O NOUĂ APLICAŢIE A NANOMATERIALULUI MAGNETITĂ PENTRU ÎNDEPĂRTAREA UNUI SURFACTANT CATIONIC DIN APA UZATĂ
NEW APPLICATION OF MAGNETITE NANOMATERIAL FOR A CATIONIC SURFACTANT REMOVAL FROM WASTEWATER

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The paper presents the adsorption capacity of magnetite nanomaterial for a cationic surfactant removal from wastewater. Kinetic studies were performed by adding the magnetite nanomaterial to a wastewater solution of benzethonium chloride having the concentrations of 2 mg/L and 20 mg/L. The wastewater systems were investigated at 1, 2, 4, 6, 24 and 48 h. The highest removal efficiency (86,98%) was obtained for wastewater containing 2 mg/L benzethonium chloride concentration. The results obtained for the magnetite nanomaterial demonstrates the possibility of applying this nanomaterial for the removal of benzethonium chloride cationic surfactant from wastewater.

Lucrarea prezintă capacitatea de adsorbție a nanomaterialului magnetită pentru îndepărtarea unui agent tensioactiv cationic din apele uzate. Studiile cinetice au fost efectuate prin adăugarea nanomaterialului magnetită într-o soluție de apă uzată care conţine clorură de benzetoniu, având concentrații de 2 mg / L și 20 mg / L. Sistemele de ape uzate au fost investigate la intervale de 1, 2, 4, 6, 24 și 48 ore. Cea mai mare eficiență de epurare (86,98%) a fost obținută pentru apele uzate care conțin concentrație de 2 mg/L de clorură de benzetoniu. Rezultatele obținute pentru nanomaterialul magnetită demonstrează posibilitatea aplicării acestui nanomaterial pentru îndepărtarea agentului tensioactiv cationic de clorură de benzetoniu din apele uzate.

Keywords: *magnetite nanomaterial, adsorbent, cationic surfactant, wastewater*

1. Introduction

An increasing number of products containing cationic surfactants are excessive used worldwide in care products (hair conditioning, cosmetics industry) and in household cleaning products (softening disinfectants, biocides). After utilization, residual amounts of surfactants and their degradation products are discharged into wastewater treatment plants or directly to surface waters and groundwater [1]. The concentration of surfactants in domestic wastewater is between 1 and 10 mg/L [2]. Cationic surfactants were frequently found in water but at lower concentrations. Some of the cationic surfactants such as quaternary ammonium salts belong to the category of emerging pollutants [3]. The presence of these compounds into environment will lead to serious environmental problems including ecological risk and human health damage [4]. In wastewater are found all type of surfactants (anionic surfactants, cationic surfactants, nonionic surfactant and amphoteric surfactants) and their interaction between them may provide an additional complexity to their removal treatment. For these reasons it is important to find the most efficient method of removing surfactants from wastewater. Three methods are used to remove surfactants from wastewaters such as physical methods, chemical methods and biological methods, but for cationic surfactant removal are recommended to find new and efficient alternative methods. Current research about the removal of surfactants were focused on the optimization of existing biological and chemical wastewater treatment [5]. Only few alternative methods have been studied to remove cationic surfactants from wastewater. Adsorption technologies have been considered most suitable for cationic surfactants removal from wastewater. Removal of cationic surfactants from wastewater using adsorption processes have been studied using a number of adsorbent materials like silica gel [6], bentonites [7], fly ash [8], clays [9], montmorillonite [10], activated carbon [11] and charcoal [12].

New adsorbent nanomaterials such as carbon nanotubes [13], unmodified multi-walled carbon nanotubes [14], zero-valent iron [15], magnetite nanomaterial [16] were investigated for applying within alternative treatment methods for removal cationic surfactants from wastewater.
Benzethonium chloride (diisobutyl-phenoxyethoxyethyl)dimethylbenzylammonium chloride), is an organic cationic surfactant, from the quaternary ammonium salt class, known as Hyamine 1622. Benzethonium chloride is utilized as antimicrobial and antibacterial

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ingredients in many consumer, industrial and medical products, including eye and nasal drops, soaps, mouthwash, and cosmetics [16]. In composition of medical products, benzethonium chloride is usually found at concentration below 1%[17]. Benzethonium chloride can be found in the food industry where it is used as a surface disinfectant [18]. The methods used for analysis of benzethonium chloride, used as preservative, in Grapefruit Seed Extract [19, 20] are based to HPLC/ UV /MS. A HPLC/DAD method for determining anionic (sodium dioctyl sulfosuccinate and sodium 1-dodecane sulfonate), amphoteric (CHAPS (3-[(3-Cholamidopropyl) dimethylammonium]-1-propanesulfonate hydrate)) and cationic (benzethonium chloride) surfactants mixture from surface water has been developed [21]. A spectrophotometric method was developed for the determination of benzethonium chloride in pharmaceutical formulation [22,23].

Although in the scientific literature are found many studies about adsorption materials used for removal from water of other quaternary ammonium salts such as benzalkonium chloride, cetylpyridinium chloride, dodecyltrimethylammonium bromide, hexadecyltrimethylammonium bromide and dodecylamine hydrochloride, the removal of benzethonium chloride from water has been poorly investigated.

In this study magnetite nanomaterial was obtained and tested as new adsorbent for removal of the cationic surfactant, benzethonium chloride, from wastewater.

2. Materials and methods

Benzethonium chloride, Hyamine 1622 (molecular formula: $C_{27}H_{42}ClNO_2$, molecular weight: 448,09 g/mol) was obtained from Sigma-Aldrich. The structure of benzethonium chloride is shown in Figure 1.

The wastewater standard solution had 1000 mg/L of benzethonium chloride.

The magnetite nanomaterial (Fe_3O_4) was synthesized through modified coprecipitation method. Ferric chloride ($FeCl_3 \cdot 6H_2O$), ferrous chloride ($FeCl_2 \cdot 6H2O$), polyvinylpyrrolidone (PVP), polyethylene glycol 400, sodium hydroxide (NaOH) were supplied from Sigma Aldrich and were used as received.

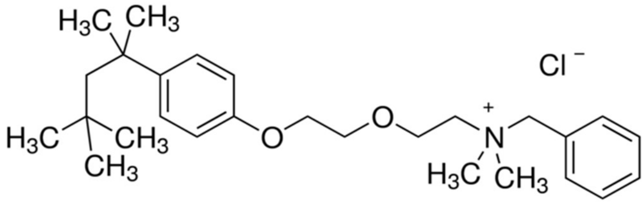


Fig. 1 - Chemical structures of benzethonium chloride./ *Structura chimică a clorurii de benzetoniu.*

The preparation of magnetite nanomaterial tested in the wastewater process was accomplished using 0.8 mol L-1 aqueous solution of sodium hydroxide and the reaction pH was 12. The molar ratio Fe^{2+}: Fe^{3+}: PEG: PVP unit was 1:2:3:4. The precipitate was separated by centrifugation and washed several times with water. Finally, Fe_3O_4 powder was obtained by precursor calcination at 410^{0}C for 2 h. The X-ray diffraction (XRD) analysis was obtained using a X'PERT PRO MPD with Cu-Kα radiation (λ = 0.15418 nm).

The morphology and crystalline properties of the Fe_3O_4 powder was assessed using a TecnaiTM F30 G^2 S–TWIN transmission electron microscope with a line–resolution of 1.2 Å and with energy dispersive X-ray (EDAX) spectrometer.

Kinetic studies were performed by adding 0,05 g of magnetite nanomaterial to 500 mL benzethonium chloride wastewater of concentrations 2 mg/L and 20 mg/L. The mixtures were homogenized at 200 rpm for 1, 2, 4, 6, 24 and 48 h. During the experiments, the collected samples were taken for analysis. The concentrations of surfactant were measured by SPECORD 205/ UV-VIS spectrophotometer, at 217 nm wavelength.

The removal efficiency (RE) of the benzethonium chloride from wastewater using magnetite nanomaterials was determined using the following equation:

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

where C_t and C_i are the benzethonium chloride t moment and initial.

3. Experimental section

X-ray characterization

The powder obtained from synthesis was analyzed by XRD. The XRD pattern (Fig.2) of oxide

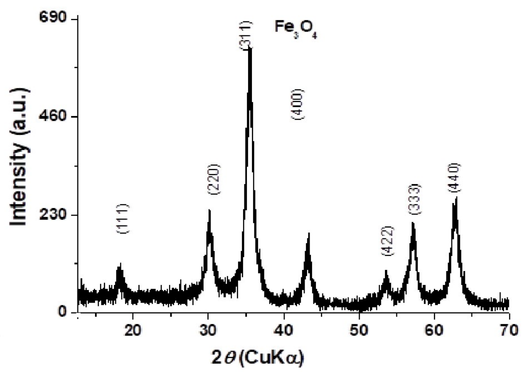


Fig. 2 - XRD patterns of Fe_3O_4 nanomaterial / *Difracția de raze X a nanomaterialului Fe_3O_4.*

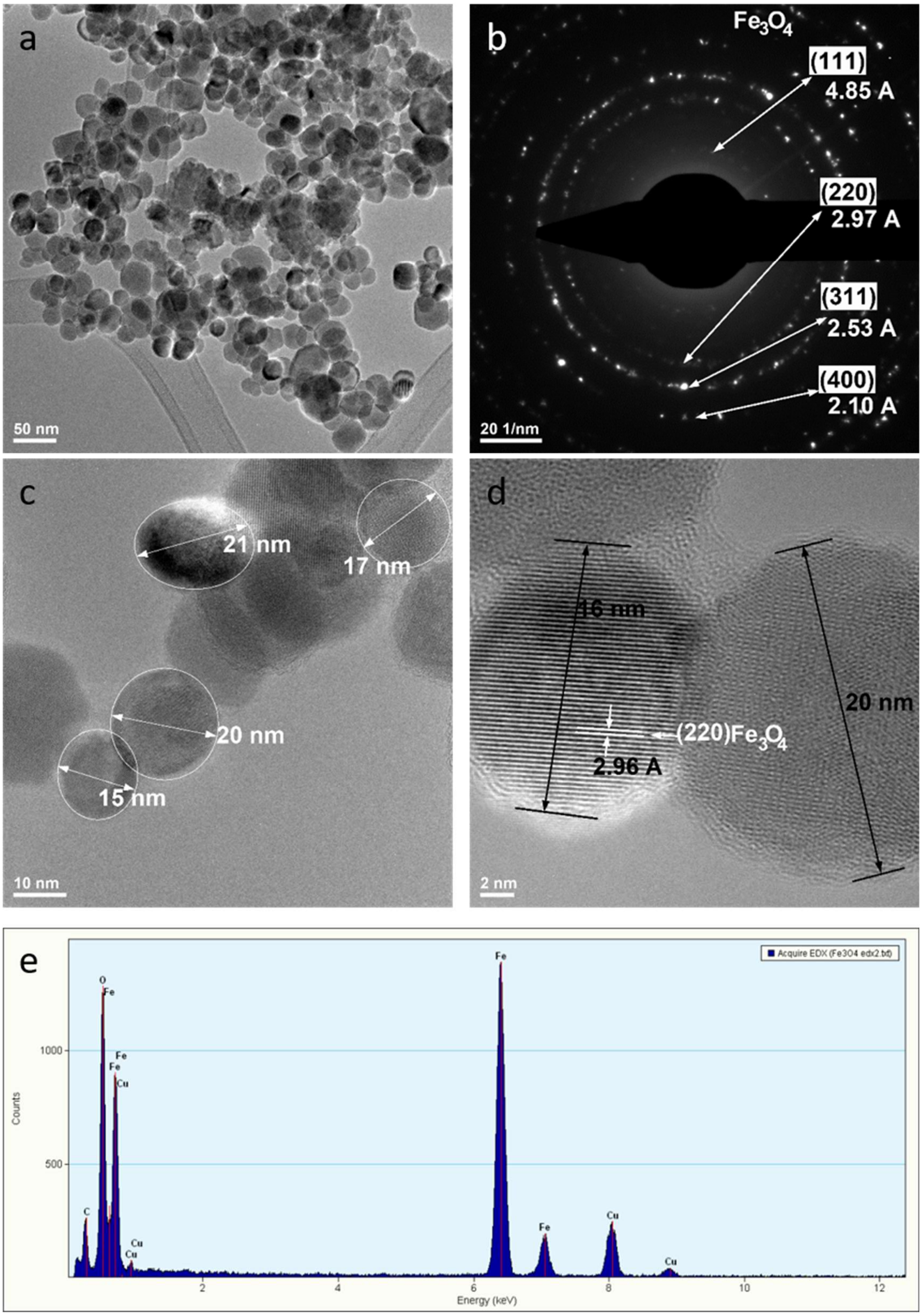


Fig. 3 - TEM of Fe_3O_4: a) BF-TEM image of Fe_3O_4 nanoparticles agglomeration; b) selected-area electron diffraction (SAED) pattern for the Fe_3O_4 powder associated to the nanoarea in image a; c), d) HR-TEM images; e) EDAX spectrum acquired on the nanoparticles agglomeration from image a. / *Rezultate TEM obținute pe nanomaterial Fe_3O_4: a) Imagine BF-TEM a unei aglomerări de nanoparticule; b) imagine de difracție de electroni (SAED) asociată nanoariei din a); c), d) imagini HR-TEM; e) spectru EDAX achiziționat pe aglomerarea de nanoparticule din a).*

powder has proved the formation of single phase compound with inverse spinel structure and cubic symmetry for Fe_3O_4, in accordance with the PDF database, ICDD file no. 01-072-8149. The average crystallite size was 15 nm.

TEM analysis

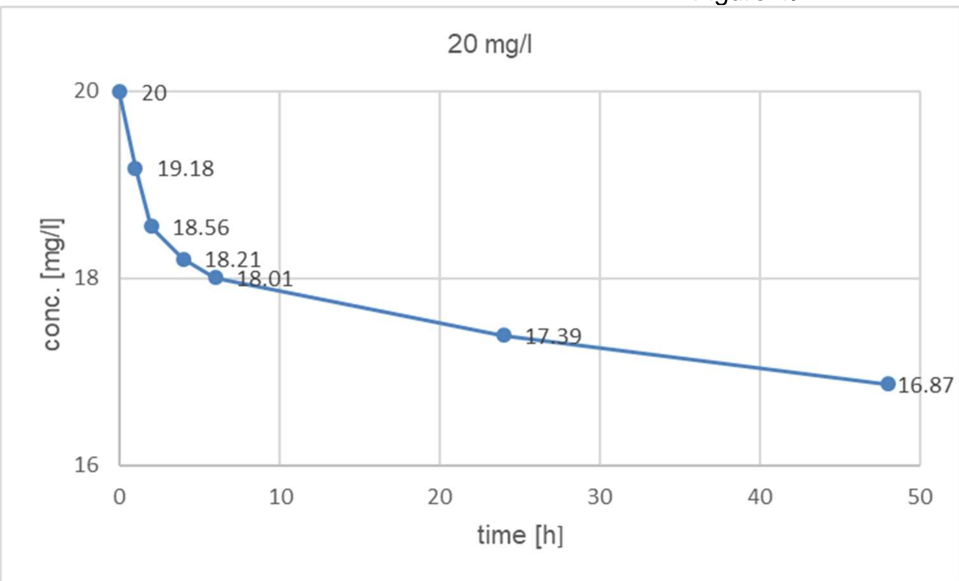
Result of transmission electron microscopy (TEM) investigation are shown in Figure 3.

Figure 3. a), c), d) are TEM micrographs of the Fe_3O_4 nanoparticles. The bright field transmission electron microscopy (BF-TEM) image (Figure 3. a) and high resolution transmission electron microscopy (HR-TEM) image (Figure 3.c) show that the Fe_3O_4 nanoparticles are nearly spherical with diameters between 15 and 25 nm. Nanocrystalline particles with diameter size between 15 and 21 nm are highlighted in Figure 3. c, d. The crystalline structure of the sample was investigated by selected area electron diffraction (SAED) and high resolution transmission electron microscopy (HRTEM). Indexing of SAED image (Figure 3. b) shows that the Fe_3O_4 sample is nanocrystalline (diffraction rings), with a typical face centered cubic (fcc) crystalline structure. The lattice spacing measured on SAED image is in accordance with the standard lattice spacing of Fe_3O_4 from the PDF database, ICDD file no. 01-072-8149. The parallel fringes existing on HRTEM images (Figure 3. c, d) show the single crystallinity of Fe_3O_4 nanoparticles. In the HRTEM image from Figure 3. d it can be seen the crystalline planes with 2.96 Å interplanar distance corresponding to crystalline family planes with (220) Miller indices of Fe_3O_4 phase.

The chemical composition of the nanoparticles analyzed has been verified by energy dispersive X-ray microanalysis (EDAX). Fe and O are major elements in EDAX spectrum (Figure 3. e) collected on Fe_3O_4 nanoparticles agglomeration from Figure 3.a, confirming the nature of nanoparticles as magnetite. The minor carbon and oxygen elements present in the EDAX spectrum come from the copper TEM grid coated with a thin amorphous carbon film.

Adsorption study

The concentration of benzethonium chloride represented versus time (hours) is presented in Figure 4.



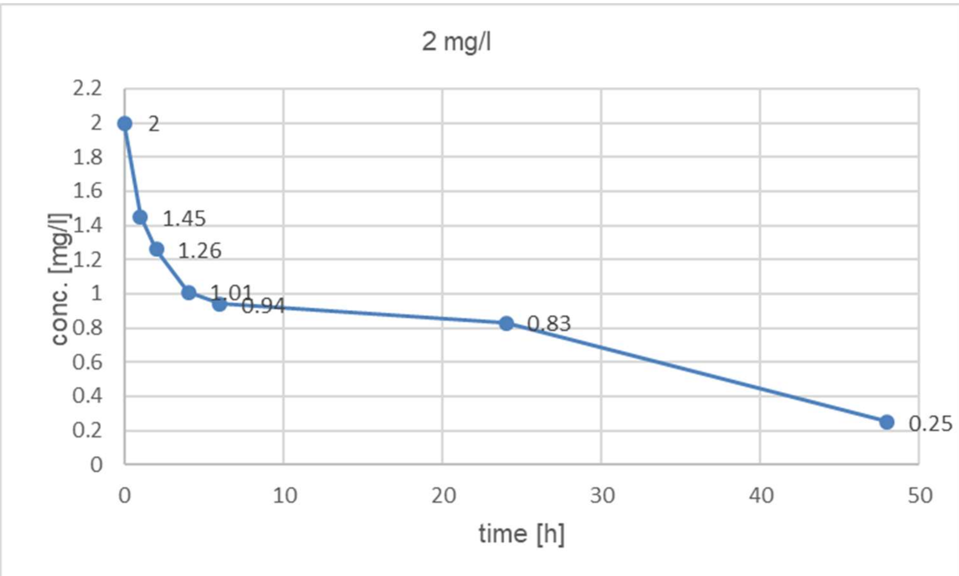


Fig. 4 - Variation of concentration of benzethonium chloride (20 mg/L and 2 mg/L) versus time (h)/ *Variația concentrației de clorură de benzetoniu (20 mg/L and 2 mg/L) versus timp (ore).*

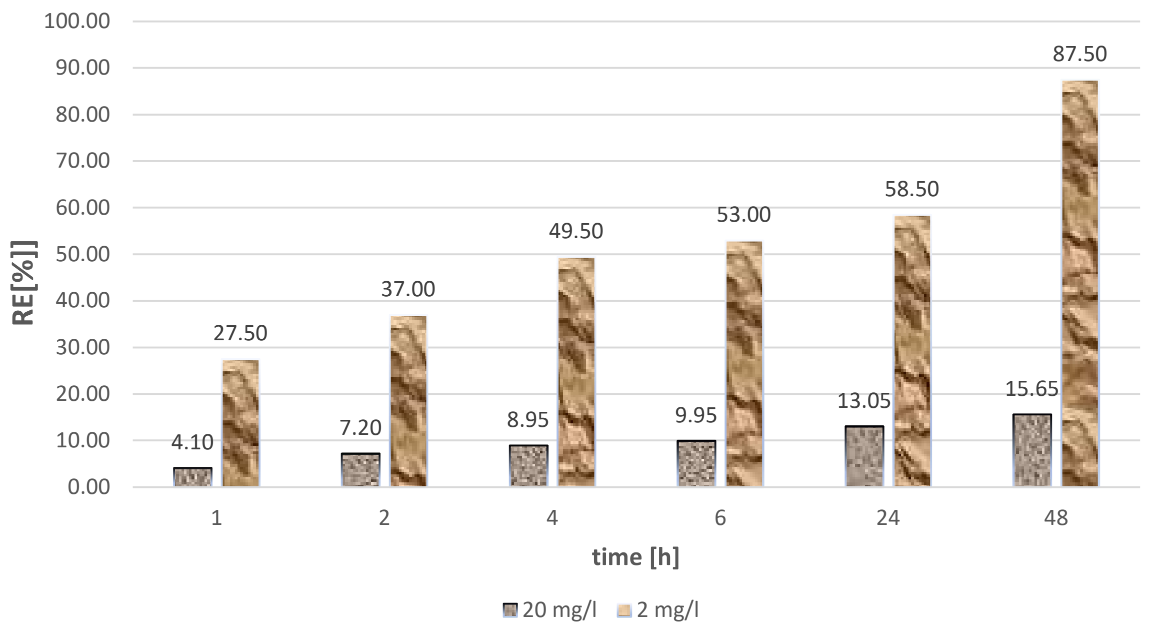


Fig. 5 - The variation of the removal efficiency (RE) % of benzethonium chloride concentration from wastewater versus time (h).
Variația eficienței de îndepărtare (RE) % a clorurii de benzetoniu din apa uzată versus timp (h)

For the wastewater having the concentration of 2 mg /L pollutant the results showed that benzethonium chloride concentration decreased to 0,25 mg /L. The difference of 1,75 mg/L benzethonium chloride represents the absorption capacity of Fe_3O_4 nanomaterial which was about 35 mg benzethonium chloride/ g Fe_3O_4 nanomaterial.

For the wastewater having the concentration of 20 mg/L benzethonium chloride, the results showed that this concentration decreased to 16,87 mg/L, which means that this concentration exceeded the adsorption capacity of Fe_3O_4 nanomaterial. The maximum amount of benzethonium chloride adsorbed on the magnetite nanomaterial was 57 mg/ g nanomaterial.

The variation of the removal efficiency (RE) % of benzethonium chloride concentration from wastewater versus time (h) was presented in Figure 5.

The maximum benzethonium chloride removal efficiency obtained was 87,5 % for wastewater containing 2 mg/L benzethonium chloride and 0,05 mg magnetite nanomaterial, after 48 h of treatment.

4.Conclusions

Increasing number of products containing cationic surfactants excessive used worldwide in care products (hair conditioning, cosmetics industry) and in household cleaning products (softening disinfectants, biocides) leads to the need of finding more efficient ways of wastewater depollution. In this regard, the study that we made was based on the use of Fe_3O_4 nanomaterial in order to remove benzethonium chloride from wastewater.

Kinetic studies were performed by adding magnetite nanomaterial adsorbent to a wastewater solution of benzethonium chloride having the concentrations of 2 mg/L and 20 mg/L. The wastewater systems were investigated during 1, 2, 4, 6, 24 and 48 h. The highest removal efficiency (86.98%) was obtained for wastewater containing 2 mg/L benzethonium chloride concentration. The results obtained for the magnetite nanomaterial sustains the possibility of applying it for the removal of benzethonium chloride cationic surfactant from wastewater.

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