MACEIÓ - ALAGOAS
EBA 15
15° ENCONTRO BRASILEIRO SOBRE ADSORÇÃO
15th Brazilian Meeting about Adsorption

Evaluation of the effect of flow on the adsorptive process of Pb^{2+} ion in a fixed bed column using prepared adsorbent from agro-industrial residue

Carolaine de Oliveira Lima Silva, Giovanna Amaral Jorge Correia Guedes, Alex Leandro Andrade de Lucena, Marina Nunes dos Santos Silva, Marta Maria Menezes Bezerra Duarte

Department of Chemical Engineering, Federal University of Pernambuco, Postcode: 50670-420, Brazil

Abstract

The disposal of effluents contaminated with metals in the environment, without proper treatment, tends to cause serious risks to the ecosystem and public health, as these have a cumulative and toxic effect. Bearing in mind that conventional treatments have low efficiency for removing metal ions, studies looking at alternatives have been carried out. Therefore, this work the objective to evaluate the influence of flow rate on the adsorption process of Pb^{2+} ions in a fixed bed using adsorbent prepared from peanut shells (CA_{H3PO4}). The CA_{H3PO4} is characterized by the presence of oxygenated, phenolic and carboxylic groups, a mesoporous structure and a pH_{PZC} equal to 7.2. Initially, fixed-bed columns were built in borosilicate glass, packed with CA_{H3PO4}. The solutions containing Pb^{2+} ions percolated through the bed, in an upward flow, and samples were collected at the top of the column at pre-established times. The flow rates evaluated were 3, 6 and 9 $mL \cdot min^{-1}$. The results obtained demonstrated that as the flow rate increases from 3 to 9 $mL \cdot min^{-1}$, higher adsorptive capacity values are obtained, 15.6% greater, despite the resistance to mass transfer increasing as indicated by the value of ZTM. In this way, the work demonstrates the potential use of CA_{H3PO4} in the removal of Pb^{2+} ions from aqueous media in continuous systems.

Keywords: Adsorption; Metal ions; Fixed bed; Peanut shell.

1. Introduction

The growth of urban occupation and industrial development has promoted an increase in the presence of heavy metals in aqueous media [1]. The dumping of effluents contaminated with harmful metal ions, without adequate treatment, poses serious risks to the ecosystem and health, due to their cumulative effect and toxicity [2].

Among the metals present in wastewater, lead (Pb) deserves to be highlighted as it is frequently found in effluents from batteries, metal alloys and coating industries[3,4]. The exposure or consuming these metallics ions can trigger multiple adverse biological effects on the human body, such as neurological disorders, depression, intelligence deficits and muscular atrophy[5].

In view of these harmful effects CONAMA Resolution Nº 430/2011 establishes conditions and standards for the discharge of effluents into receiving bodies, defining the maximum limit of lead ions as 0.5 $mg \cdot L^{-1}$[6].

In this way, the need for processes aimed at removing this ion from effluents before their disposal in a receiving body is highlighted. Among the treatments applied to remove metals from aqueous media, adsorption is one of the most efficient, versatile as well as easy to operate[7].

Large-scale adsorption tends to be more viable in continuous systems than in finite baths, due to its operational flexibility, high efficiency and low maintenance requirements [8]. Thus, aiming to increase the sustainability of the adsorptive process, studies have been carried out with the aim of using agricultural waste as precursors for the production of adsorbents, due to their abundance, effectiveness and renewable origin[9,10].

Among agro-industrial waste, peanut shells stand out, since in Brazil peanut (*Arachis hypigaea Linn*) is one of the main oilseeds cultivated in the country, reaching 893.2 thousand tons in the 2022/2023 harvest [11].

The peels represent Around 30% of the legume, and are 80% fiber, which makes it suitable for applications such as fuel in boilers, animal feed ingredients, among others. However, the quantity produced exceeds existing demand, making it possible to use the peels in the production of adsorbents, reintegrating them into the production chain[12].

In view if the above, the objective of this work is to evaluate the effect of flow rate on the fixed bed adsorption process of Pb^{2+} ions by peanut shells chemically activated with phosphoric acid.

2. Methodology

Stock solutions of 1000 mg·L^{-1} (4.8 mmol·L^{-1}) were prepared from $Pb(NO_3)_2$ (Dinâmica, 99%). The working solutions were obtained by diluting the stock solutions. The tests were carried out at pH 5, considering that in previous studies by the research group[13] it was found that at this pH there is no precipitation of ions, thus allowing the evaluation of only the adsorptive process. All reagents used to adjust pH and carry out the tests were of analytical grade.

The ion levels were quantified before and after the experiments in the Flame Atomic Absorption Spectrophotometer (Varian, AA 240 FS - Fast Sequencial Atomic Absorption Sprectrometer) at a wavelength of 261.4 nm. The analytical curve presented a linear range between 0.025 and 2.25 mmol·L^{-1} with a linear correlation coefficient (r) greater than 0.99, coefficient of variation (CV%) equal to 5%, limit of detection and limit of quantification of 0.004 and 0.014 mmol·L^{-1}, respectively. The adsorbed amount of the Pb^{2+} ion (adsorptive capacity q) was calculated by Equation 1.

$$q = \frac{C_0 Q}{1000 m_s} \int_0^t \left(1 - \frac{C}{C_0}\right) dt \qquad (1)$$

In which: q (mmol·g^{-1}) the adsorption capacity of the adsorbent; C (mmol·L^{-1}) the adsorbate concentration at the column outlet; C_0 (mmol·L^{-1}) the initial concentration at the column inlet; m_s (g) the amount of adsorbent in the bed; Q (mL·min^{-1}) the volumetric flow rate of the fluid phase.

The peanut shells were obtained from commercial establishments in the metropolitan region of Recife-PE/Brazil. The Chemical activation of the peanut shells with phosphoric acid followed the procedure described by Santos *et al.* (2022)[12]. The prepared adsorbents were macerated, with the aid of a mortar and pestle, and classified in particle size of 0.15-0.21 nm using a series of Tyler sieves.

Based on the characterization carried out, the presence of oxygenated, phenolic and carboxylic groups on the surface of CA_{H3PO4} was verified.

Furthermore, it was found that its structure is mesoporous and the pH at the point of zero charge (pH_{PZC}) is equal to 7.2, favorable characteristics for the adsorption of metal ions.

2.1 Fixed bed column adsorption tests

The tests were carried out in a borosilicate glass fixed bed column (30 x 0.3 cm), packed with CA_{H3PO4}. In order to obtain the fluid travel times in the system, ultrapure water was pumped in an upward flow in the column previously in each experiment. The mass/volume of solution ratio, initial concentration and minimum contact time adopted in this work were based on data obtained in finite bath tests.

The solutions were pumped, with the aid of a peristaltic dosing pump (Milan, model 202), in an upward flow, traveling through the adsorptive bed at room temperature (25 ± 2ºC). Sample collection was carried out at the top of the column, at pre-established times.

The tests to evaluate the influence of flow on the adsorptive process were carried out by varying the flow of the feed solution by 3, 6 and 9 mL·min^{-1}, f or solutions with a concentration of 2.0 mmol·L^{-1}.

Finally, to obtain the value of the Mass Transfer Zone (MTZ), the methodology developed by Geankoplis (2003)[13] was used. For this, the calculation of useful time, total time and total and useful heights is taken as a basis so that the MTZ can then be determined.

3. Results and discussion

The rupture curves obtained to study the effect of flow rate (3, 6 and 9 mL·min^{-1}) on the removal of Pb^{2+} ion from aqueous solutions by CA_{H3PO4} in a fixed bed column are shown in Figure 1.

It can be seen from Figure 1 that, as the flow rate increased, the rupture curves became steeper, with a reduction in the rupture time (t_r) and saturation time (t_s) of the bed. At the highest flow rate, there was a decreased in t_s of 15,4% in relation to the flow rate of 3 mL·min^{-1}.

According to Gama *et al.* (2022)[14], this can be attributed to the shorter residence time of the fluid in the bed and greater contact with the adsorbent.

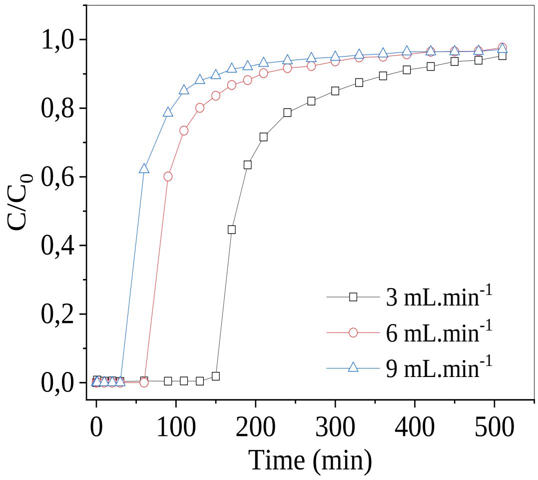

Fig.1. Effect of the feed flow rate of the Pb^{2+} ion solution on the adsorptive process in a fixed bed column. Conditions: C_0 = 2.0 mmol·L^{-1}, Q = 3, 6 and 9 mL·min^{-1}, m_S = 2.0 g, Z = 30 cm, t = 1 to 510 min.

The calculated values for t_r, t_s, q and MTZ in the evaluated flows are shown in Table 1.

Table 1. Values of t_r, t_s, q and MTZ for the study of the feed flow of Pb^{2+} ions in a fixed bed column.

Flow rate (mL·min^{-1})	t_r (min)	t_s (min)	q (mmol·g^{-1})	*MTZ*
3	150	450	0.65	9.05
6	60	330	0.72	14.00
9	30	270	0.77	18.28

From Table 1, it is possible to see that the adsorptive capacity values increased according to the increase in the feed flow, with a percentage difference between the extremes of 15.6%.

According to Asadullah *et al.* (2022)[15], this fact may be associated with the increase in the Applied flow rate, which provided faster mass transfer with a shorter residence time in the bed, enabling the occupation of active sites by the adsorbate.

Still according to Table 1, higher values for the MTZ were observed as the flow rate increased. Thus, even with greater resistance to mass transfer, the increase in flow rate enables greater occupation of sites and, consequently, an increase in adsorptive capacity values.

4. Conclusion

In view of the above, it is possible to infer that the adsorbent prepared from peanut shells (CA_{H3PO4}) is a viable material for adsorption of Pb^{2+} ions.

It was found that for the highest flow rate used in the studies, a higher adsorptive capacity value was obtained, due to a faster mass transfer with a shorter residence time in the bed, which accelerated the occupation of active sites by the adsorbate.

In view of the results obtained, it can be concluded that, similar to studies in a finite bath, the CA_{H3PO4} adsorbent presented favorable characteristics for the remediation of Pb^{2+} ions in aqueous media by an adsorption process in a fixed bed. This property adds value and can be reinserted into the production chain, making the process more sustainable.

Acknowledgements

The authors would like to thank *Nucleo de Química Analítica Avançada de Pernambuco* – NUQAAPE (FACEPE, process APQ-0346-1.06/14), the *Conselho Nacional de Desenvolvimento Científico e Tecnológico* – Brazil (CNPq) and *Programa Institucional de Bolsas de Iniciação Científica* (PIBIC) of UFPE.

References

[1] Baskaran P, Abrahan M. Adsorption of cadmium (Cd) and lead (Pb) using powdered activated carbon derived from Coco Nucifera waste: A Kinetics and equilibrium study for long-term sustainability. Sustain. Energy Technol. Assessments 2022; 53: 102709.
[2] Sharma P, Kumar S. Bioremediation of heavy metals from industrial efluents by endophytes and their metabolic activity: Recent advances. Bioresour. Technol 2021; 339: 125589.
[3] Kushwaha A, Hans N, Kumar S, Rani S. A critical review on speciation, mobilization and toxicity of lead in soil-microbe plant system and bioremediation strategies. Ecotoxicol Environ Saf 2018; 147: 1035-45.
[4] USGS - UNITED STATES GEOLOGICAL SURVEY. Mineral Commodity Sumaries: cádmium and lead. p. 50-51 and 104-105, 2023. Available in: <https://pubs.er.usgs.gov/publication/mcs2023>. Accessed in: 27/05/2023.
[5] Lima MLBS, Santos KO, Santana LSOS, Silva IRJ, Silva LEA, Lemos MCLS, Lopes RM, Junior JLP. Intoxication by heavy metals and pharmaceutical intervention. Braz J Health Rev 2021; 4(3): 11049-53.

[6] BRASIL. Ministério do Meio Ambiente. Resolução nº 430, d e13 de maio de 2011. Conselho Nacional do Meio Ambiente (CONAMA), Brasília, DF, 2011.

[7] Acorde M, Khiari B, Zagrouba F. Textile wastewater treatment by agroindustrial waste: Equilibrium modeling, thermodynamics and mass transfer mechanisms of cationic dyes adsorption onto low-cost lignocellulosic adsorbent. J Taiwan Inst Chem 2019; 96: 439-52.

[8] Vilardi G, Rodriguez-Rodriguez J, Ochando-pulido JM, Palma LD, Verdone N. Fixed-bed reactor scale-up and modeling for Cr(VI) removal using nano iron-based coated biomass as packing material. Chem Eng J 2019; 361: 990-8.

[9] Amalina F, Razak ASA, Krishnan S, Zularisam AW, Nasrullah M. The effects of chemical modification adsorbent performance on water and wastewater treatment - A review. Bioresource Technology Reports 2022; 20: 101259.

[10] Raji Z, Karim A, Karam A, Khalloufu S. A review on the heavy metal adsorption capacity of dietary fibers derived from agro-based wastes: Opportunities and challenges for practical applications in the food industry. Trends Food Sci. Technol 2023; 137: 74-91.

[11] CONAB - Companhia Nacional de Abastecimento. Acompanhamento da Safra Brasileira de Grãos, Brasília, DF, v.10 - safra 2022/2023, n. 8, Oitavo levantamento, p. 1-106, maio 2023. Available in: <https://www.conab.gov.br/info-agro/safras/graos>. Acessed in: 26/05/2023.

[12] Santos VH, Nascimento GE, Sales DCS, Santos JHL, Rodríguez-Díaz JM, Duarte MMMB. Preparation of adsorbents from agro-industrial wastes and their application in the removal of Cd^{2+} and Pb^{2+} ions from a binary mixture: Evaluation of ionic competition. Chem Eng Res Des 2022; 184: 152-64.

[13] Geankoplis CJ. Transport processes and separation process principles, 4th ed. Prentice Hall Press, 2003.

[14] Gama BMV, Sales DCS, Nascimento GE, Rodrígues-Díaz JM, Barbosa CMBM, Duarte MMMB. Modeling mono and multicomponent adsorption of phenol and cadmium from aqueous solution by peanut shell biochar. Ind Eng Chem Res 2022; 61: 18833-42.

[15] Asadullah, Kaewsichan L, Techato K, Qaisrani ZN, Chowdhuru MS, Yilmaz M. Elimination of selected heavy metals from aqueous solutions using biochar and bentonite composite monolith in a fixed-bed operation. J Environ Chem Eng 2022; 10: 106963.