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BENZALKONIUM CHLORIDES SORPTION ONTO ACTIVATED CARBON AND ION-EXCHANGE RESINS. EQUILIBRIUM ANALYSIS

Benzalkonium chlorides (BACs) are cationic surfactants with amphiphilic structure and relatively large molecular size, which strongly influences their interaction with sorbent materials. This study compares the sorption of BACs onto cation-exchange resins and activated carbons. The highest sorption capacities were observed for macroporous resins (up to 370 mg/g), while activated carbons showed lower performance due to limited pore accessibility. The results indicate that sorption efficiency is governed by pore structure, functional groups, and BAC molecular characteristics. Overall, macroporous cation-exchange resins were identified as the most effective materials for BAC removal from aqueous solutions.

1. INTRODUCTION

The continuous release of anthropogenic micropollutants into aquatic systems represents a significant environmental and engineering challenge. Many of these compounds are not efficiently removed by conventional wastewater treatment due to their low biodegradability and complex structures. Among these pollutants, surfactants form a distinct and environmentally relevant group, owing to their widespread use and unique physicochemical properties [1–3].

Surfactants are commonly present in industrial products, pharmaceuticals, personal care items, and cleaning and disinfection agents. Their amphiphilic nature enables interactions with both nonpolar (hydrophobic) and polar (hydrophilic) components of aquatic environments, thereby influencing transport, bioavailability, and potential toxicity. Cationic

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surfactants, in particular, exhibit high toxicity to aquatic organisms and microbial communities, complicating their removal in biological treatment systems [4–6]. Quaternary ammonium compounds (QACs), including benzalkonium chlorides (BACs), are widely used due to their strong antimicrobial properties. Their use has increased significantly in recent years, resulting in widespread occurrence in municipal and industrial wastewater. During treatment, some BACs may be partially removed via sorption onto activated sludge; however, this process rarely achieves complete elimination, and notable amounts may still enter surface waters or remain in the sludge [7–9]. Effective post-treatment or complementary removal strategies are therefore necessary.

Several physicochemical methods have been investigated for cationic surfactant removal, including advanced oxidation processes (AOPs), membrane separations (ultrafiltration, nanofiltration, reverse osmosis), coagulation–flocculation, and electrochemical treatments [10–14]. While AOPs degrade surfactants through highly reactive species, their application is limited by cost and potential by-product formation. High-pressure membrane processes are highly effective but face challenges such as fouling, concentrate handling, and high energy demand. Conventional coagulation–flocculation achieves only partial removal and is generally insufficient for dissolved micropollutants.

Adsorption and ion exchange are promising methods for the removal of cationic surfactants, such as benzalkonium chlorides (BACs), whose amphiphilic nature and positive charge facilitate their removal via both processes. These approaches are operationally simple, efficient, and adaptable to different water matrices, and can serve as polishing steps in advanced treatment trains. Activated carbons and ion-exchange resins operate via distinct mechanisms: adsorption is primarily driven by physical forces (van der Waals interactions, hydrophobic effects, and, in some cases, electrostatic or hydrogen-bonding interactions), whereas ion-exchange resins remove ionic compounds via reversible exchange of charged species, sometimes enhanced by hydrophobic domains. The relative contribution of each mechanism depends on the sorbent type, surface chemistry, and micropollutant properties [15–18].

Although adsorption of surfactants has been reported in the literature, available studies often focus on single materials or selected conditions, and systematic comparisons between different types of cation-exchange resins and activated carbon remain scarce. To address this gap, the removal of BACs from aqueous solutions was investigated using selected activated carbons and cation-exchange resins. Equilibrium experiments were conducted using classical adsorption isotherms (Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich) to characterize sorption behavior and assess the relative contributions of adsorption and ion exchange, enabling a direct comparison of the effectiveness of the different sorbent types. The work focused on evaluating adsorption and ion-exchange mechanisms and assessing the influence of sorbent properties on BAC uptake.

2. MATERIALS AND METHODS

Sorbents. Four brand-new cation-exchange resins (C150H, Dowex 88, Marathon 1200, and C104 Plus) and two activated carbons (PAC and GAC) were used. The characteristics of the sorbents are summarized in Table 1.

Cation-exchange resins were converted to their sodium form by immersing them in a 12% NaCl solution for 1 hour under gentle stirring (40 rpm), followed by thorough rinsing with distilled water until no residual brine remained. The resins and granular activated carbon were measured volumetrically in the hydrated state using a graduated cylinder, while powdered activated carbon was weighed directly and then transferred into separate containers for adsorption experiments. Before the experimental series, granular activated carbon was pre-soaked in distilled water and thoroughly pre-washed before being introduced into reactors to remove fines and ensure uniform wetting. To unify the results, the sorption capacities of all materials were expressed per dry mass of sorbent. Therefore, the resins were dried separately, and the dry mass corresponding to the applied resin volume was determined.

C150H, Dowex 88, and C104 Plus are macroporous resins, with pore structures expected to permit penetration of small molecules. The gel-type Marathon 1200 resin possesses a microporous network with a uniform distribution of functional sites. WG-12 has a microporous and heterogeneous structure, while PWA-HA exhibits a high external surface area. These structural differences may influence the accessibility of adsorption sites for BAC molecules.

Adsorbate. Benzalkonium chlorides (BACs) are widely used quaternary ammonium compounds (QACs) with antiseptic and disinfectant properties. BAC molecules consist of a quaternary ammonium center attached to hydrophobic alkyl chains and a hydrophilic ammonium group, making them amphiphilic and able to interact with both polar and non-polar phases. BAC solutions were prepared in distilled water (80% purity, mixture of C_8–C_{18} alkylbenzyldimethyl ammonium chlorides, CMC = 350 mg/L, *MW* = 283.80–423.97 Da, monomer length = 5.9±0.5 nm [19]). The solution pH was adjusted to 6.5±0.2, and experiments were performed at 25±1 °C. BAC concentrations were determined at a wavelength of 215 nm using a UV Mini1240 UV-Vis spectrophotometer (Shimadzu, Japan). A calibration curve (R^2 = 0.997) was prepared over a concentration range up to 200 mg/L.

Sorption capacity tests. Batch adsorption experiments were conducted to evaluate the sorption capacities of the selected materials. Specific volumes of each sorbent were added to BAC solutions with initial concentrations ranging from 0 to 350 mg/L. The samples were agitated on a laboratory shaker (WL-2000, JW Electronic, Poland) to reach equilibrium. Based on preliminary kinetic tests, a contact time of 24 h was chosen, as it ensured that BAC concentrations stabilized and equilibrium was achieved for all sorbents. After equilibration, samples were filtered through 0.45 µm cellulose acetate membranes, and residual BAC concentrations were measured spectrophotometrically.

Table 1

Physicochemical properties of activated carbons and cation-exchange resins applied for benzalkonium chloride sorption

Sorbent	Type	Structure/Polymer	Functional group	Dominant pore type /structure	Particle size [μm]	Specific surface area [m^2/g]	Bulk density [g/cm^3]
PWA-HA (Chemviron)	powdered activated carbon (PAC)	carbon	–	microporous	≥ 65% particles smaller than 44 μm	900–1000	0.45
WG-12 (Gryfskan)	granular activated carbon (GAC)	carbon	–	microporous, heterogeneous	1000–1500	1005	0.44
$C_{15}OH$ (Purolite)	cation-exchange resin	styrene-divinylbenzene	sulfonic acid	macroporous	300–1200	N/A	0.72
Marathon 1200		styrene--divinylbenzene	sulfonic acid	gel	535–635	N/A	0.68
Dowex 88 (Dow)		styrene--divinylbenzene	sulfonate	macroporous	500–600	N/A	0.70
C104 Plus (Purolite)		styrene-divinylbenzene	carboxylic acid	macroporous	300–1600	N/A	0.71

N/A – not available.

Table 2

Equilibrium adsorption parameters of BAC on studied sorbents

Material		Model												
		Langmuir			Freundlich			Temkin				Dubinin–Radushkevich		
		q_{max} [mg/g]	K_L [L/mg]	R^2	K_f [L/g]	n	R^2	A [L/g]	B [mg/g]	b_T [J/mol]	R^2	q_m [mg/g]	E [kJ/mol]	R^2
Activated carbons	PWA-HA	217	0.045	0.999	83	5.59	0.969	4.28	28.99	84.7	0.973	200	0.050	0.968
	WG-12	121	0.082	0.987	39	4.96	0.988	8.47	14.20	164.5	0.945	95	0.845	0.768
Cation-exchange resins	C150H	370	0.064	0.903	137	1.40	0.945	7.74	75.22	32.6	0.931	196	2.500	0.903
	Marathon 1200	313	0.390	0.996	81	1.56	0.987	4.61	64.36	38.1	0.982	170	2.236	0.911
	Dowex 88	256	0.080	0.995	57	3.22	0.809	3.13	36.70	66.9	0.939	165	0.707	0.931
	C104 Plus	278	0.439	0.991	72	2.40	0.825	5.94	50.51	48.6	0.987	159	1.581	0.126

Equilibrium adsorption data were fitted using classical isotherm models, including Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R). Each model characterizes different aspects of adsorption:

- Langmuir assumes monolayer adsorption on homogeneous active sites and allows estimation of the maximum adsorption capacity (q_{max}).
- Freundlich accounts for adsorption on heterogeneous surfaces with variable site energies.
- Temkin evaluates the effect of adsorbate–adsorbent interactions on the distribution of adsorption energies.
- Dubinin–Radushkevich provides an estimate of adsorption energy, which may be used to infer the nature of adsorption interactions and provides insight into the dominant interaction types (van der Waals, electrostatic, or ion-exchange).

3. RESULTS AND DISCUSSION

This study aimed to investigate the sorption mechanism of benzalkonium chloride (BAC) onto four cation-exchange resins (C150H, Marathon 1200, Dowex 88, and C104 Plus), as well as two types of activated carbons (powdered PWA-HA (PAC) and granular WG-12 (GAC)). The applied concentration range was at or below the reported CMC; therefore, BAC was expected to remain predominantly in monomeric form, although partial aggregation near the upper concentration limit cannot be excluded.

The equilibrium adsorption parameters obtained from the applied isotherm models are summarized in Table 2. Langmuir provided a good fit to the experimental data and allowed estimation of q_{max}, suggesting monolayer-type adsorption behavior; Freundlich described surface heterogeneity; Temkin captured adsorption energy variation; and Dubinin–Radushkevich provided insight into the possible nature of adsorption interactions based on calculated adsorption energy.

Macroporous cation-exchange resins, including C150H, C104 Plus, and Dowex 88, exhibited high sorption capacities due to the combination of accessible ion-exchange sites, chemically defined functional groups, and favorable hydrophobic interactions with BAC monomers. Among them, C150H reached the highest q_{max} of 370 mg/g, while C104 Plus and Dowex 88 reached 278 mg/g and 256 mg/g, respectively. Langmuir R^2 values were generally high (0.903–0.995), indicating that the model adequately describes the experimental data, consistent with monolayer-type adsorption assumptions, although the fit for C150H was slightly lower ($R^2 = 0.903$). Freundlich heterogeneity values ($n = 1.40–3.22$) indicate favorable adsorption, but R^2 values for some resins (0.809 for Dowex 88; 0.825 for C104 Plus) suggest moderately less ideal fitting, while C150H ($R^2 = 0.945$) shows reasonably good agreement. These observations align with previous reports demonstrating that full accessibility of active sites enhances adsorption efficiency. Well-developed

porous structures and high surface area facilitate access to these active binding sites, improving the interaction between adsorbent and adsorbate, and leading to higher adsorption capacities [15, 17, 20].

The gel-type Marathon 1200 resin, microporous but lacking macropores, exhibited q_{max} of 313 mg/g. Despite slightly lower capacity than C150H, its uniform distribution of ion-exchange sites allowed relatively predictable adsorption behavior consistent with monolayer assumptions. High Langmuir R^2 (0.996) and moderate Freundlich heterogeneity (n = 1.56, R^2 = 0.987) reflect efficient site utilization despite limited pore size.

Activated carbons showed lower sorption capacities due to micropore limitations and heterogeneous surface energies. PWA-HA (PAC) achieved q_{max} of 217 mg/g, while WG-12 (GAC) reached only 121 mg/g. The relatively uniform microporous structure of PWA-HA allowed effective access of BAC monomers to adsorption sites, whereas the variable pores of WG-12 may restrict penetration, particularly for longer BAC homologues. The adsorption on activated carbons was likely influenced primarily by van der Waals interactions, with electrostatic contributions playing a secondary role. Langmuir R^2 values were high (PWA-HA = 0.999; WG-12 = 0.987), indicating a good fit of the Langmuir model. Steric hindrance due to the relatively large size of BAC molecules, combined with limited pore accessibility, further restricted adsorption, particularly for longer-chain homologues [21].

The observed trends reflect the interplay between the sorbent pore structure and the size of BAC monomers. Shorter homologues (C_8–C_{12}) can more easily access smaller pores, whereas longer homologues (C_{14}–C_{18}) preferentially adsorb on macroporous resins (e.g., C150H, C104 Plus) or on gel-type resins (e.g., Marathon 1200), where the uniform distribution of ion-exchange sites allows effective adsorption despite the limited pore size. Macroporous resins provide greater accessibility to BAC molecules and facilitate utilization of ion-exchange sites, while gel-type resins promote more uniform monolayer adsorption due to their homogeneous active site distribution. Microporous activated carbons (PWA-HA, WG-12) mainly favor physical adsorption, as indicated by low D–R adsorption energies (E < 1 kJ/mol), which suggests weak interaction energies and limited uptake of larger BAC homologues.

Adsorption capacities are likely influenced by a combination of electrostatic attraction, hydrophobic interactions, steric effects, and ion-exchange processes. High Langmuir R^2 values (0.987–0.999) across most sorbents suggest that monolayer-type adsorption may be a dominant approximation for the studied systems, while a slightly lower fit for C150H (R^2 = 0.903) indicates partial surface heterogeneity. Freundlich modeling better describes activated carbons, especially GAC (R^2 = 0.988), reflecting heterogeneous surfaces with variable site accessibility. High n values for PAC (5.59) and GAC (4.96) confirm favorable adsorption dominated by physical interactions, whereas lower n values for resins (1.40–3.22) suggest a more homogeneous distribution of adsorption sites. Temkin parameters (b_T = 32.6–48.6 J/mol for resins; 84.7–164.5 J/mol for activated carbons) reflect variations in apparent adsorption energy, consistent with coexisting electrostatic, hydrophobic, and ion-exchange interactions, and greater energetic heterogeneity for activated carbons. The

Dubinin–Radushkevich model suggests that physical adsorption is likely to be a dominant mechanism, although contributions from other interactions cannot be excluded, with additional electrostatic and ion-exchange contributions in resins. The very low R^2 for C104 Plus (0.126) indicates that the D–R model does not adequately describe adsorption for this macroporous resin, likely due to its heterogeneous pore structure and mixed adsorption mechanisms. An additional factor affecting BAC sorption on C104 Plus is the weak-acid nature of this resin, associated with the presence of carboxylic groups. Unlike strongly acidic sulfonic resins, the degree of dissociation of carboxylic groups depends on pH, which may result in less uniform ion-exchange behavior. Thus, the sorption performance of C104 Plus is likely determined not only by its macroporous structure, but also by the pH-dependent reactivity of its functional groups. In contrast, higher R^2 values for other macroporous resins (C150H, Dowex 88) may reflect a more uniform distribution of active sites and a relatively simpler adsorption mechanism, allowing better model fit.

Overall, BAC sorption appears to be governed by its amphiphilic structure and relatively large molecular size, which dictate pore accessibility and interaction mechanisms. Macroporous resins enable efficient utilization of active sites due to improved accessibility. Gel-type resins provide uniform and predictable monolayer adsorption, while activated carbons restrict access to micropores, resulting predominantly in physical adsorption, with possible contributions from other interactions. From a practical perspective, macroporous resins are optimal for high-capacity BAC removal, gel-type resins provide stable and predictable performance, and activated carbons are better suited for partial or slower adsorption processes.

4. CONCLUSIONS

Macroporous cation-exchange resins C150H and C104 Plus, along with the gel-type Marathon 1200 resin, showed high BAC adsorption capacities (q_{max} of 370, 278, and 313 mg/g, respectively), highlighting the importance of accessible ion-exchange sites and uniform functional group distribution. In contrast, activated carbons (PWA-HA and WG-12) displayed lower capacities (q_{max} of 217 and 121 mg/g) due to micropore limitations and heterogeneous surfaces, where sorption was mainly associated with physical interactions. The amphiphilic structure and relatively large monomer size of BAC further influenced adsorption, suggesting that sorption efficiency results from the combined effects of sorbent morphology and BAC properties.

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