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Benzalkonium Chloride Removal: Insights into Mechanisms, Ecotoxicity Assessment, and Viability of Fixed-Bed Treatment in Aqueous Environments

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Abstract

The study concerns regarding the presence of benzalkonium chloride (BZK) and its contamination of urban waters, which pose risks to aquatic organisms and human health while affecting water treatment plant efficiency. Investigating BZK's toxicity in aqueous matrices, the study proposes adsorption as a tertiary treatment method, evaluating its feasibility and scaling while emphasizing sustainability through solid adsorbent regeneration. In silico toxicity analysis reveals BZK's moderate toxicity, irritating to the eyes and potentially causing skin sensitization. Batch adsorption removes 83.7% of BZK under pH 8.1, with optimal conditions observed at 120 min and carbon concentration = 2 g/100mL. Bayesian analysis highlights the pseudo-first-order kinetic model and the Sips hybrid model with Langmuir characteristics as the best fits for experimental data. Thermodynamic analysis shows favorable adsorption, with endothermic and spontaneous process, primarily via physisorption. Regeneration efficiency reaches 74.2% after 60 minutes at 300°C, with 50% efficiency after 5 cycles. Fixed-bed tests demonstrate stable efficiency, fitting the Log-Gompetz model, with an adsorptive capacity of 1.5 mg/g, making them suitable for continuous industrial-scale operation. Overall, the study underscores the potential of adsorption as a tertiary treatment method, highlighting its effectiveness, scalability, and sustainability.

Keywords: adsorption; benzalkonium chloride; personal care products; toxicity; wastewater.

1. Introduction

Benzalkonium chloride (BZK), is extensively utilized in pharmaceuticals, healthcare, and cleaning products due to its beneficial properties. However, the toxic effects of this compound have been documented in the literature [1]. Tertiary treatments are essential for meeting regulations, ensuring water quality, and promoting sustainable water reuse [2].

Adsorption is an effective method for resolve the problem, due the high efficiency, wide applicability, and easy implementation. It can be conducted in batch or in fixed-bed processes, and have the possibility to regenerate the solid.

In this context, the study investigates the toxicity of BZK in water using in silico analysis and suggests adsorption as a tertiary treatment method for BZK-contaminated matrices. It examines batch and continuous adsorption mode and regeneration of activated carbon (AC) is included to ensure sustainability and effectiveness in BZK removal.

2. Experimental Procedure

2.1 Eco-Toxicity Assessment

An in-silico approach using QSAR was employed to assess the ecotoxicity of TC before the adsorption process. The analysis was conducted using the OECD Toolbox, Version 4.3.1.

2.2 Batch Adsorption Experiments

Batch adsorption tests were conducted using 100 mL solution of BZK (20 mg/L). The sample was placed on an orbital shaker at 150 rpm, with a temperature of 25°C, following the methodology adopted by Costa et al. [3]. For each test, the adsorbent, previously characterized, was added to the solution, and removal efficiency was assessed based on pH, contact time, and solid concentration parameters. All experiments were conducted in duplicate, and the standard deviation was calculated to assess the dispersion of experimental points. After the equilibrium time, samples were filtered and analyzed using ultraviolet spectrophotometry, in the detection range of 254 nm.

To understand the adsorption process and the mechanism of BZK, analyses of adsorption kinetics, isotherms, and thermodynamics were conducted. Adsorption isotherms were constructed by varying the initial concentration of BZK, at temperatures of 15, 25, 40, and 50°C, at 150 rpm for 24 hours. Four isotherm models were examined in their nonlinear form: Langmuir, Freundlich, Sips, and Redlich-Peterson. The thermodynamic characteristics were expressed through the variations of its parameters.

2.3 Regeneration of the Adsorbent Solid

To regeneration of the adsorbent solid, thermal oxidation at 300 °C, during 60 minutes, was employed without controlled atmosphere, and subsequent cycles was applied until removal efficiency decreased by approximately 50%.

2.4 Fixed-Bed Adsorption Experiments

Fixed-bed experiments were conducted using a borosilicate glass column with dimensions of 12 mm internal diameter and 20 cm total length. The BZK solution was pumped upward through the column using a peristaltic pump in a controlled flow mode. Distilled water was used to rinse and equilibrate the column before each operation. Experimental conditions included a flow rate of 0.6 L/min and a bed height of 2 cm, representing 2.5 g of solid. The 80 mg/L pollutant concentration was tested, and breakthrough curves was obtained. Mathematical models such as Thomas, Yoon-Nelson, Clark, Yan, Gompertz and Log-Gompertz were used to simulate breakthrough curve.

3. Results and Discussion

3.1 Evaluation of toxicity before BZK treatment

BZK has moderate acute toxicity with an LD50 of 1.42E+03 mg/kg when ingested, suggesting relatively low toxicity. However, it poses significant risks of ocular irritation (Category 1) upon exposure [4]. It showed negative results for genetic mutation but tested positive for skin sensitization, indicating the potential to induce skin allergies. In terms of aquatic toxicity, BZK at concentrations between 0.14 and 2.5 mg/L led to approximately 50% mortality in *Morone saxatilis* after 72 hours of exposure. The LOEC ranged between 17.8 and 0.068 mg/L for different microorganisms (*Oncorhynchus kisutch and Raphidocelis subcapitata*), indicating adverse effects on mortality, growth, reproduction, or other health and behavioral aspects [5]. NOEC was below 0.69 mg/L, showing no observable adverse effects in tested organisms.

3.2 Determination of Adsorption Conditions

After the experiments, it was possible to determine the optimal batch adsorption conditions for efficiently BZK removal. It was observed that the highest BZK removal rates occurred at pH 8, 120 minutes and solid adsorbent concentration of 2.0 g/100 mL. These conditions led to a maximum percentage removal of BZK of 83.7%, with a residual concentration of 3.6 mg/L.

Given BZK's positive charge in aqueous environments, it exhibits a propensity to adsorb onto negatively charged surfaces, particularly evident below the solid's pH_{PZC} of 7.47, resulting in diminished adsorption capacity. The initial rapid adsorption observed within the first 45 minutes can be attributed to the abundance of available surface sites [6], gradually tapering off as the BZK concentration reaches equilibrium in the reaction medium. Moreover, the augmentation in solid adsorbent concentration initially augments removal efficiency, reflecting the typical behavior observed in porous materials, albeit showing a decline post the 2.0 g/100 mL mark [7].

3.3 Adsorption Mechanism

Figure 1 displays the adsorption data of BZK on AC over varying contact times, along with fittings to pseudo-first-order, pseudo-second-order, and Elovich kinetic models, in a non-linear format.

Notably, all three models exhibit suitable and comparable behavior, with coefficient of determination values approximating 0.99, 0.98, and 0.96 for the pseudo-first-order, pseudo-second-order, and Elovich models, respectively. Statistical parameter analysis indicates that the pseudo-first-order model outperformed others, yielding R^2= 0.988, R^2ajstd= 0.987, AIC=199.64, AIC_C= 200.64, and BIC= 201.05. These results suggest that the adsorption rate is directly proportional to the difference in BZK adsorbed amounts at equilibrium for a given time. The maximum adsorption capacity of the solid, was approximately 0.92 mg_{BZK}/g_{AC}.

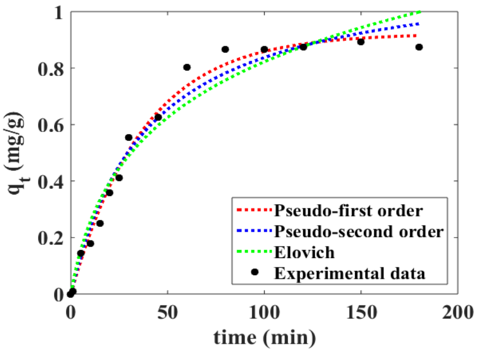

Fig. 1. Adjustment of kinetic models to experimental data.

Figure 2 presents the experimental equilibrium adsorption data of BZK at temperatures of 15, 25, 40, and 50 °C.

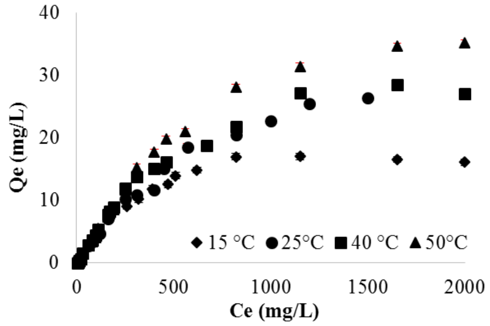

Fig. 2. Experimental isotherms.

It was illustrated that increasing the adsorption temperature results in higher amounts of BZK adsorbed, consistent with findings reported for other pollutants like tetracycline [3] and caffeine [8]. Based on the models, it was possible to verify that the Sips model accurately predicts experimental data at 15 °C, while the Langmuir model performs best at 25 °C, 40 °C, and 50 °C, indicating a temperature-dependent shift in the adsorption mechanism. Bayesian analysis confirms the Sips model's superior accuracy [9].

The thermodynamic parameters are in Table 1.

Table 1. Thermodynamic parameters.

ΔG*				ΔH*	ΔS**
15°C	25°C	40°C	50°C		
-17.6	-19.1	-21.4	-22.9	25.5	149.6

*kJ/mol; **J/mol.T

The values for ΔG at the temperatures were consistently negative, demonstrating that the adsorption process is spontaneous, favorable, and more facile at higher temperatures. The positive values of ΔH and ΔS indicate that adsorption is endothermic and involves a significant change in the internal structure of the adsorbent.

3.4 Solid regeneration

The application of thermal treatment at 300°C for the regeneration of AC saturated with BZK was presented in Figure 3.

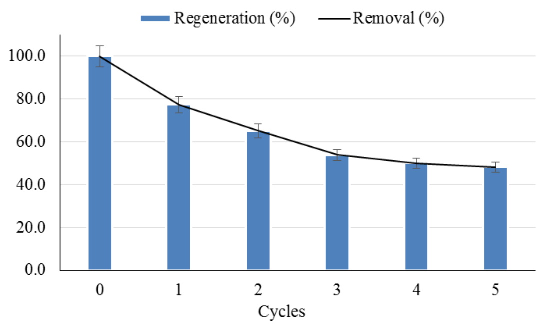

Fig. 3. Adsorption/desorption cycles of AC.

The efficiency of AC in removing and regenerating BZK gradually decreases over successive cycles. Initially, the adsorbent achieves 100% removal efficiency, showing after the first cycle, a desorption potential of 75.8%. This declines over time, reaching 50% regeneration efficiency after the 4th cycle. Factors contributing to this decline include the deposition of non-regenerated pollutants on the adsorbent surface, inadequate desorption time, and the formation of chemical bonds between adsorbed molecules and active sites on the adsorbent surface [10].

3.5 Application in Fixed Bed process

Figure 4 depicts the breakthrough curve obtained for 80 mg/L BZK with the fitting of the curve to all models applied in this study. The proposed technique accurately predicts the breakthrough curve behavior for BZK adsorption, with a characteristic sigmoidal shape ideal for breakthrough curves. Models as Thomas and Yoon-Nelson are inadequate in prediction the asymmetry seen in breakthrough curves. Clark, Gompertz and Log-Gompertz models offer improved fits by accounting for this behavior and, the Log-Gompertz model achieves a satisfactory fit and is suitable for practical application.

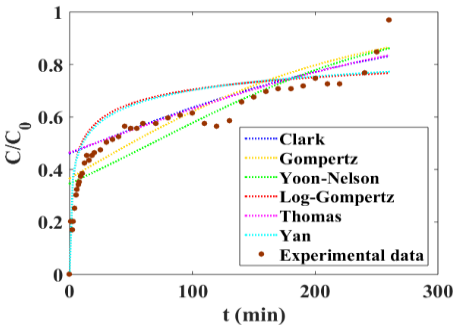

Fig. 4. Breakthrough curve of BZK adsorption and graphical fitting to the models applied.

Comparing batch and fixed-bed processes reveals significant differences. While batch tests demonstrate high efficiency in short periods, fixed-bed tests exhibit stable efficiency over time, making them suitable for continuous industrial-scale operation.

Conclusion

The study provides a promising solution for mitigating BZK contamination in urban water systems. Operational viability was confirmed by 83.7% removal efficiency and a successful regeneration over five cycles. The Bayesian analysis highlights the predominance of physical adsorption, and fixed-bed experiments demonstrate industrial applicability.

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