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ECOLOGICAL TREATMENT OF WASTEWATER CONTAINING A CATIONIC SURFACTANT POLLUTANT

Leon Dumitru COVALIU[1], Iuliana PAUN[1,2], Vasile Ion IANCU[2], Ecaterina MATEI[1], Razvan TEODORESCU[3], Valerica TUDOR[3], Gigel PARASCHIV[1], Cristina Ileana COVALIU-MIERLA[1]

[1]National University of Science and Technology POLITEHNICA Bucharest, 313 Splaiul Independentei Street, District 6, Bucharest, Romania
[2]National Research and Development Institute for Industrial Ecology – ECOIND, 71-73 Drumul Podu Dambovitei Street, District 6, Bucharest, Romania
[3]University of Agronomic Sciences and Veterinary Medicine of Bucharest, 59 Marasti Blvd, District 1, Bucharest, Romania

Corresponding author email: cristina_covaliu@yahoo.com

Abstract

Increasing pollution from organic substances that are difficult to biodegrade has led scientists to search for solutions to prevent them from entering the environment. A type of pollutant widely found in the environment is quaternary ammonium compounds, with benzalkonium chlorides being the main representative. Among the benzalkonium chlorides class, was chosen to study the method of removal of benzyldimethyldodecylammonium chloride (C12-BAC) from wastewater. One efficient method for the removal of organic compounds from wastewater is by using adsorbent material. For this reason, this paper presents the treatment of wastewater containing benzyldimethyldodecylammonium chloride (C12-BAC) by activated carbon material.

Key words: *activated carbon powder, benzalkonium chloride, quaternary ammonium salt, wastewater treatment.*

INTRODUCTION

One of the major challenges in wastewater treatment is the treatment of emerging contaminants such as surfactants. The reason for that lies in the fact that tensides are used extensively and widely and that they have an adverse effect on the wastewater treatment process and, above all, on the environment. This requires continuous improvement of wastewater treatment technologies (Dracea et al., 2022) and constant monitoring of water quality (Sandu et al., 2023). Various techniques including physical, chemical, biological and membrane treatment are used to remove surfactants from wastewater. The use of adsorbent materials has proven to be the most effective and cost-efficient approach for eliminating organic pollutants from wastewater. A significant advantage of this method is its ability to prevent the generation of additional pollutants, which can sometimes be even more toxic than the substances being removed. Surfactants are very persistent and water-soluble contaminants. They can pose a serious health risk to humans, animals and aquatic life by passing through wastewater treatment processes (Bautista-Toledo et al., 2008). One crucial class of pollutants that find their way into the environment includes organic compounds like cationic surfactants (Marković et al., 2017). Among these, benzalkonium chlorides are extensively utilized due to their dual attributes as both biocides and surfactants. They primarily serve as active ingredients in disinfection and cleaning products, with applications extending to surface disinfection, equipment sanitation, and device cleaning in hospitals and the food industry. Furthermore, they are employed in wood preservation. Notably, during the COVID-19 pandemic, there has been a significant surge in the use of these products, resulting in their detection in wastewater.

Benzalkonium chloride boasts a wide array of applications, serving as a versatile cationic surfactant, disinfectant, and bactericide. Additionally, its synergy with natural zeolites has given rise to organozeolites that are effectively employed for the adsorption and elimination of various non-polar organic substances, including drugs and mycotoxins.

In one study, natural zeolite clinoptilolite was subjected to modification with three different concentrations of benzalkonium chloride, with the resulting material being utilized for the in vitro adsorption of mycotoxins, specifically ochratoxin A and zearalenone (Marković et al., 2017). In another context, zeolites were modified with varying quantities of benzalkonium chloride and cetylpyridine chloride to facilitate the adsorption of the mycotoxin zearalenone (Daković et al., 2013)

Furthermore, the combined use of natural zeolite-clinoptilolite and benzalkonium chloride demonstrated efficacy in adsorbing a range of substances, including two drugs, sulfamethoxazole, and metronidazole (Rivera & Farias, 2005), aspirin (Lam & Rivera, 2006), diclofenac diethylamine (Krajišnik et al., 2011), and in conjunction with natural kaolinite, they formed an adsorbent material for the removal of the pesticide diazinon from wastewater (Tilakia et al., 2020).

A tailored zeolite material was engineered by combining natural mordenite zeolite with benzalkonium chloride, and this composite was effectively employed for the removal of Congo red dye (Astuti et al., 2020).

Functionalized zeolites were crafted through the synergistic combination of cationic surfactants (cetylpyridinium chloride, tetrapropylammonium chloride, and benzalkonium chloride) with two zeolites of the FAU zeotype, enabling them to be utilized for the adsorption of tannic acid and the insecticide acetamiprid (Jevremović et al., 2020).

Given the coexistence of pesticides, heavy metals, and cationic surfactants in wastewater, a study focused on the adsorption of benzalkonium chloride surfactant, paraquat cationic herbicide, and cadmium metal onto montmorillonite. Notably, it was observed that the cationic surfactant augmented the adsorption capacity of the herbicide without affecting the metal's adsorption capacity (Ilari et al., 2014).

A comparative investigation involving montmorillonite phyllosilicate clay was carried out to assess the adsorption of benzyl dodecyldimethyl ammonium chloride and benzyl tetradecyldimethyl ammonium chloride (Zanini et al., 2013). A zeolitic tuff with a Si/Al ratio of 2/4 was used to absorb the cationic surfactant benzyldimethyldodecyl ammonium chloride (Leone & Iovino, 2016; Covaliu et al., 2017; Paun & Covaliu-Mierla, 2023).

Due to its bactericidal properties, benzalkonium chloride together with kaolinite produced an absorbent material with bactericidal properties that was used against *Staphylococcus aureus* by inactivating 60% of the bacteria in 10 minutes (Zhang et al., 2023).

Modified zeolites with bactericidal properties against Bacillus subtilis bacteria were derived from synthetic zeolites A, X, and Y in combination with quaternary ammonium compounds, specifically hexadecyltrimethyl ammonium bromide and benzalkonium chloride (Maleka & Maleka, 2012).

Activated carbon exhibits a negative charge when submerged in water, making it capable of removing only cations from the water. Activated carbon is a non-toxic material to the environment and can be regenerated and reused in wastewater treatment technology.

The introduction of quaternary ammonium compounds, primarily benzalkonium chloride, transforms the charge from negative to positive in the resulting activated carbon material modified with cationic surfactant. This newly developed material can effectively eliminate anions from water, including substances like fluorides (Liang et al., 2022), perchlorates (Hou et al., 2013), hexavalent chromium compounds (Tilaki & Motlagh, 2017), and even non-polar compounds such as volatile organic substances Li et al., 2020).

Hospital wastewater containing benzalkonium chloride was successfully treated by adsorption using granular activated carbon (Tanada et al., 1991). Additionally, powdered activated carbon was employed for the removal of binary and ternary combinations of BAC12, BAC14, and BAC16 from water (Kim et al., 2022).

The removal of benzalkonium chloride was achieved using four ion exchange resins, comprising three strongly acidic resins with sulfonate functional groups and one weakly acidic resin with a carboxylic functional group. Across all ion exchange resins, removal rates exceeded 80%, with contact times ranging from 40 to 60 minutes (Klimonda et al., 2019).

The hydrophobic polymer adsorbent Amberlite XAD-16 was applied for the removal of

benzalkonium chloride (BAC), which is a commercial product containing mixtures of C12-BAC and C14-BAC counterparts (Turku & Sainio, 2009).
Adsorbent materials, like zeolites, find application in the removal of benzalkonium chlorides from wastewater. In a related context, two natural zeolites, smectite, and kaolinite, were employed as adsorbents for two quaternary alkylammonium compounds, namely benzyl dimethyl dodecyl ammonium chloride (C12-BAC) and dodecyl dimethyl ammonium chloride. Simultaneously, the study delved into the bacterial growth of eight bacterial taxa on adsorbent materials containing quaternary alkylammonium compounds. It was revealed that the adsorbent material plays a pivotal role in mitigating the toxicity of quaternary ammonium salts to bacteria (Fortunato et al., 2019).
For a deeper understanding of the adsorption mechanisms of C12-BAC, C14-BAC, and C16-BAC from water, powdered activated carbon was employed. Following the adsorption of BACs onto powdered activated carbon, a partial detoxification of water was observed, as indicated by a Microtox assay (Kim et al., 2022).
The removal of cationic surfactants primarily revolves around adsorption methods, employing a variety of adsorbent materials, including silica gel (Zhu et al., 2010), bentonites (Banerjee et al., 2006), fly ash (Zanini et al., 2013), clays (Mykola et al., 2016), montmorillonite, charcoal (Kozak & Domka, 2004), as well as nanomaterials like carbon nanotubes (Mahmoud et al., 1999), untreated multi-walled carbon nanotubes (Lopez-Lopez et al., 2016) , and nano zero-valent iron (Ncibi et al., 2015). Increasingly, natural zeolites are being used as eco-friendly adsorbents to extract cationic surfactants from wastewater (El-Lateef et al., 2018; Hasan & El-Gawad, 2014; Liu et al., 2015).
This study addresses the removal of the prevalent benzalkonium chloride, specifically benzyl dodecyl dimethyl ammonium chloride (C12-BAC) presented in Figure 1, using environmentally friendly adsorbent materials like activated carbon. It explores the influence of experimental parameters such as pH, contact time, C12-BAC concentration, and the quantity of adsorbent material on the process.

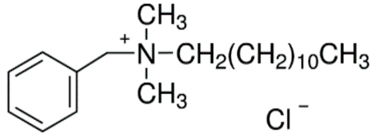

Figure 1. Molecular structure of C12-BAC

MATERIALS AND METHODS

Reagents and adsorbent materials
Benzyldimethyldodecylammonium chloride (C12-BAC) was purchased from Sigma-Aldrich, and Figure 1 shows its molecular structure.
The activated carbon was purchased from Trace Elemental Instruments with a particle size between 10 and 50 µm. The adsorbent material (activated carbon) presents a specific surface area of 256 m^2/g, a pore size of 12.7 Å, and a total pore area of 870 m^2/g.

C12-BAC analysis
The chromatographic method used to determine the concentrations of C12-BAC was developed in another paper (Covaliu et al., 2017) and the equipment used was an Agilent 1200 liquid chromatograph equipped with a DAD detector operating at a wavelength of 262 nm, and an Acclaim Surfactant chromatographic column Plus, 3 µm, length 150 mm, inner diameter 3 mm. The operating parameters of the method were column temperature of 30°C, injection volume of 20 µL, mobile phase of ammonium acetate 0.2 M: acetonitrile in the ratio 50:50 (v/v), mobile phase flow of 0.5 mL/min, elution time for C12-BAC was 2.4 minutes.

The cinetic studies
Kinetic studies were performed by adding: 250 mg of PAC to 500 mL synthetic wastewater with C12-BAC concentrations of 50 mg/L, 100 mg/L and 250 mg/L.
The mixtures were shaken at 250 rpm for 60 minutes. The samples were taken every 10 minutes and analyzed.

pH influence
To investigate the effect of pH on C12-BAC adsorption, the experiments were carried out at the same concentration of 50 mg/L of C12-BAC and two different amounts of the absorbent

material, respectively 200 mg and 250 mg at three pH values: pH=4, pH=6 and pH=10.

The adsorption studies

C12-BAC is absorbed on adsorbent material, namely PAC (powder activated carbon).

The experiments were carried out in 500 mL of synthetic wastewater with a concentration of 50 mg/L of C12-BAC.The three amounts of adsorbent material were used for the adsorption of C12-BAC: 100 mg, 200 mg and 250 mg. The experiments were performed at pH=10. The mixtures were homogenized at 250 rpm for 60 minutes. The samples were taken every 10 minutes and analyzed.

The removal efficiency (RE) can be determined using the following equation:

$$RE\% = 100\ x\ \left(1 - \frac{C_t}{C_i}\right) \tag{1}$$

where:

- Ct and Ci are the concentration of C12-BAC at t moment and initial moment.

The amount of C12-BAC adsorbed on the adsorbent material at equilibrium used was calculated using the following equation:

$$Qe = \frac{(Ci - Ce) * V}{m} \tag{2}$$

where:

- *Qe* - adsorption capacity at equilibrium, mg/g;
- Ci and Ce - the C12-BAC concentrations in the initial wastewater and at equilibrium (mg/L);
- m - the mass of adsorbent material (g);
- V - the C12-BAC volume initially used in the study (L).

Sorption isotherms are used to explain adsorption processes, and in addition calculate the adsorption capacity of the adsorbent material used using mathematical modelling. The most used adsorption isotherm models are Langmuir (Langmuir, 1918; Allen et al., 2004) and Freundlich (Freundlich,1906) isotherms.

Langmuir isotherm is based on the following mathematical equation:

$$Q_e = \frac{Q_{max} K_L c_e}{1 + K_L c_e} \tag{3}$$

where:

- C_e is concentration of C12-BAC at equilibrium (mg/L);
- K_L is the equilibrium constant of the Langmuir model (L/mg);
- Q_e is the adsorption capacity at equilibrium (mg/g);
- Q_{max} is the maximum adsorption capacity (mg/g);
- 1 is the maximum capacity occupied by adsorption for a given set of conditions to balance the entire monomolecular layer, mg/g.

The Freundlich isotherm equation is based on the following mathematical equation (Freundlich, 1906):

$$Q_e = K_F\ x\ C_e^{\frac{1}{n}} \tag{4}$$

where:

- K_F is adsorption capacity determined from Freundlich equation (mg/g);
- 1/n represents Freundlich parameter with respect to adsorption intensity;
- Ce is the concentration of C12-BAC at equilibrium (mg/L).

RESULTS AND DISCUSSIONS

The cinetic studies

The calculated removal efficiency for each concentration of C12-BAC was 92.3% for the concentration of 50 mg C12-BAC/L, 67.5% for the concentration of 100 mg C12-BAC/L and 39.92% for the concentration of 250 mg/L as seen in Figure 2.

For wastewater containing 50 mg/L C12-BAC and PAC adsorbent material, after 60 minutes of contact time the determined concentration was 0.40 mg C12-BAC/L. The adsorption capacity of PAC was 0.20 mg C12-BAC/mg PAC. For the concentration of 100 mg C12-BAC/L in wastewater, the concentration remaining in the treated wastewater was 0.38 mg C12-BAC/mg PAC, and the adsorption capacity of PAC was 0.38 mg C12-BAC/mg PAC. For the wastewater containing 250 mg C12-BAC/L, 26 mgC12-BAC/L was determined in the wastewater, which corresponds to a PAC adsorption capacity of 0.90 mgC12-BAC/mg PAC.

As can be seen in Figure 2, the removal yields are over 90% for all three concentrations of wastewater used in the experiments.

Influence of pH

The effects of pH on the removal efficiency of C12-BAC using powdered activated carbon, was determined by the interaction of 200 mg and 250 mg of adsorbent material with a concentration of 50 mg/L of C12-BAC at three pH values, namely pH=4, pH=6 and pH=10. The results of the quantitative dosing of C12-BAC showed that at pH=4 the removal efficiency was below 50%, at pH=6 the removal efficiency was over 50%, and at pH=10 the removal efficiency was over 90%, as seen in Figure 3.

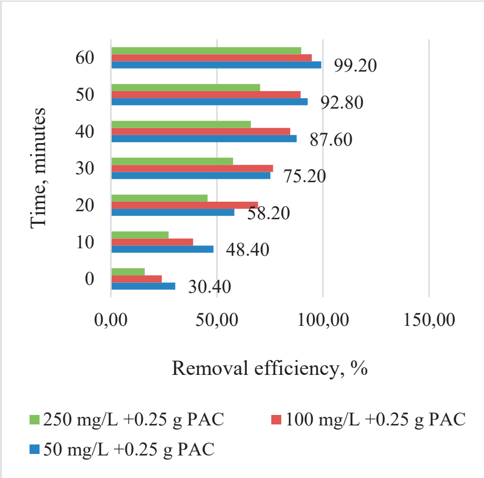

Figure 2. The removal efficiency for C12-BAC when using 0.25 g PAC adsorbent material

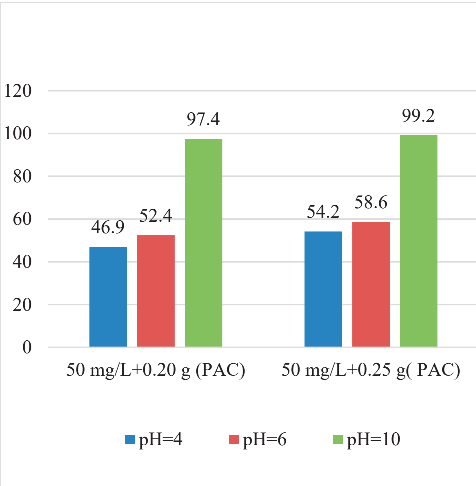

Figure 3. The influence of pH in the removal efficiency of C12-BAC by powdered activated carbon (PAC)

The adsorption studies

The removal efficiency of C12-BAC on different amounts of PAC material increased with the amount of adsorbent material as can be seen in Figure 4. The experimental data obtained in the adsorption study were used to calculate the adsorption isotherms for each adsorbent material used.

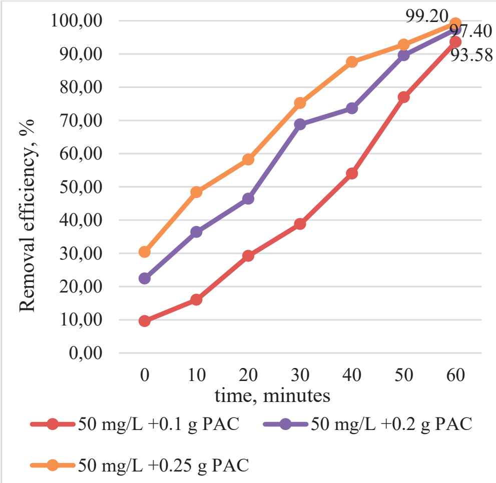

Figure 4. Removal efficiency of C12-BAC as a function of time for different amounts of PAC material

The adsorption capacity of PAC material increased depending on the contact time, as can be seen in Figure 5.

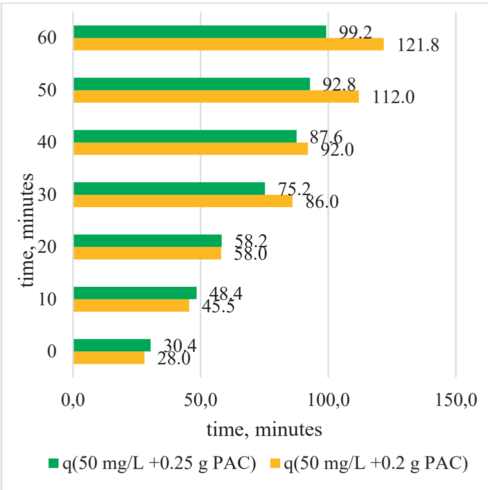

Figure 5. Adsorption capacity of PAC ecomaterial in time

The Langmuir isotherm proposes that adsorption occurs on homogeneous active sites of a monolayer adsorption surface with a finite number of identical sites, with no interactions between adsorbed molecules. Freundlich isothermal model can be used for multilayer adsorption on heterogeneous sites. Heterogeneous adsorption is when the pollutant enters the adsorbent material in such a way that the adsorption is continuously increased, and the adsorption equilibrium is not reached.

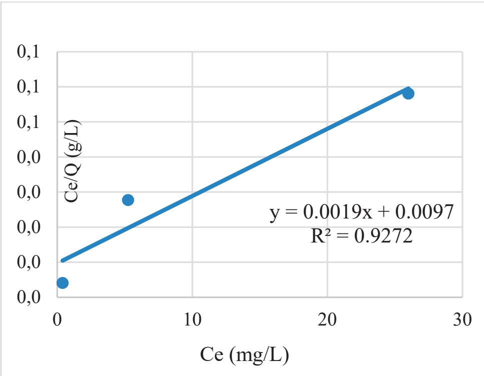

Figure 6. Langmuir isotherm for PAC

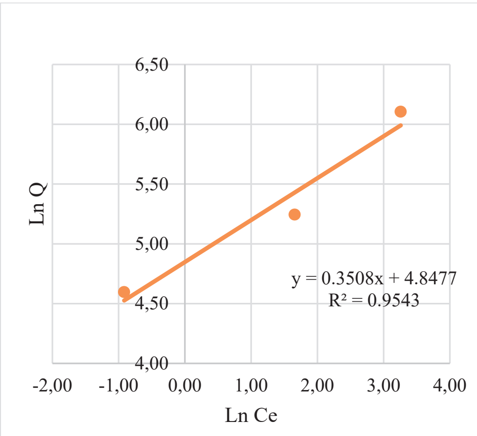

Figure 7. Freundlich isotherm for PAC ecomaterial

Table 1. Langmuir and Freundlich adsorption parameters

	Langmuir parameters			Freundlich parameters		
Adsorbent material	Q_{max} (mg/g)	K_L (L/mg)	R^2	K_F (L/g)	1/n	R^2
PAC	526	0.196	0.9272	2.85	127	0.9543

As can be seen from Figures 6 and 7 and Table 1, the correlation coefficients (R2) and the values of the isotherm parameters used show that all the adsorption data for the PAC adsorbent material fit better with the Freundlich model.

CONCLUSIONS

The adsorption of C12-BAC increases with the increase in the pH of the wastewater and the maximum adsorption of C12-BAC is obtained at a pH of 10.
The PAC adsorbent ecomaterial had the highest adsorption capacity of 526 mg/g, and the removal efficiency was 99.2% for 250 mg of adsorbent material, for the concentration of 50 mg C12-BAC/L and pH =10.
The correlation coefficients (R^2) and the values of the isotherm parameters for the PAC adsorbent ecomaterial fit better with the Freundlich model which is applied to explain the adsorption for the heterogeneous surface.

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