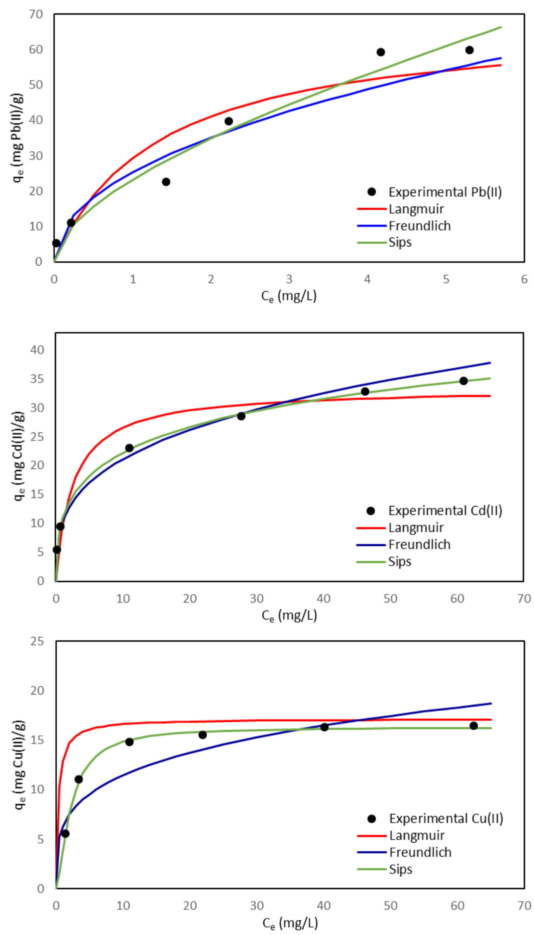

Fig. 4. Sorption isotherms for Pb(II), Cd(II) and Cu(II) bioadsorptive removal using agrowaste biomass from globe artichoke.

Fig. 4 shows the adsorption capacity of the sorbent as a function of the solution equilibrium concentration of Pb(II), Cu(II) and Cd(II). The suggested optimal operating conditions of the Taguchi approach were used in these experiments. The equilibrium sorption isotherms are important for characterizing the sorption capacity and ascertain the mechanism of adsorption onto the artichoke agrowaste sorbent. The sorption process was quantified from the equilibrium parameters obtained by fitting the experimental data using the most commonly used mathematical models: Langmuir, Freundlich and Sips (Vijayaraghavan et al., 2006; Foo and Hameed, 2010; Tang et al., 2018), which correspond to both homogeneous (Langmuir) and heterogeneous (Freundlich, Sips) sorbent surfaces (Zolfaghari et al., 2011).

Table 6 presents the values of the relative constants for the three models considered. The Langmuir constant (K_L) provides information about the affinity of the sorbent for the metal ions and is further used to calculate the dimensionless separation factor (R_L), defined by Weber and Chakravorti (1974), and expressed by Eq. (9):

$$R_L = \frac{1}{1 + K_L \cdot C_0} \tag{9}$$

where C_0 is the initial metal ion concentration. When $0 < R_L < 1$ the sorption process is thermodynamically favorable. The three metal ions investigated showed R_L values ranging from 0.02 to 0.31 for the whole concentration range, confirming the favorable uptake by the artichoke agrowaste biomass. The maximum adsorption capacities for Pb(II), Cu(II) and Cd(II) expressed by the Langmuir coefficient q_{max} shows that the adsorption capacity increased in the sequence Cu(II) (27.2 mg.g^{-1}) < Cd(II) (43.3 mg.g^{-1}) < Pb(II) (88.5 mg.g^{-1}). The three metal ions investigated in this study are divalent, and the sequence can be directly correlated with their increasing atomic radii (0.128, 0.154 and 0.175 nm, respectively) (Sulaymon et al., 2013). The selectivity of metal sorption can also be linked to the hydration energies of the metal ions Pb(II) (−1481 kJ.mol^{-1}), Cd(II) (−1807 kJ.mol^{-1}) and Cu(II) (−2100 kJ.mol^{-1}) (Benettayeb et al., 2017). Despite all this, it should not be forgotten that in the analysis of the sorption capacity, the characteristics of the sorbent are the most important factor to be considered.

The high degree of fitness of Langmuir model on the experimental data of Cd(II) and Cu(II), supported by the high R^2 coefficient values (>0.98), illustrates that monolayer adsorption is the main sorption process in these two metal ions (Li et al., 2017).

Table 6.

Sorption isotherms. Parameters of the Langmuir, Freundlich and Sips models

		Pb(II)	***Cd(II)***	***Cu(II)***
Langmuir	q_{max} $(mg.g^{-1})$	88.5 ± 0.9	44.3 ± 0.4	27.2 ± 0.4
	K_L $(L.mg^{-1})$	0.75 ± 0.07	0.39 ± 0.08	3.0 ±0.2
	R^2	0.738	0.989	0.989
Freundlich	K_F $(mg^{\frac{n-1}{n}}.g^{-1}.L^{1/n})$	35.3 ± 0.8	11.3 ± 0.7	9.9 ± 0.8
	n	2.1 ± 0.6	3.2 ± 0.6	3.8 ± 0.7
	R^2	0.970	0.997	0.848
Sips	K_S $(mg^{1-\beta}.g^{-1}.L^{\beta})$	23.8 ± 0.5	12.6 ± 0.5	5.0 ± 0.4
	β_s	0.6 ± 0.1	0.4 ± 0.1	1.5± 0.2
	a_s $(L.mg^{-1})^{\beta}$	0.03 ± 0.01	0.17 ± 0.05	0.30 ± 0.08
	R^2	0.978	0.999	0.999

The Freundlich coefficient, K_F, which describes the sorption capacity, was found to increase in the order Cu(II) (9.9 mg.g^{-1}) < Cd(II) (11.3 mg.g^{-1}) < Pb(II) (35.3 mg.g^{-1}), which agrees with that established by the Langmuir coefficient q_{max} (Table 6). The empirical parameter $1/n$, derived from the Freundlich equation provides information on the sorption intensity (Karnitz et al., 2007) and the heterogeneity of the sorption process. A variation of 0 to 1 in $1/n$ is associated with a chemisorption process that become more heterogeneous as the value gets closer to 0. The values of $1/n$ increased in the order Cu(II) (0.26) < Cd(II) (0.31) < Pb(II) (0.47), which illustrates the favorable adsorption conditions, whilst simultaneously revealing the highest heterogeneity for the sorption of Cu(II).

The Sips isotherm model is suitable for predicting adsorption on heterogeneous surfaces, thereby avoiding the limitation of increased adsorbate concentration normally associated with the Freundlich model. Therefore, when metal ion concentrations are low this model reduces to the Freundlich model, but at high metal ion concentrations it predicts the Langmuir model. The K_S coefficient, which is directly related to the sorption capacity, also increased in the order Cu(II) <

Cd(II) < Pb(II). Comparatively higher R^2 values ($0.978<R^2<0.999$) among the tested isotherms, suggest that the sorption equilibrium data can be best explained by Sips isotherm (Fig. 4).

3.4. Sorption kinetics

The rate of sorption of a metal ion onto a surface can be expressed in the same manner as any other kinetic process. Kinetic studies are essential for estimating the time dependence of the sorption process, to investigate the rate controlling steps, and to obtain valuable insights into the sorption mechanism. Sorption kinetics can be determined for several stages including bulk diffusion, film diffusion, intraparticle diffusion, and the proper reaction rate (Reddad et al., 2002). In general, the sorption rate depends on: 1) the chemical composition, structural properties and active sites of the sorbent; 2) the concentration of the metal ion and its diffusion on the sorbent; and 3) experimental conditions such as temperature, pH and stirring speed (Lezcano et al., 2011). All the kinetic experiments were performed for different contact times in the optimal conditions suggested for each metal ion by the Taguchi approach.

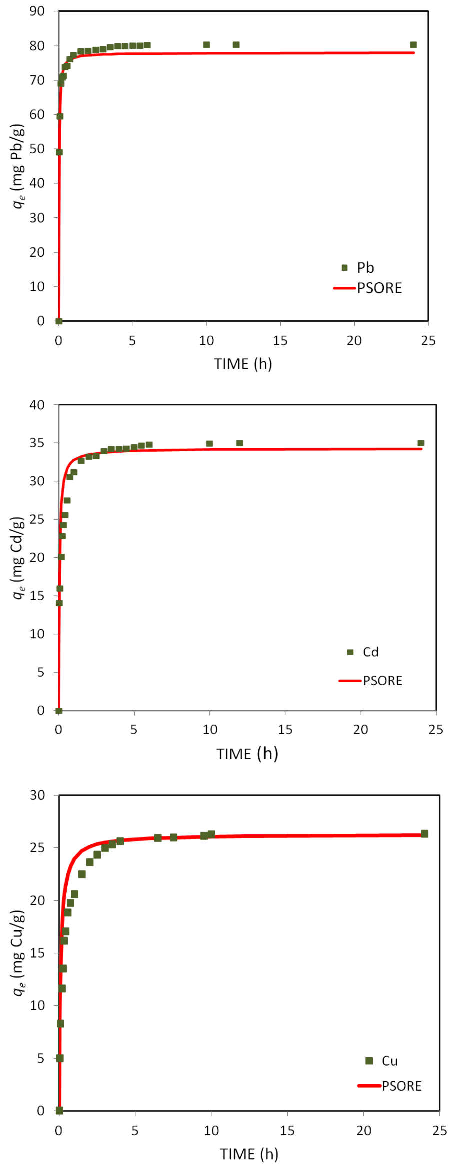

Fig. 5. Kinetics of Pb(II), Cd(II) and Cu(II) sorption by agrowaste biomass from globe artichoke.

As illustrated in Fig. 5, the adsorption edge experienced a fast stage in the initial 60 min and then slowed down until the sorption reached equilibrium at 2.5 h. The rapid sorption rates could be attributed to surface sorption which is facilitated by the free active sites at the sorbent surface. As these active sites are occupied, the sorption process slowed down and the sorption rates were limited by diffusion processes. The results revealed that, irrespective of the metal ion assayed, the sorption process reached equilibrium in about 2.5 hours (Fig. 5). Typically, 93-96 % of the ultimate adsorption occurred within this time.

Lagergreen equation (PFORE, pseudo-first-order kinetic model), Ho and McKay equation (PSORE, pseudo-second-order kinetic model) and Weber and Morris equation (IPD, intraparticle diffusion model) were used for investigating the controlling mechanism of Pb(II), Cd(II) and Cu(II) adsorption on artichoke agrowaste biomass. It was proved, according to the R^2 coefficient, that intraparticle diffusion model does not fit the results. Uptake-kinetic parameters and coefficients of determination (R^2) corresponding to PFORE and PSORE models are listed in Table 7. PSORE model predicted maximum adsorbed amounts relatively close to the experimental ones for the three metal ions investigated, and also this model provided higher coefficients of determination ($0.944 < R^2 < 0.989$) than the pseudo-first order model. This result confirms that PSORE model best describes the sorption process of Pb(II), Cu(II) and Cd(II), which suggests that the bioadsorptive removal of these metal ions by artichoke agrowaste biomass involves chemisorption related to valence forces through electron exchange or sharing.

Table 7.

Uptake kinetic-modeling parameters (mean ± SD) of PFORE and PSORE models.

Metal ion	**Pseudo first-order**			**Pseudo second-order**		
	q_e ($mg \cdot g^{-1}$)	k_1 (h^{-1})	R^2	q_e ($mg \cdot g^{-1}$)	k_2 ($g \cdot mg^{-1} \cdot h^{-1}$)	R^2
Pb(II)	19.2 ± 0.4	0.33 ± 0.05	0.783	78.3 ± 0.8	0.65 ± 0.07	0.966
Cd(II)	13.6 ± 0.3	0.85 ± 0.07	0.921	34.3 ± 0.6	0.68 ± 0.08	0.944
Cu(II)	10.2 ± 0.3	0.50 ± 0.06	0.930	26.3 ± 0.6	0.39 ± 0.05	0.989

4. Conclusions

There is a great deal of ongoing research into the use of inexpensive lignocellulosic biomass from agrowastes and by-products as an environmentally friendly alternative sorbent for removing pollutants from aquatic systems. This study has shown that agroindustrial waste biomass from globe artichoke can be effective for the bioremoval of Pb(II), Cu(II) and Cd(II) ions from aqueous solutions. The FTIR spectrum of the sorbent indicated the presence of alcoholic, carboxylic, sulphonic and amine groups which are responsible for the chemisorption processes. The Taguchi approach has proved to be a reliable tool for improving the sorption process by providing a systematic, simple and suitable methodology. This approach facilitated understanding of the interaction of four factors (pH, temperature, sorbent dosage and initial metal concentration) at three levels each with a reduced number of experiments, and suggested optimal operating conditions for each metal ion. The initial metal concentration made the highest percentage contribution to the sorption of the three metal ions studied (43−49 %). In the optimal operating conditions, the sorbent showed a greater sorption capacity for Pb(II) (86.2 mg.g^{-1}) than for Cd(II) (35.8 mg.g^{-1}) and Cu(II) (24.4 mg.g^{-1}). The Sips model better fitted the equilibrium isotherm for the three metal ions investigated. The pseudo-second order kinetic model, which was best model for describing the sorption behavior for all the metal ions, indicated that chemical sorption was the rate-controlling mechanism. However, it should be noted that metal adsorption onto agricultural wastes is a rather complex process influenced by numerous factors. The results of this study confirm that Taguchi methodology is a suitable tool for enhancing the bioremoval capacity of heavy metals by artichoke agrowaste biomass, a sorbent potentially suitable for removing Pb(II), Cu(II) and Cd(II) from aqueous solutions. Desorption studies are currently being finalized, which will allow the reusability of the biomass and the metals recovery in order to achieve the improvement of the system´s overall sustainability.

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