Synthesis and Characterization of Alginate-Cysteine (Alg-Cys) Beads for the Removal of Naproxen from Aqueous Solutions

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Resumen

El naproxeno es un contaminante emergente que se encuentra en pequeñas cantidades en las aguas superficiales y subterráneas. Es un fármaco de uso generalizado y los procesos convencionales de tratamiento de aguas residuales no lo eliminan de manera eficiente. Sintetizamos perlas de Alg-Cys biodegradables para la adsorción de naproxeno y utilizamos los modelos de isotermas de Freundlich debido a la rugosidad y heterogeneidad de la superficie. El parámetro de Freundlich k_f fue de 16.39 (mg/g)(L/mg)^{n,} lo que indica una eficiencia de la capacidad de remoción. Nuestro trabajo presenta las perlas de Alg-Cys como un nuevo adsorbente para la eliminación de naproxeno de soluciones acuosas.

Palabras clave: naproxeno, perlas de Alg-Cys, adsorción, contaminantes emergentes

Abstract

Naproxen is an emerging contaminant found at trace amounts in surface and groundwaters. It is a widespread used drug and conventional wastewater treatment processes do not remove it efficiently. We synthesize a biodegradable Alg-Cys beads for the adsorption of naproxen and use the Freundlich isotherms models due to the roughness and heterogeneity of the surface. The Freundlich parameter k_f was 16.39 (mg/g)(L/mg)^n , indicating an efficiency of removal capacity. Our work presents the Alg-Cys Beads as a novel adsorbent for the removal of naproxen from aqueous solutions.

Keywords: naproxen, Alg-Cys beads, adsorption, emerging contaminants

1. Introduction

Naproxen, a non-steroidal anti-inflammatory drug (NSAID), is an emerging contaminant found in surface and groundwater due to its widespread use and incomplete removal during conventional wastewater treatment processes (Lach & Szymonik, 2019). The presence of naproxen in water bodies has been found at ng/L to µg/L levels, whereas is a potential risk to aquatic ecosystems and human health due to relatively high stability and lack of effective remediation strategies to mitigate its impact. Methods such as photochemical degradation seems to create compounds more toxic and persistent in the environment (Wojcieszyńska & Guzik, 2020). Adsorption, as a promising method for water treatment, has gained significant attention for the removal of pharmaceutical compounds, including naproxen, from water matrices. Adsorption involves the adherence of contaminants onto the surface of solid materials, known as adsorbents, leading to the reduction of their concentration in the aqueous phase. The selection of an adequate adsorbents is critical in the success of the remediation process. Factors such as surface area and chemical composition play fundamental roles in the adsorption capacity and efficiency of the materials. Commonly employed adsorbents for naproxen removal include activated carbon, metal organic frameworks, and nano clay composite all with characteristics and mechanisms influencing the adsorption process (Ozcan & Saloglu, 2020), (Hasan, Jeon, & Hwa Jhung, 2012) and (Rafati, Ehrampoush, Rafati, Mokhtari, & Mahvi, 2016). These materials usually offer a high surface area and a diverse range of functional groups, enhancing their affinity for naproxen molecules.

Instead, their synthesis complexity, applications and variable cost are drawbacks on real scenarios (Mpongwana & Rathilal, 2022). This research focuses on the synthesis of biodegradable and versatile easy to scale-up adsorbent to remove naproxen from water sources, thus contributing to the development of sustainable and efficient water treatment technology. In this research, we used alginate, a natural and biodegradable polymer, that had been used to encapsulate a vast of materials and drugs as a base for the adsorbent (Nalini, 2019; Caetano, Almeida, & Gonçalves, 2016). This research is novel adding cysteine, an amino acid containing sulfur, to the alginate beads. Cysteine and others amino acids have been used to enhance the adsorption of emerging contaminants and heavy metals (Zhang, Liangguo, Jing, & Haiqin, 2019; Mantovani, et al., 2023). Furthermore, this research contributes to the growing body of knowledge in the field of water treatment, offering insights into the development of efficient and sustainable solutions to address the challenges posed by emerging contaminants like naproxen in aquatic environments.

2. Procedures

2.1 Alg-Cys Beads Synthesis

The synthesis of Alg-Cys beads was performed with 0.10% w/v cysteine and 0.1 M calcium chloride. These are quantitatively transferred to a 250 mL volumetric flask and filled with distilled-deionized water (sol. A). This solution A was poured into a 1000 mL beaker. Alginic acid (2% w/v) was weighed and added to a 400 mL beaker containing 196 mL distilled-deionized water (solution B). This solution B was added dropwise to solution A at slow magnetic agitation. The 1000 mL beaker was covered and gently shaken for twenty-four hours. After that period, the beads were filtered with small portions of distilled water, using a Büchner funnel and left to air dry on a covered watch crystal for a week or placed in the oven at 60-70 °C for 4-6 hours.

2.2 Characterization

The Alg-Cys beads were analyzed with scanning electron microscopy energy dispersive X-ray spectroscopy (SEM-EDS) which provides information about the size, beads surface and morphology and elemental composition. The analysis was carried out at the Center for Materials

Characterization of the UPR Rio Piedras Campus.

2.3 Adsorption isotherms

Naproxen duplicate solutions in 10% ethanol at concentrations of 1-60 ppm were placed in amber bottles with 10 g/L of Alg-Cys beads at the desired pH, generally 6.0. All analysis were made under room temperature (25º C) in a water shaker bath at 100 rpm where samples of 1.00 mL were withdrawn at certain time intervals until the equilibrium time was reached. All samples were measured in a Shimadzu 1900i UV-VIS Spectrometer.

2.3.1 Adsorption isotherms

Adsorption phenomena, integral to the field of surface chemistry, have garnered significant attention due to their fundamental roles in environmental remediation, catalysis, and separation processes. Within the expansive landscape of adsorption isotherm modeling, Freundlich has emerged as an indispensable tool for understanding the intricacies of adsorption processes.

Herbert Freundlich's original work in 1906 gave rise to the Freundlich isotherm, an empirical model that accommodates heterogeneous surfaces and multilayer adsorption scenarios. The equation is expressed as

$$q_e = k_f \, C_e^{\frac{1}{n}} \quad (1)$$

The Freundlich linear equation is expressed as

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (2)$$

k_f = is a Freundlich parameter with units of $(mg/g)(L/mg)^n$, that predicts the relative adsorption capacity of the adsorbent under the studied conditions

n = is a Freundlich parameter related to the surface heterogeneity. Typical values ranges from 0 to 1. The intensity of adsorption increases as the value of $1/n$ is greater. (Ayawei, Ebelegi, & Wankasi, 2017) and (Murphy, Vashishtha, Palanisamy, & Kumar, 2023).

The Freundlich isotherm assumes multilayer adsorption onto a heterogeneous surface, making it suitable for describing adsorption on a variety of surfaces. The model is particularly useful for understanding the non-ideal nature of adsorption processes between naproxen and Alg-Cys beads.

3. Results and discussions

3.1 Characterization

As seen in Figure 1, SEM images show the roughness and heterogeneous nature from the beads surface before (Fig. 1.a) and after naproxen exposure (Fig. 1.b), confirming that a better adsorption model is the Freundlich isotherm. The EDS spectra (Fig. 1.c) shows the main elements composition (% mass) present in the Alg-Cys beads are oxygen (39.90 ± 0.19%), carbon (36.33 ± 0.09 %), calcium (16.44 ± 0.06 %), chloride (5.89 ± 0.03 %), and sulfur (0.14 ± 0.01%). After the exposure, the EDS spectra (Fig. 1.d) shows an increase of the % mass for oxygen (42.67 ± 0.10 %) and carbon (52.84 ± 0.04 %), thus confirming the adsorption of naproxen on the Alg-Cys surface.

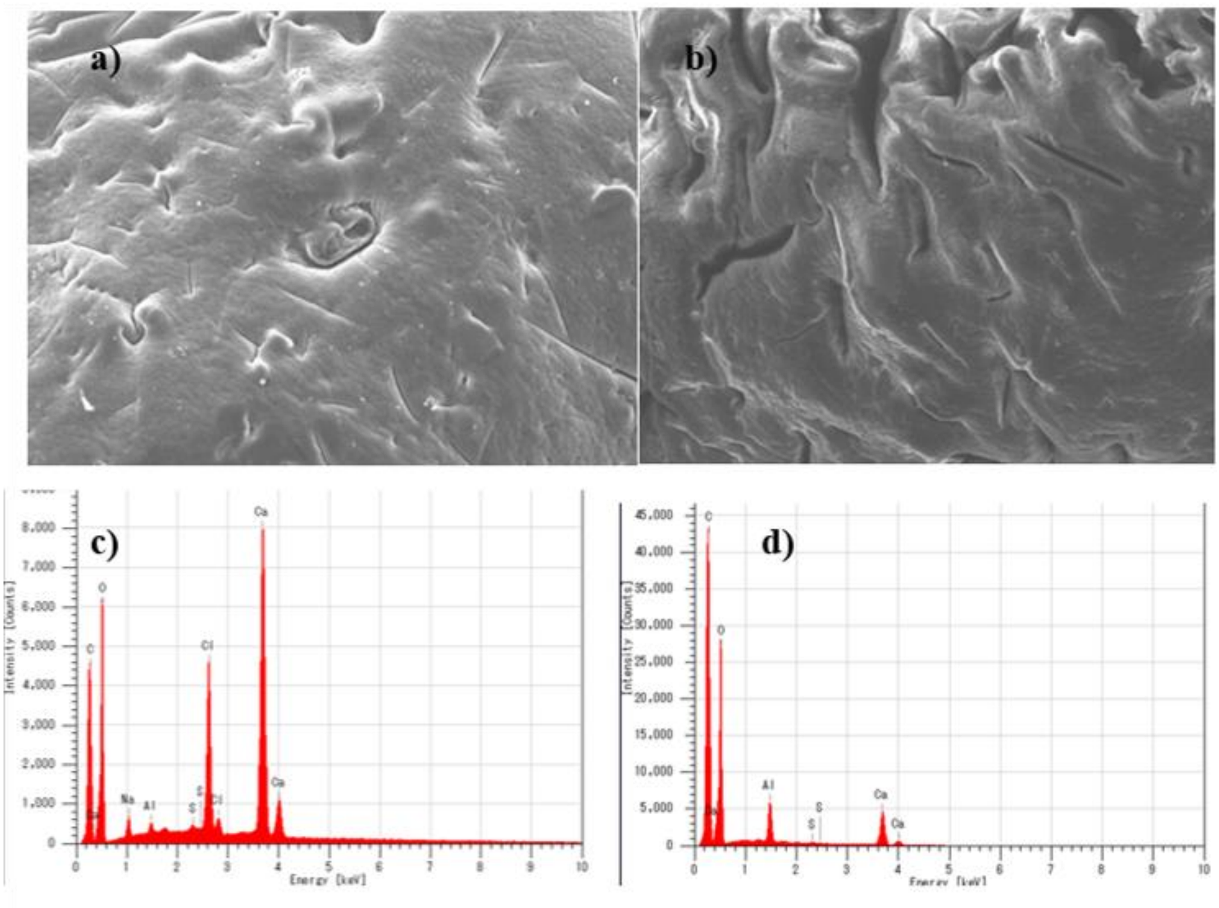

Figure 1: a) SEM image (300x) Alg-Cys beads b) with naproxen c) EDS spectra Alg-Cys beads d) with naproxen

3.2 Adsorption isotherms

Freundlich model was used to describe the adsorption behavior of naproxen onto the Alg-Cys beads due to the surface heterogeneity. Freundlich n values shown on Table 1 are typical for adsorption isotherms. The value of 1/n is related to the adsorption intensity seems that there is a greater adsorption intensity for natural clay, Al-Cys beads and the less intense adsorption for MGOSBA adsorbent. Another important parameter is the kf that predicts the relative maximum adsorption capacity of the adsorbents is seems that for natural clay has teh low and for MGOSBA and Alg-Cys Beads are similar in values, meaning a greater adsorption capacity. As seen, our adsorbent is easy to synthesize and biodegradable, and is efficient in the removal of naproxen from aqueous solutions in comparison with others in literature. Also, the adsorption intensity seems to be adequate to recover the naproxen and reuse of the beads.

The pKa of naproxen is 4.2, meaning that at pH 6.0 exist primary as an anion and like the majority of the functional groups in alginic acid are carboxylic groups and alcohols we do not expected electrostatic attraction at the studied pH. Instead, other interactions could enhance the removal of naproxen like H bonding between -COOH and -OH groups (Mohammadi Nodeh, et al., 2021).

Table 1: Freundlich isotherms parameters comparison for naproxen adsorption

k_f	*n*	Adsorbent	Author
16.39	0.84	Alg-Cys Beads (pH 6.0)	This study
19.09	1.66	Magnetic Graphene Oxide Silica Based Adsorbent (MGOSBA) (pH 5.0)	(Mohammadi Nodeh, et al., 2021)
1.68	0.52	Natural Clay	(Khazri, Ghorbel-Abid, Kalfat, & Trabelsi-Ayad, 2017)

4. CONCLUSIONS

The results show an effective synthesis of Alg-Cys Beads for the removal of naproxen from aqueous solutions. The SEM analysis of the heterogeneous surface is consistent with the applicability of the Freundlich isotherm. The Freundlich parameter, *kf*, was calculated with the result of 16.39 and with an *n* parameter of 0.84. Tthe first value predicts a good adsorption capacity of the adsorbent and the second parameter predicts a typical adsorption value. The proposed removal mechanism are due to hydrogen bonds between (-COOH and -OH) functional groups. We synthesize a novel material for the removal of emerging contaminants in real scenarios.

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