

## Special Edition

# Optimization of Pb<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup> and Ba<sup>2+</sup> adsorption onto light expanded clay aggregate (LECA)

Otimização da adsorção de íons Pb<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup> e Ba<sup>2+</sup> em argila expandida (LECA)

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## ABSTRACT

The possibility of Pb<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup> and Ba<sup>2+</sup> ions removal from aqueous solution using light expanded clay aggregate (LECA) was investigated in this work. The central composite design (CCD) in response surface methodology (RSM) was used to optimize the operating parameters (adsorbent granulometry, adsorption time and initial metal ions concentration) to reach the maximum ions removal in single and multi-elemental solutions. After optimization, the results shows that the removal efficiency decrease following the ion sequence Pb<sup>2+</sup> > Ba<sup>2+</sup> > Cd<sup>2+</sup> > Ni<sup>2+</sup> ions. The better efficiency (~95%) is observed for the Pb<sup>2+</sup>. The Langmuir and Freundlich isotherm models were applied to the equilibrium data at room temperature. The results revealed that data on LECA was very well fitted with Langmuir equations. The real interest of this work is to demonstrate that a simple material such as LECA can be used to remove extremely small levels of toxic metals, such as those found in drinking water. So our results could be the starting point for the development of a low-cost filtration system to remove toxic metals.

**Keywords:** Adsorption; Toxic Metals; Light Expanded Clay Aggregate

## RESUMO

Este trabalho investiga a possibilidade de remoção de íons Pb<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup> e Ba<sup>2+</sup>, em soluções aquosas, utilizando Argila Expandida (LECA). Os experimentos de adsorção foram estabelecidos por um Planejamento Composto Central (CCD) onde através das Superfícies de Resposta (RSM) foram otimizados os parâmetros de adsorção, tais como: granulometria do material adsorvente, tempo de adsorção e concentração inicial dos íons metálicos a serem removidos. Os experimentos de adsorção foram realizados em soluções multielementares e também em soluções contendo apenas um metal em

questão. Os resultados mostraram que a eficiência de adsorção, pela argila expandida, decresce em eficiência segundo a sequência de metais Pb<sup>2+</sup> > Ba<sup>2+</sup> > Cd<sup>2+</sup> > Ni<sup>2+</sup>, sendo a melhor eficiência de remoção encontrada para o íon Pb<sup>2+</sup>. Os resultados foram ajustados segundo os modelos para as isotermas de Langmuir e Freundlich, sendo o de Langmuir o que mais se adequou aos valores de metais adsorvidos em LECA. O real objetivo deste trabalho foi demonstrar que um material simples e barato, como a argila expandida, pode ser usado para remover níveis extremamente pequenos de metais tóxicos, como os encontrados em água potável. Portanto, nossos resultados podem ser o ponto de partida para o desenvolvimento de um sistema de filtragem de baixo custo para remover metais tóxicos de sistemas de abastecimento.

**Palavras-chave:** Adsorção; Metais tóxicos; Argila Expandida

## 1 INTRODUCTION

The release of industrial effluents and domestic wastewater, containing potentially toxic metals, into water bodies has become one of the major environmental concerns nowadays. The most commonly found toxic metals in wastewater include arsenic, barium, cadmium, chromium, copper, lead, nickel, and zinc. Although a few metals are essential for human health, an excess amount of these materials can have negative effects, even at very low concentrations (AKPOMIE *et al.*, 2015; HANI, 2009; RAI and TRIPATHI, 2008). The main problem is that the human body cannot totally discharge these metals and they continue amassing inside it, which can cause harm to the brain, lungs, liver, kidneys, and other vital organs. In addition, heavy metals are also known as carcinogenic materials.

Unfortunately, the presence of these materials is not exclusive to domestic and industrial rejects and is often found in drinking water. Potable water sources, such as surface, groundwater and seawater, are likely to be polluted by toxic metals, which are not entirely removed by conventional treatment systems. Therefore, it is necessary to use advanced methods to remove these metals, even in very low concentrations.

In order to improve water quality for human supply, several treatment techniques have been used to remove these potentially toxic metals, such as filtration, ion exchange, membrane processes, electrocoagulation, biofiltration and

biological oxidation (INCE and KAPLAN, 2019; GUNATILAKE and MULTIDISCI, 2015). However, most of these methods are high operational and maintenance costs. Based on this, the use of adsorbent materials, for toxic metal removal, has been considered as a better alternative in water and wastewater treatment because of convenience, low cost and high efficiency.

In particular, natural adsorbent materials, such as biomass and mineral clays, are very promising due to their high ability to interact with chemical functional groups present in the polluting waste molecules.

The use of clay minerals as adsorbent materials has received a lot of attention due to their high efficiency, low cost, high cation exchange capacity, large specific contact area, chemical stability and non-toxicity. Several studies report the effectiveness of clay application in the adsorption of various contaminants compounds, such as in the removal of pesticides, potentially toxic metal ions, organic compounds and textile dyes (ASHIQ *et al.*, 2021; EL KASSIMI *et al.*, 2021; DASGUPTA *et al.*, 2021; ĐUKIĆ *et al.*, 2013; ZAGHLOUL *et al.*, 2021; HIRADE *et al.*, 2021).

In particular, light expanded clay aggregate (LECA) is a material widely used in gardening for soil moisture retention and has been also used for treating water, for human consumption, and wastewater (HAQUE *et al.*, 2008; SHOJAEIMEHR *et al.*, 2014; AMIRI *et al.*, 2011; YAGHI and HARTIKAINEN H., 2018.; FERREIRA *et al.*, 2017, SHARIFNIA *et al.*, 2016). LECA is produced by burning clay aggregates in high temperatures, which causes them to expand, leading to a very porous material with high mechanical and thermal resistance (SHOJAEIMEHR *et al.*, 2014). Expanded clay also has a characteristic to be very reactive, which is related to their surface charge and their pH interdependence; at lower pH their charge is predominantly positive and at high pH is negative (AMIRI *et al.*, 2011).

The use of LECA as adsorbents for water and effluents treatment has shown great relevance due to their high adsorption capacity and low maintenance costs (HAQUE *et al.*, 2008; SHOJAEIMEHR *et al.*, 2014; AMIRI *et al.*, 2011; YAGHI and

HARTIKAINEN H., 2018.; FERREIRA *et al.*, 2017, SHARIFNIA *et al.*, 2016). Based on this, in this article, we report the use of LECA as adsorbent for Pb<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup> and Ba<sup>2+</sup> from aqueous solutions. The interest of this work is to demonstrate that a simple material such as LECA can be used to remove extremely small levels of toxic metals, such as those found in drinking water.

## 2 MATERIALS AND METHODS

The raw material used for adsorbent was commercial light expanded clay aggregate such as showed in the Figure 1.

Figure 1 – Commercial light expanded clay aggregate



Source: Authors, 2021

Those balls were crushed with a subsequently attendant increase in surface area and population of particles. The particle size distribution of crushed granules was performed using an electromagnetic sieve shaker with the larger sieve on top from 4# to 100# sieve (4#, 10#, 16#, 30#, 40#, 48#, 50#, 80# and 100#). Each sieve, along with the retained particles was characterized individually after shaking.

The microstructural, chemical and mineralogical characterization of expanded clay were performed using a Scanning Electron Microscopy (SEM), Energy Spectroscopy (EDS) and X-ray Powder Diffraction (XRD), respectively.

The multi-elemental stock solution containing the metals ions  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Ni^{2+}$  and  $Ba^{2+}$  at  $125\text{ mg}\cdot\text{L}^{-1}$  (each one) was prepared using chloride salts of these metals:  $BaCl_2\cdot 2H_2O$  (MERCK, 99,98%),  $CdCl_2\cdot 2H_2O$  (MERCK, 99,95%),  $NiCl_2\cdot 6H_2O$  (MERCK, 98,96%) and  $PbCl_2\cdot H_2O$  (MERCK, 99,95%) and ultra-pure water. An elementary stock solution at  $125\text{ mg}\cdot\text{L}^{-1}$  was also prepared for each individual metal ion. All stock solutions were prepared without adjusting the pH.

The central composite design (CCD) in response surface methodology (RSM) was used to optimize the operating parameters for the maximum removal of  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Ni^{2+}$  and  $Ba^{2+}$  ions. CCD was applied to investigate the effects of three independent variables, such as, adsorbent granulometry ( $X_1$ ), absorption time ( $X_2$ ) and initial metal ions concentration ( $X_3$ ). The levels of each designed variable are illustrated in Table 1, selected based on preliminary experiments. Each significant variable was examined at five levels ( $-\alpha$ ,  $-1$ ,  $0$ ,  $+1$ ,  $+\alpha$ ).

Table 1 – Designed variables and their coded and actual values used for experimental design ( $\pm\alpha$ : axial points)

Variable	Symbol	Actual value of coded level				
		$-\alpha$ ( $-2$ )	Low ( $-1$ )	Central ( $0$ )	High ( $+1$ )	$+\alpha$ ( $+2$ )
Adsorbent granulometry (#)	$X_1$	4	20	48	75	100
Absorption time (min)	$X_2$	10	20	35	50	60
Initial ions concentration ( $\text{mg}\cdot\text{L}^{-1}$ )	$X_3$	6	30	65	100	125

Source: Authors, 2021

In Table 2, the 17 experiments are presented based on five levels and 3 variables, including eight orthogonal design points (23 full factorial design), 6 star points to form a CCD with  $\alpha=2$ . In order to define experimental error, three replications were made at the central values.

In this study, the Statistica 7.0 software, by StatSof was used to construct the experimental design. In order to refine our results, after running the 17 experiments listed below, we decide to fix the initial ion concentration at the

central value of 65 mg/L<sup>-1</sup>, varying the adsorbent granulometry (X<sub>1</sub>) and the absorption time (X<sub>2</sub>). The levels of each designed variable are shown in Table 3.

Table 2 – CCD of three variables

Runs	Coded values of independent variables		
	X <sub>1</sub> (#)	X <sub>2</sub> (min)	X <sub>3</sub> (mg L <sup>-1</sup> )
1	20 (-1)	20 (-1)	30 (-1)
2	75 (+1)	20 (-1)	30 (-1)
3	20 (-1)	20 (-1)	100 (+1)
4	75 (+1)	20 (-1)	100 (+1)
5	20 (-1)	50 (+1)	30 (-1)
6	75 (+1)	50 (+1)	30 (-1)
7	20 (-1)	50 (+1)	100 (+1)
8	75 (+1)	50 (+1)	100 (+1)
9	48 (0)	35 (0)	65 (0)
10	48 (0)	10 (-α)	65 (0)
11	48 (0)	60 (+α)	65 (0)
12	48 (0)	35 (0)	6 (-α)
13	48 (0)	35 (0)	125 (+α)
14	4 (-α)	35 (0)	65 (0)
15	100 (+α)	35 (0)	65 (0)
16	48 (0)	35 (0)	65 (0)
17	#48 (0)	35 (0)	65 (0)

Source: Authors, 2021

Table 3 – Designed variables and their coded and actual values used for experimental design (±α: axial points)

Variable	Symbol	Actual value of coded level		
		Low (-1)	Central (0)	High (+1)
Adsorbent granulometry (#)	X <sub>1</sub>	20	30	80
Absorption time (min)	X <sub>2</sub>	20	30	40

Source: Authors, 2021

Table 4 shows the 11 experiments, including four orthogonal design points (23 full factorial design), four star points to form a CCD with  $\alpha=1$  and three replications at the central values.

Table 4 – CCD of two variables

Runs	Coded values of independent variables	
	X <sub>1</sub> (#)	X <sub>2</sub> (min)
1	20 (-1)	20 (-1)
2	80 (+1)	20 (-1)
3	20 (-1)	20 (-1)
4	80 (+1)	20 (-1)
5	12 (-1)	50 (+1)
6	100 (+1)	50 (+1)
7	30 (-1)	50 (+1)
8	30 (+1)	50 (+1)
9	30 (0)	35 (0)
10	30 (0)	10 (- $\alpha$ )
11	30 (0)	60 (- $\alpha$ )

Source: Authors, 2021

The amount of Pb<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup> and Ba<sup>2+</sup> adsorption per unit mass of adsorbent and removal efficiency were calculated using the equations 1 and 2, respectively:

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (1)$$

$$\text{Removal efficiency (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where  $q_e$  is the adsorption capacity (mg/g),  $C_0$  is the initial concentration of ions (mg/L) in the solutions and  $C_e$  is final concentration of ions in the solutions (mg/L),  $V$  is the volume of solutions (L), and  $m$  is the mass of LEICA powder (g).

The kinetic studies of Pb<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup> and Ba<sup>2+</sup> adsorption on the LEICA powder were carried out to determine the influence of concentration and temperature on the rates of adsorption reaction. To do so, the data were analysed using the Langmuir and Freundlich adsorption isotherms in which mathematical equations are used to describe the relationship between the adsorbed and the absorbent. Isotherms are also used to determine the required amount of absorbent material. The Langmuir equation is the most widely used two-parameter model, commonly expressed by the equation:

$$\frac{C}{q} = \frac{1}{q_{max}K_{ads}} + \frac{C}{q_{max}} \quad (3)$$

where C is the equilibrium concentration of metal ion remaining in the solution (mgL<sup>-1</sup>), q is the amount of adsorbate adsorbed per mass unit of adsorbent at equilibrium (mgkg<sup>-1</sup>),  $q_{max}$  and  $K_{ads}$  are Langmuir constants.

Freundlich isotherm is shown the following:

$$\log(q) = \frac{1}{n}\log(C) + \log(k_f) \quad (4)$$

where C and q have the same meaning as in equation 3;  $k_f$  and  $1/n$  are constants that are considered to be relatively indicators of adsorption capacity and adsorption intensity, respectively.

The experiments were taken in different Erlenmeyer flasks, 50 mL of dye solution of known concentration with definite pH and known amount of adsorbent was taken at 25°C at fixed agitation speed.

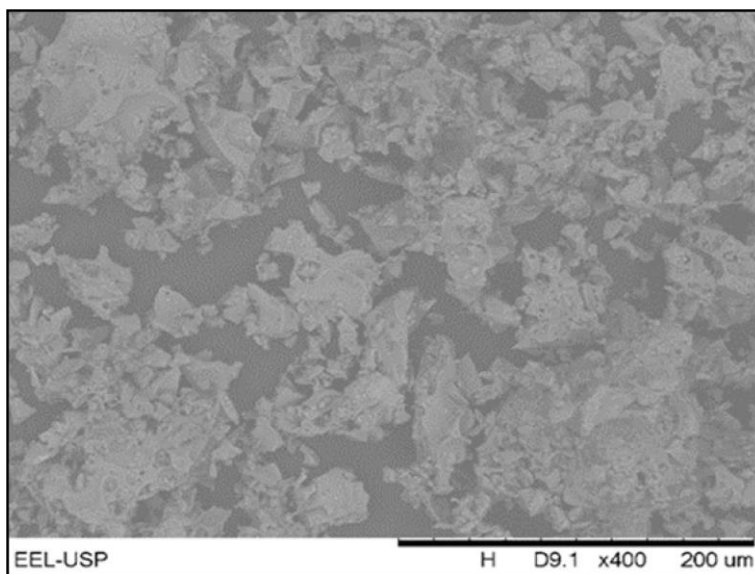
The elemental ratio in all the experiments were analyzed using MP-AES (microwave plasma atomic emission spectroscopy, Agilent 4200, USA) after digestion with HNO<sub>3</sub> and HCl. Sample replicates, reagent blanks, and standard samples with known concentrations were included in each batch of analysis to ensure its quality.



### 3 RESULTS AND DISCUSSION

Figure 2 shows the SEM image of LECA powder. The images captured from LECA powder surface confirm the high porosity of the particles. Moreover, LECA composition was characterized using EDS analysis. Accordingly, the most part of LECA composition was O (58.68 %w), Mg (2.16%w), Al (9.96%w), Si (21.19%w) and Fe (5.01%w).

Figure 2 – SEM image of LECA powder

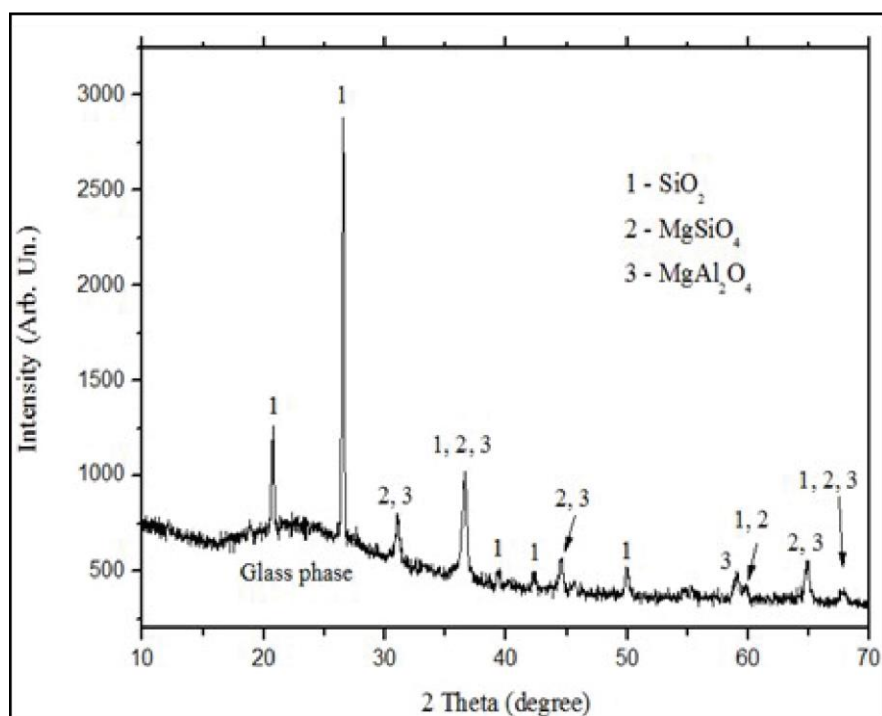


Source: Authors, 2021

Figure 3 shows the X-ray Powder diffractogram and the main chemical phases of LECA, such as silica ( $\text{SiO}_2$ ) in the  $\alpha$ -quartz form,  $\text{MgSiO}_4$  and the spinel  $\text{MgAl}_2\text{O}_4$ . In the diffractogram, an elevation of the line can be observed between approximately  $15^\circ$  and  $30^\circ$ , indicating the presence of amorphous phases in the expanded clay.

Table 5 shows the adsorption results for the 17 experiments, design in tables 2 and 4, for the multi-elemental and elementary solutions. It can be observed that the adsorption capacities vary strongly depending on the values of the influential factors.

Figure 3 – X Ray Powder Diffraction of LECA



Source: Authors, 2021

Regarding to the analyzed multi-element solution, except for the Pb<sup>2+</sup>, the values presented in Table 5 shows low removal efficiency. The Pb<sup>2+</sup> ions showed the best removal rates, followed by the Ba<sup>2+</sup> and Cd<sup>2+</sup> ions, while the Ni<sup>2+</sup> ion present the lower removal rate. As it is well known, the co-presence of metals led to a decrease in the sorption of ions due to competition for adsorption sites (HE *et al.*, 2020). So, the increased competition between metal ions for the available permanent negative sorption sites is responsible for the low removal efficiency. Although competition reduced sorption of the two metals, the magnitude of this effect was different for each one Ba<sup>2+</sup>, Cd<sup>2+</sup> and Ni<sup>2+</sup> ions.

For elementary solutions, the removal efficiency increase for the Ba<sup>2+</sup>, Cd<sup>2+</sup> and Ni<sup>2+</sup> ions, but still low. The better efficiency is observed for the Pb<sup>2+</sup>, which reaches 100% in some experiments.

Based on the results of table 5, shown in the last section, an optimized batch of experiments was done fixing the initial ion concentration of 65 mg L<sup>-1</sup>, following the CCD of two variables presented in Table 4.

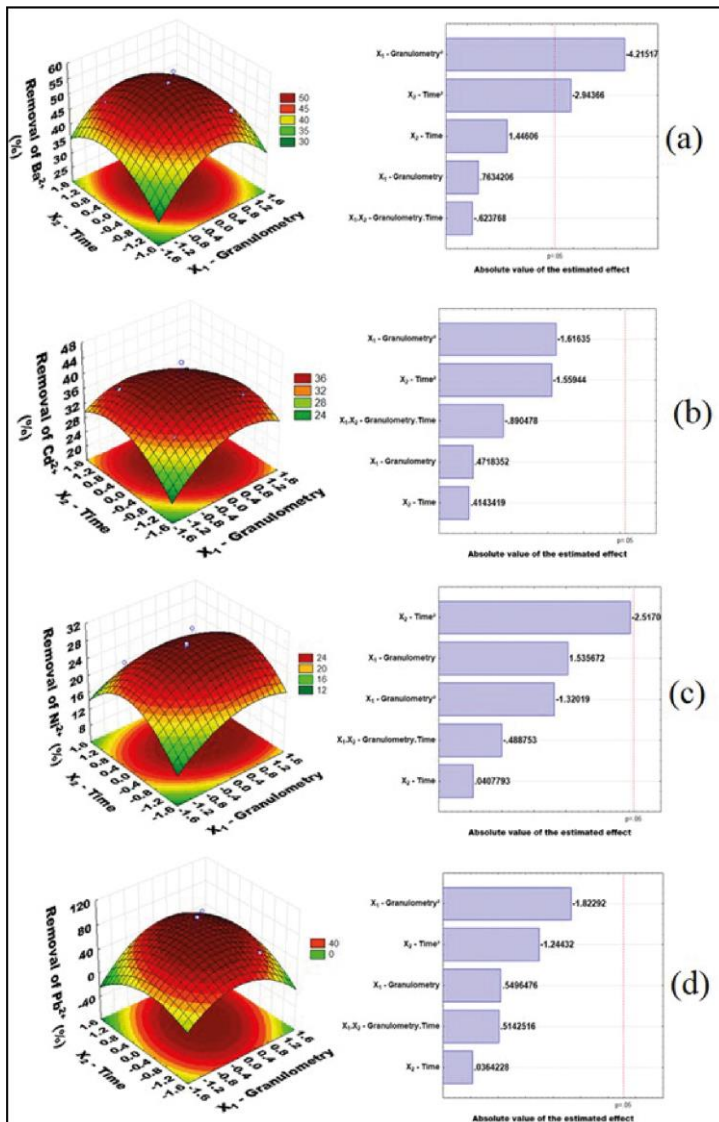
Three dimensions (3D) surface plots are employed in order to show the interaction between two variables better. The combine effect of absorption time and granulometry in the  $Pb^{2+}$ ,  $Ba^{2+}$ ,  $Cd^{2+}$  and  $Ni^{2+}$  ions is exhibited in Figure 4 and 5. To highlight the statistical significance of the two variables, these figures also shows the Pareto chart of all ions.

Table 5 – Adsorption efficiency for the CCD of three variables

Runs	<i>Removal efficiency (%)</i>				<i>Removal efficiency (%)</i>			
	Multi-Elemental solution				Elementary solution			
	Ba <sup>2+</sup>	Cd <sup>2+</sup>	Ni <sup>2+</sup>	Pb <sup>2+</sup>	Ba <sup>2+</sup>	Cd <sup>2+</sup>	Ni <sup>2+</sup>	Pb <sup>2+</sup>
1	31.33	5.50	2.33	92.50	29.17	32.00	15.50	95.17
2	34.33	11.01	9.38	93.50	35.83	35.67	20.33	98.00
3	29.6	20.02	2.45	54.05	27.85	50.45	16.55	73.25
4	29.15	17.25	1.55	62.20	29.35	49.45	16.50	69.60
5	31.00	9.82	1.67	95.33	30.83	32.67	20.17	95.33
6	31.17	4.50	3.02	97.67	36.17	38.50	24.33	98.67
7	33.50	22.35	8.40	93.05	32.25	50.35	18.85	78.65
8	30.10	15.90	2.05	96.55	28.35	48.35	19.25	91.25
9	31.15	7.12	2.69	94.85	29.00	40.62	18.15	93.54
10	32.23	11.38	2.69	93.46	24.85	40.38	15.92	83.85
11	26.85	7.69	0.00	96.38	38.31	41.62	19.69	97.46
12	40.01	0.00	0.00	93.33	34.17	44.17	56.67	100
13	28.12	22.68	0.16	63.28	32.28	53.88	24.72	41.88
14	27.46	6.23	0.00	88.77	29.85	47.00	18.77	70.23
15	35.15	15.62	3.69	98.46	36.38	49.08	27.85	98.23
16	31.77	11.28	0.62	96.15	30.31	40.08	18.77	92.62
17	30.69	11.08	0.00	95.54	26.23	42.15	21.15	93.62

Source: Authors, 2021

Figure 4 – 3D graphs plots of effect of absorption time and granulometry on  $Ba^{2+}$  (a),  $Cd^{2+}$  (b)  $Ni^{2+}$  (c) and  $Pb^{2+}$  (d), removal percentage, for the multi-elemental solution. Pareto graphic analysis for the percentage effect of the investigated factors are also shown

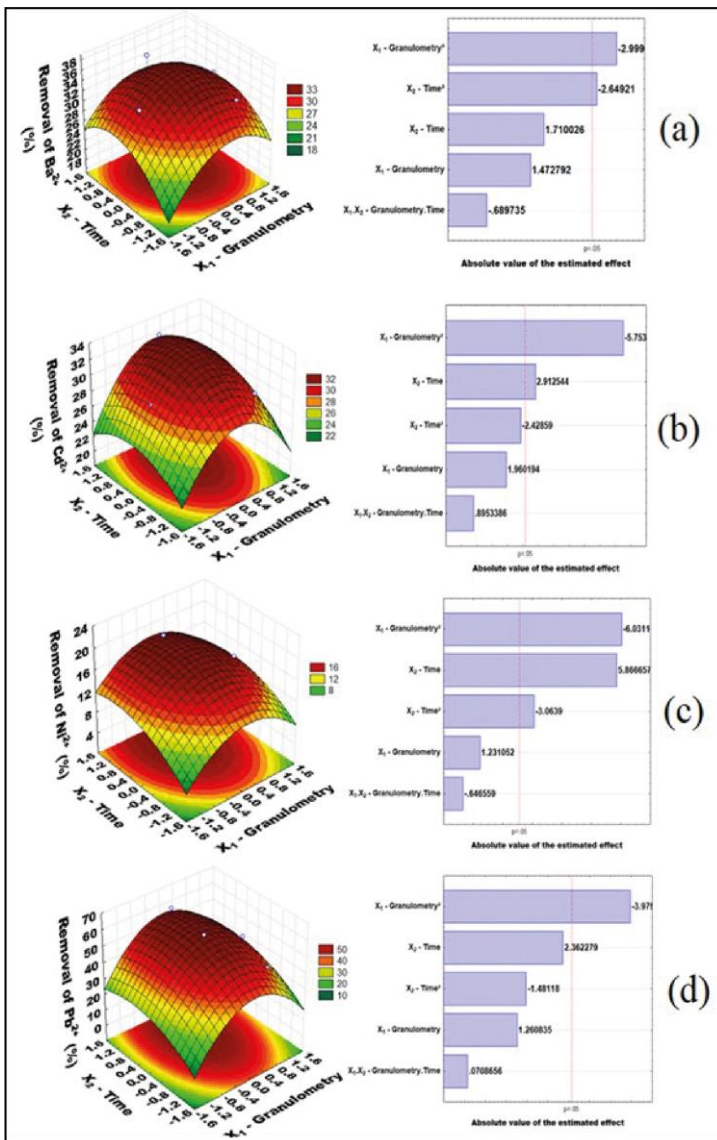


Source: Authors, 2021

Figure 5 shows the 3D graphs plots of effect of absorption time and granulometry on  $Ba^{2+}$  (a),  $Cd^{2+}$  (b)  $Ni^{2+}$  (c) and  $Pb^{2+}$  (d), removal percentage, for the elementary solution. Figure 5a indicates a quadratic behavior profiles for the absorption time and granulometry. The 3D graphs shows a maximum  $Ba^{2+}$  removal rates for granulometry of #50 and ~39 minutes of adsorption. According to the Pareto chart, granulometry  $\times$  granulometry and time  $\times$  time are the most effective

on Ba<sup>2+</sup> removal with confidence level of 95 %. For Cd<sup>2+</sup> a maximum removal rate can be obtained for granulometry of #35 and ~29 minutes of adsorption, (see figure 5b). No significant interactions were observed into a confidence level of 95 %. The same can be observed, in the figure 5c, for Ni<sup>2+</sup> removal. Finally, in Figure 5d, maximum removal of Pb<sup>2+</sup> was found to #40 and ~31 minutes of adsorption time, with no significant interactions (see the Pareto chart).

Figure 5 – 3D graphs plots of effect of absorption time and granulometry on Ba<sup>2+</sup> (a), Cd<sup>2+</sup> (b) Ni<sup>2+</sup> (c) and Pb<sup>2+</sup> (d), removal percentage, for the elementary solution. Pareto graphic analysis for the percentage effect of the investigated factors is also shown



Source: Authors, 2021

The optimal results at different granulometry and adsorption times (last section) were used to obtain Langmuir and Freundlich adsorption isotherm by using the well-known equations 3 and 4 (HE *et al.*, 2020). Table 6 shows the result of adsorption isotherm for Ba<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup> and Pb<sup>2+</sup> using a low cost LECA as adsorbent at 25°C. Comparison of R<sup>2</sup> values in Table 6 reveals that, for all ions, the adsorption data on LECA was very well fitted with both Freundlich and Langmuir equations. However, Langmuir isotherm shows to be better face to the lower value of the Freundlich constant  $n$  and also  $k_f$ .

Table 6 – Adsorption Isotherm Parameters using LECA as adsorbent material

Ions	Langmuir			Freundlich		
	Q <sub>max</sub>	K <sub>ads</sub>	R <sup>2</sup>	n	K <sub>f</sub>	R <sup>2</sup>
Ba <sup>2+</sup>	1.08	4.01	0.95	1.18	0.04	0.84
Cd <sup>2+</sup>	1.56	17.72	0.98	0.65	0.06	0.96
Ni <sup>2+</sup>	1.45	13.66	0.97	1.08	0.02	0.95
Pb <sup>2+</sup>	2.63	52.40	0.99	1.41	1.63	0.97

Source: Authors, 2021

## 4 CONCLUSIONS

The experimental investigation conducted here demonstrates that the Expanded Clay Aggregate is able to reduce concentrations of heavy metals in aqueous solutions concurrently. We recommend this material as an economical and efficient sorbent for heavy metals in uses related to the isolation of heavy metals derived from urban waste.

## ACKNOWLEDGMENTS

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