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Benzalkonium Bromide Cationic Surfactant Removal from Wastewater Using Magnetite Nanomaterial

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Abstract: *The cationic surfactants have various applications being found in personal care products, detergents, cleaning products, disinfectants, hair conditioners, etc. Cationic surfactants are presented in domestic or industrial wastewater, being very resistant pollutants to biodegradation during conventional wastewater treatment (WT) methods, which generated the need to develop new efficient alternative methods. One of the alternative to conventional WT methods involves the utilization of the adsorbent nanomaterials, which are highly efficient, easy to operate, environmental friendly and cost effective. In this study, it was investigated the adsorption process of a cationic surfactant, benzyldodecyldimethylammonium bromide (benzalkonium bromide) from wastewater on magnetite nanomaterial. The adsorption investigation of benzalkonium bromide was analyzed by TOC analysis and the maximum adsorption efficiency obtained was 91.4 %. The experimental data fitted very well with Langmuir model, the correlation coefficient (R^2) being 0.9792.*

Keywords: *benzyldodecyldimethylammonium bromide, benzalkonium bromide, cationic surfactant, magnetite nanomaterial, adsorbtion, wastewater.*

1. Introduction

Surfactants are the most used organic substances in many household and industrial products. The cationic surfactants, especially quaternary ammonium compounds [1], such as cetylpyridinium chloride can be used in the wastewater treatment plant (WWTP) together with other adsorbent materials to remove organic pollutants [2] such, reactive dyes [3-5]. It has been shown that cationic surfactants have a toxic action to the environment due to the attachment of their positive charge with the predominantly negatively charged particles from sewage sludge, soil and sediments [6]. Overall, the cationic surfactants have negative influences on the environment by increasing the eutrophication of lakes [7,8] or by disturbing the wastewater treatment process through the decreasing of microbial communities and subsequently disturbing the biochemical reactions of the activated sludge [9,10]. Up to now, there are many studies to evaluate the ecotoxicity of anionic and non-ionic surfactants, but ecotoxicological profile of cationic and amphoteric surfactants is still largely unknown [11].

Benzyldodecyldimethylammonium bromide, the chemical name of benzalkonium bromide is a cationic surfactant used as biocide in cosmetic products (hair conditioners and hair coloring preparations), detergent products, pesticide or as an inactive ingredient in pharmaceuticals. It was introduced on the market in 1953 and it has been widely used in chemical disinfectants due to its low price. In China, benzalkonium bromide, although it is known as a neurotoxic, is more used than the benzalkonium chloride, another popular disinfectant used in Germany, USA and UK. The methods used for analysis of benzalkonium bromide in disinfectants products are based on capillary electrophoresis (CE) and high-performance liquid chromatography (HPLC) with UV detector [12]. Today, HPLC, combined with various detectors, is used for the analysis of surfactants and their degradation products [13].

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Compared with on benzalkonium chloride many ecotoxicity studies have been performed, but the study of benzalkonium bromide has been poorly investigated. There are many studies in literature about the adsorption of benzalkonium chloride, but not on the benzalkonium bromide. At the present, in the scientific literature, the removal of benzalkonium chloride was analyzed in presence of a hydrophobic polymer adsorbent called Amberlite XAD-16 [14], a granular activated carbon [15], pristine and organo-bentonite [16].

Removal of cationic surfactants from wastewater has been a priority and many physical, chemical and biological methods have been tested [1-32]. Adsorption has been recognized as an effective and promising technique and has been used in wastewater tertiary treatment step [17]. Moreover, adsorption has been proposed as one of the most appropriate technique for the removal of surfactants due to its high efficiently, easy to operate, environmentally friendly and cost effective.

The retaining of various cationic surfactants was studied previously using various adsorbents such as: a) granular charcoal for cetylpyridinium chloride) [18], b) activated carbon cloth for the following cationic surfactants: benzyltrimethylammonium chloride, benzyltriethylammonium chloride, benzyltributylammonium chloride, benzyldimethyldecylammonium chloride, benzyldimethyltetradecyl ammonium chloride, benzyldimethylhexadecylammonium chloride, N-dodecyl pyridinium chloride N-cetyl pyridinium chloride [19], c) powdered activated carbon for cetyltrimethylammonium bromide [20], d) microporous and mesoporous activated carbons prepared from vinylidene chloride copolymer for tetraethyl-, tetrapropyl-, hexadecyltrimetyl- and tetrahexylammonium bromide [21], e) activated carbon for cationic–anionic surfactant mixtures: octyltriethylammonium bromide/sodium dodecylbenzenesulfonate dodecylpyridinium chloride/sodium octanesulfonate) [22], f) activated carbons -TH90 activated carbon with a lower ash content for cetyltrimethylammonium bromide (C16TABr), myristyltrimethylammonium bromide (C14TABr), dodecyl trimethy lammonium bromide (C12TABr), decyl trimethyl ammonium bromide (C10TABr))[23].

Other adsorbent materials used for the removal of cationic surfactant [24] were based on: a) clay minerals such as attapulgite for removal of cetyltrimethylammonium chloride) [17], b) perlite for elimination of cetyltrimethylammonium bromide) [25], c) sepiolite for elimination of dodecyltrimethylammonium bromide, hexadecyltrimethylammonium bromide and dodecylamine hydrochloride [26] and d) other adsorbent materials powders of hematite and magnetite with dimension pores 0.5, 1 and 5 μm for alkyl ester ammonium and Kemfluid EQ18) [27], SiO_2 for dodecylpyridinium bromide [28], silica alumina for removal of cationic alkylpyridinium and alkyloxyethylenepyridinium chlorides [29].

The objective of this study was the utilization of magnetite nanomaterials as adsorbent for the removal from wastewater of a resilient cationic surfactant, benzyldodecyldimethylammonium bromide (benzalkonium bromide). Taking into consideration the disadvantages of conventional methods and conventional adsorbent materials used for the wastewater treatment such as low efficiency for pollutants removal at low concentration, it was chosen a nanomaterial which have more advantages compared with the conventional ones: small particle size, increased surface area, therefore improving adsorption capacities for the removal of pollutants form wastewater [30, 31]. Treatment of wastewater containing surfactants by adsorbent nanomaterials offered a non-polluting alternative to the standard one. Other advantages of using adsorbent nanomaterials have been recovery, the regeneration and reuse of adsorbent used in domestic and industrial wastewater treatment processes. In our study, it has been shown that the magnetite nanomaterial was an efficient adsorbent for the cationic surfactant, it could be easily regenerated by desorbing the surfactants and the surfactant could be decomposed by using photocatalysis or advanced oxidation using UV and O_3 or H_2O_2.

In this study the adsorption process of cationic surfactant, benzyldodecyldimethylammonium bromide (BB) on magnetite nanomaterial was investigated. Also, were studied: the influence of wastewater pH, BB concentration and magnetite quantity upon the wastewater treatment process.

2. Materials and methods

2.1. Reagents and standard solutions

Benzyldodecyldimethylammonium bromide (benzalkonium bromide) (BB) (molecular formula: $C_{21}H_{38}BrN$) was purchased from Sigma Aldrich.

Magnetite nanomaterial (Fe_3O_4 nanomaterial) synthesis according to the protocol described by scientific literature [32].

2.2. TOC analysis

TOC was performed with a total organic carbon analyzer, TOC/TN-LCPN (Shimadzu) controlled by TOC-Control V Software. Briefly, the method consisted in heating the samples to 680^0C in an oxygen-rich environment inside combustion tubes filled with a platinum catalyst. The carbon dioxide generated by oxidation was detected using an infrared gas analyzer.

2.3. BB kinetic studies

Kinetic studies were performed by adding 25 mg of Fe_3O_4 nanomaterial to 250 mL BB solution of various concentrations: 5 mg/L (BB1), 10 mg/L (BB2) and 20 mg/L (BB3) then the samples of pH 6 were mixed at 200 rpm for 1; 2; 4; 6; 24 and 48 h. The BB concentrations were analyzed with TOC.

2.4. Influence of *p*H

In order to investigate the effect of pH on the BB adsorption the experiments were performed, at two pH values: 6 and 9.

2.5. BB adsorption studies

The adsorption studies were performed in presence of various amounts of Fe_3O_4 adsorbent nanomaterial. An amount of 25, 20, 15, 10 and 5 mg Fe_3O_4 nanomaterial was added to 250 mL of 5 mg/L BB1. The samples were mixed at 200 rpm for 2 h. The BB concentration was analyzed with TOC as mg of total organic carbon per liter (mg C/L)

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

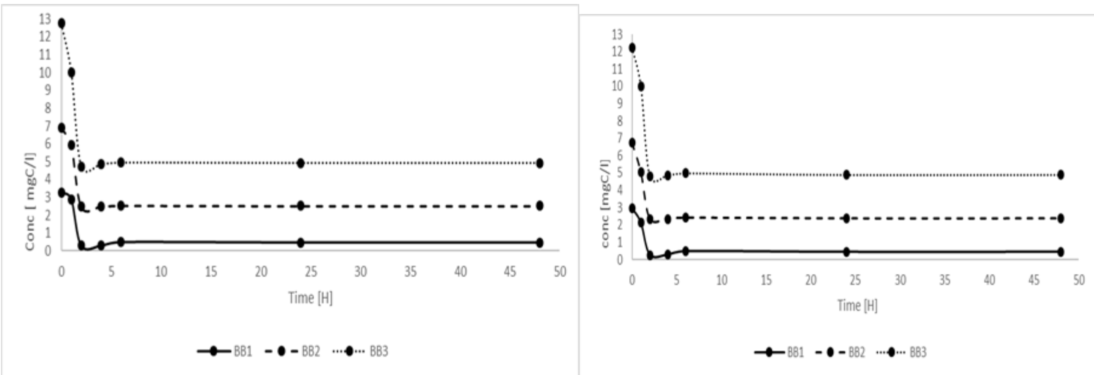
$$RE\% = 100\ x\ \left(1 - \frac{C_t}{C_i}\right) \qquad (1)$$

where: Ct is the BB concentration at t moment and Ci is the BB initial concentration.

3. Results and discussions

3.1. BB kinetic studies

The variation of different BB concentrations absorbed in presence of magnetite nanomaterial adsorbent in time showed a rapid decrease up to 2 h, then no significant variations were observed (Figure 1).



a) *p*H=9 b) *p*H=6

Figure 1. Variation of BB concentration (mg C/L) in time (h) at: *p*H=9 (a) and *p*H=6 (b).

It was worth mentioning the fact that absorption capacity of Fe_3O_4 nanomaterial was higher than the BB1 amount from wastewater because BB1 concentration dropped to zero after interaction with the nanomaterial. Moreover, the BB2 and BB3 concentrations exceeded the absorption capacity of Fe_3O_4 nanomaterial, since the remanent concentrations was around 2 mg C/L for BB2 and 5 mg C/L for BB3 (Figure 1). The results showed that BB concentration decreased at *p*H 9 from 3.27 mg C/L (BB1) to 0.28 mg C/L. The difference of 2.99 mg C/L was the absorption capacity of Fe_3O_4 nanomaterial which was about 0.74 mg C/mg Fe_3O_4 nanomaterial. The amount of BB adsorbed on the Fe_3O_4 nanomaterial were 0.74 mg C for BB1 (from 0.75 mg C, initial amount) at *p*H=9; 0.67 mg C for BB1 at *p*H=6; 1.11 mg C for BB2 (from 1.72 mg C, initial amount) *p*H=9; 1.10 mg C for BB2 at *p*H=6; 2.01 mg C for BB3 (from 3.19 mg C, initial amount) *p*H=9; 1.84 mg C for BB3 at *p*H=6. Overall, the maximum amount of BB adsorbed on the Fe_3O_4 nanomaterial was 0.027 mg C/mg nanomaterial.

3.2. Influence of pH

The effects of pH on the RE of the nanomaterial was established by interacting 25 mg Fe_3O_4 nanomaterial with various concentrations of BB (BB1, BB2 and BB3) for 2h. Two *p*H values (*p*H 6 and 9) were analyzed. The results showed insignificant effects of the *p*H on the RE (Figure 2) and subsequently no significant BB adsorption on adsorbent nanomaterial. However, it was observed that the values of the RE were slightly higher at the *p*H 9 compared to *p*H 6.

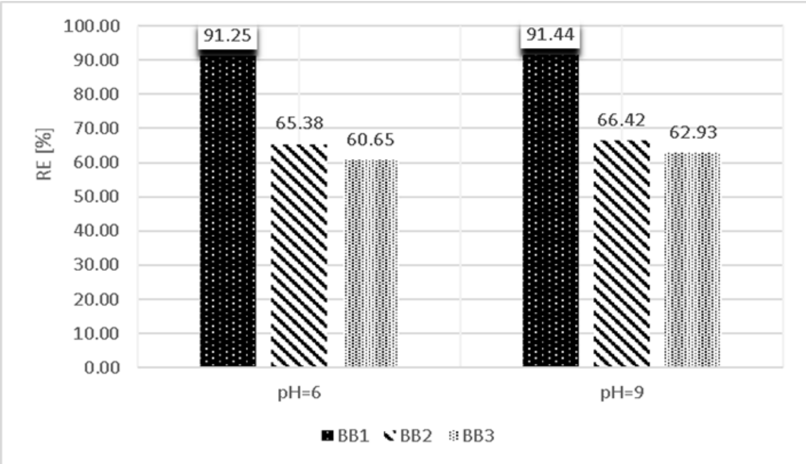


Figure 2. The influence of *p*H upon the removal efficiency (RE) % of BB by the nanomaterial

3.3. BB adsorption studies

The removal efficiency of BB on various amounts of adsorbent nanomaterial showed a significant effect of the removal efficiency which increased with the amount of magnetite nanomaterial (Figure 3).

The experimental data of the BB adsorption study were used in order to calculate the adsorption isotherm (Figure 4). The concentration of BB adsorbed on Fe_3O_4 nanomaterial at equilibrium was determined experimentally and it was calculated with the following equation:

$$a = \frac{(C_i - C_e) * V}{m} \qquad (2)$$

where Ci and Ce were the BB concentrations in the initial wastewater and at equilibrium (mg/L), m was the mass of Fe_3O_4 nanomaterial (g), V was the BB volume initially used in the study (L). The adsorption capacity of Fe_3O_4 nanomaterial increased with the increase in the amount of magnetite used in the experiments (Figure 4).

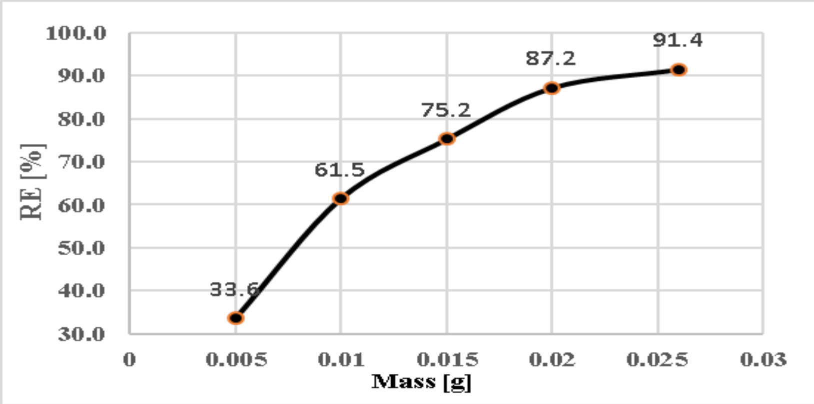


Figure 3. The removal efficiency (RE) of BB during 2h at *p*H 9 on various amount of Fe_3O_4 nanomaterial (0.005, 0.01, 0.01, 0.02 and 0.025 g)

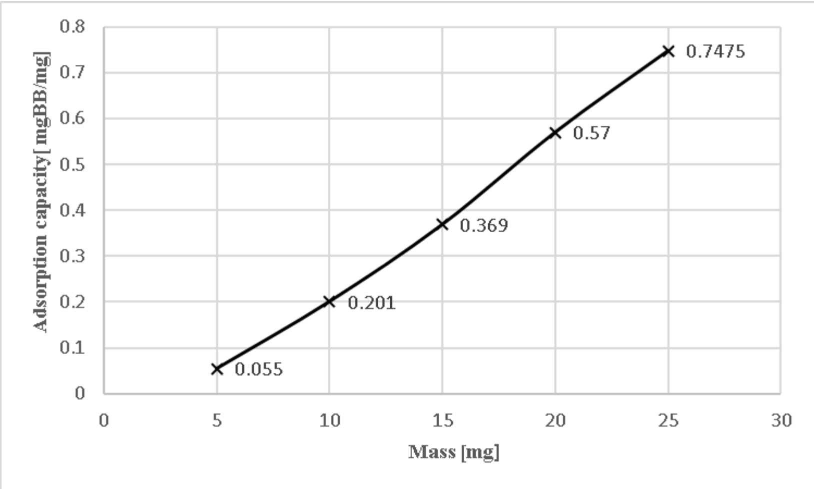


Figure 4. BB1 adsorption capacity by 5-10-15-20-25 mg magnetite nanomaterial (Fe_3O_4) during 2 h at *p*H 9

The Langmuir isotherm proposed that adsorption occurs on homogenous active sites by monolayer adsorption surface with a finite number of identical sites without interactions between adsorbed molecules.

Langmuir isotherm characteristic equation was:

$$a = \frac{b\, a_m C_e}{1 + b\, C_e} \quad (3)$$

where: a - adsorption capacity at equilibrium, mg/g; 1 - maximum adsorption capacity for a given set of conditions to balance the entire monomolecular layer was occupied, mg/g; Ce - concentration of solute in the system at equilibrium, mg/L; b - equilibrium constant that depends on the nature of the adsorption system.

Langmuir equation can be written as a linearized form as follows:

$$\frac{1}{a} = \frac{1}{a_m} + \frac{1}{b\, a_m C_e} \quad (4)$$

The “b” constant and the maxim adsorption capacity “am”, can be determined from experimental data if the plot 1/a by 1/Ce. Graphical representation is a line that intersects with the point Oy (1/am) thus determining the “am”. Knowing ‘‘am’’ was determined the “b” of the value of tangent right angle that makes with the axis Ox [33].

Langmuir equation representation by the 1/a = f (1/Ce) for BB is shown in Figure 5. The characteristic equation of experimental data is:

$$\frac{1}{a} = 5{,}1624\frac{1}{C_e} + 16{,}349 \qquad (5)$$

R^2 = 0.9792 is the regression coefficient.

The experimental data fitted well with the Langmuir model.

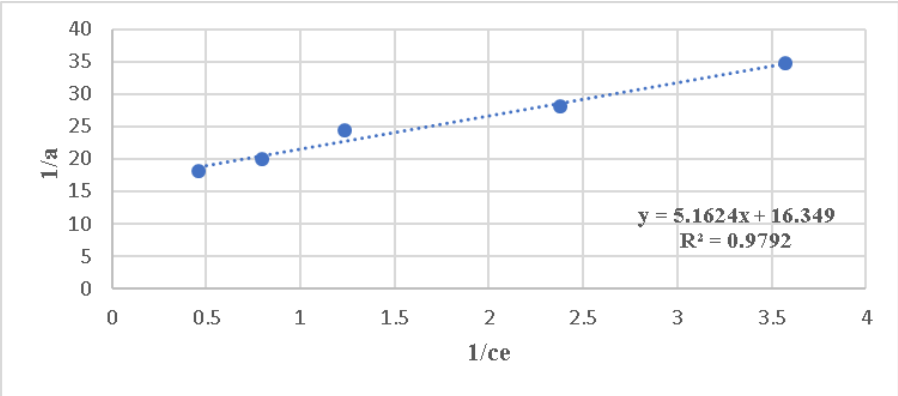


Figure 5. Variation of the Langmuir adsorption isotherm of benzalkonium bromide on magnetite nanomaterial

4. Conclusions

The magnetite nanomaterial was tested for removal of benzalkonium bromide cationic surfactant from wastewater. The maximum BB removal efficiency obtained was 91.4 % on magnetite nanomaterial after 2h interaction at *p*H 9 of wastewater. The experimental data fitted very well with Langmuir model, the correlation coefficient (R^2) being 0.9792. The adsorption process of benzalkonium bromide was found to follow a first-order kinetics. The benzalkonium bromide removal efficiency in the batch process was found to increase with the increasing of the amount of magnetite and *p*H.

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