

ORIGINAL RESEARCH PAPER

Removing Sodium Dodecyl Benzene Sulfonate Using a Hybrid Electrocoagulation/Flotation and Photocatalytic System

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ABSTRACT

This study was conducted to evaluate sodium dodecyl benzene sulfonate removal using electrocoagulation/flotation and photocatalytic nano-TiO₂ slurry systems. The parameters which are effective on the surfactant removal were investigated and optimized. Electrocoagulation/flotation system included meshed and mono-polar stainless steel electrodes which installed horizontally. According to the results, after 60 minutes in pH of 8, electrodes distance of 1 cm, initial SDBS concentration of 750 mg/L, SDBS and COD removal rates were achieved to 93.54 and 90%, respectively. In photocatalytic system, during 48 h, SDBS and COD removed 98.7 and 95%, respectively, while pH was around 8, initial concentration of SDBS was 300 mg/L and nano-TiO₂ particles concentration was 0.5 mg/L. In the hybrid system, after 12 minutes, SDBS concentration reached 329 mg/L which entered to the photocatalytic system that resulted in SDBS and COD removal efficiency of 99 and 96.27%, respectively. Compared to the single systems, by using the hybrid system, the removal efficiencies were improved.

Keywords: Anionic Surfactant; Anode Dissolution; Detergent; Electrocoagulation/Flotation; TiO₂

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INTRODUCTION

Today, surfactants are considered as one of the most important compounds that have extensive domestic and industrial usage [1]. Annually, about 12 million tons of surfactants are produced. Discharges of these chemicals are toxic to aquatic life and soil, which can cause significant environmental problems. Thus, they can be considered as one of the most important hazards to the environment [2].

Detergent wastewater has a high COD concentration (600-4000 mg/L) [3]. High pH and temperature are other specifications of this wastewater [4]. There are a few methods to treat this type of wastewater.

Surfactants have large molecules that cause various environmental impacts such as eutrophication, foam generation [5] and decrease in dissolved oxygen of the receiving water [6]. According to the high cleaning power

of sodium dodecylbenzene sulfonate (SDBS), it is used vastly in different industries such as food, pesticides, and pharmaceuticals. It is also one of the main constituents of detergents [7]. So far, different physical, chemical and biological methods such as coagulation, UV photo-catalysis [8], biofilm reactor [9], carbon nanotubes [10] and artificial wetlands [11] have been used to remove detergents. Each method has its own advantages and disadvantages. For instance, physical methods are less efficient and economical to remove high concentrations of pollutants from wastewater. Usually, biological processes are highly dependent on environmental conditions. Therefore, it is very appropriate to combine chemical methods, to benefit from the advantages of each system.

Electrocoagulation/flotation is one of the flotation methods, in which tiny bubbles are

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generated through water electrolysis. When two electrodes are entered in the solution, the electric current produces an electric field between anode and cathode. Therefore, primary coagulation occurs, and negative and positive particles generate flocs. Also, under electrical stimulation conditions, because water is hydrolyzed, tiny hydrogen and oxygen bubbles are generated and come up vertically [12, 13]. In this method, high-quality gases are generated and the volume and distribution of electrolyte gases can be controlled. These are the main advantages of this method. Furthermore, a large number of strong oxidants such as hypochlorite can be produced. This can remove mineral and non-mineral pollution [14].

Other methods for wastewater treatment are advanced oxidation processes such as photocatalytic systems. In these methods, hydroxyl radicals produce a strong oxidant to decompose and destruct a wide range of pollutants [15]. TiO_2 is used frequently due to its optical-electrical properties, high photocatalytic activity, high chemical stability, non-toxicity, frequency, availability and the lack of erosion and corrosion in the light [16]. It has also a high surface area and proper particle size distribution [17].

The main aim of this study was to remove an anionic surfactant, sodium dodecylbenzene sulfonate (SDBS), using a combination of electrocoagulation/flotation and photocatalytic systems in order to minimize energy consumption and anode dissolution as economic criteria.

EXPERIMENTAL

Materials and Equipment

The materials used in this study included sodium dodecylbenzene sulfonate (SDBS) produced by Aldrich Company, NaCl to supply conductivity, HCl and NaOH to adjust the pH of the system, Acridine Orange and Toluene, all produced by Merck Company, and TiO_2 nanoparticles produced by Degussa Company, Germany.

The main equipment applied in this study were Hach spectrophotometer DR 4000, Megatek PM-3005D Power Supply for supplying electric current, ultrasonic cleaner (UE-6SFD), IKA magnetic stirrer RH-Basic2 for mixing the solution, Mettler digital pH meter 691 for pH determination, three 8-watt Philips ultraviolet (UV) lamps with 253.7 nm wavelength, Xpert-MPD LC-MS for determining possible combinations and Mira3 Tescan Microscope.

Methods

The laboratory-scale electrocoagulation/flotation system was a cube made of Plexiglas with the dimensions of 15*7*7 cm and 500 mL of effective volume. To create more efficiency in the electro-floatation system, the mono-polar electrodes were placed horizontally. They were made of stainless steel and were meshed using a grid with holes diameters of 8 mm. Also, since the cathode plays a key role in hydrogen generation, it was placed above the anode.

In the photocatalytic system, after using ultrasonic cleaner to de-agglomerate TiO_2 nanoparticles for 30 minutes, SDBS wastewater was added to the mixture. Then it was placed on the magnetic stirrer (150 rpm) under the UV lamp.

In this study, SDBS concentration was measured by Acridine Orange method, developed by Rajer [18] and Adak [19]. This method is highly accurate for measuring samples containing anionic surfactant at concentrations of 0.1-0.6 mg/L. The measurement process was as follows: 10 mL of sample was added to a 50 mL separatory funnel. After that, 100 μL of Acridine Orange solution (0.050 molar), 100 μL of acetic acid and 5 mL of toluene were added. The whole mixture was shaken for one minute. The absorption of the uppermost solution in the separatory funnel (toluene) was measured by spectrophotometer at a wavelength of 467 nm. The samples which required dilution were diluted in appropriate volumes.

SDBS and COD removal efficiencies were calculated according to equation (1). In this equation, C_0 is the initial concentration of SDBS or COD, and C is the concentration of SDBS or COD [20].

$$R = [(C_0 - C) / C_0] \cdot 100 \quad (1)$$

The amount of specific energy (kWh/kg removed SDBS), which can be a significant factor in justifying the process, has been calculated through equation (2). In this equation, U is the potential difference (V), I is current intensity (A), t is reaction time (h), V is the volume of wastewater (L), and C_0 and C are initial and final concentrations (gr/L) [20].

$$\text{SEC} = U \cdot I \cdot t / (V \cdot (C_0 - C)) \quad (2)$$

The amounts of metals dissolution and anode decomposition were calculated by Faraday's law according to equation (3). In this equation, m is the

mass of dissolved anode (g), I is current intensity (A), t is electrolysis duration (s), M is molar mass (Fe= 56), F (Faraday constant) is 96485 C/mole, and z is metal capacity (Fe=2) [20].

$$m=I.t.M/(F.z) \quad (3)$$

All experiments were repeated for three times in laboratory temperature (around 25°C) and their average was reported.

RESULTS AND DISCUSSION

Electrocoagulation/Flotation System

In the electrocoagulation/flotation system, the effect of electrodes distance, initial SDBS concentration, initial pH and electric current intensity were studied. Summary of the results in different levels is shown in Table 1 [21].

According to the results, the electrode distance of 1 cm was chosen as the optimal amount. Because by increasing electrode distance to more than 1 cm, due to the delay in flocs formation and its dependence on mobility of materials and ions produced in the electrodes, the efficiency decreased [22,23]. Also, less electrode distance is not economical because of non-favorable transfer of material and fluid, accumulation of bubbles and solid particles between anode and cathode

and probability of short-circuiting in the electric current [24,25]. In the next part of the research, initial SDBS concentration of 750 mg/L was chosen as the optimal amount because with a known increase in SDBS concentrations, energy consumption decreased, as also reported by other researchers [26]. According to the studies, both coagulation/flocculation and absorption of SDBS molecules on the generated flocs contribute to the removal efficiency [27].

Although it is always preferred to use initial pH without adding chemicals to the solution, since pH is an important parameter in electrochemical processes [26, 28], the experiments were carried out at different pHs. In various pHs, generation of monomeric and polymeric species of iron is different, and the coagulation mechanism depends on solution pH. Production of $Fe(OH)_3$ flocs as adsorbent in the solution and their performance at various pH are important. The amount and size of produced bubbles are also pH-dependent. Due to pH variation during process and by examining the mentioned mechanisms, the effect of pH on removal rate can be explained by flotation processes [29]. As a result, because there is no need to add chemicals to set pH to 8, and also according to the high removal efficiency, this pH was considered as the optimal amount.

Table 1. Results of Electro Flotation System

Parameter	Studied Amounts	Maximum COD Removal Efficiency (%)	Maximum SDBS Removal Efficiency (%)	Energy Consumption (kWh/kg for 90% SDBS removal)	Anode Dissolution (kg Fe/ kg SDBS Removal for 90% SDBS removal)	Optimal Value
Electrode Distance (cm)	0.5	50.8	85.6	603.2	2.3	1
	0.75	64.75	84.1	1025.5	2.15	
	1	18.76	84.9	923	2.08	
	1.5	50.87	81.9	746	2.2	
Initial SDBS Concentration (mg/L)	50	79.1	83.9	970	1.8	750
	100	76.3	93.8	905	2.08	
	250	77.5	88.7	236	2.35	
	500	88.75	97.29	100	0.07	
	750	90.6	93.84	35	1.04	
Initial pH	1000	78.1	93.6	53	1.41	8
	3	89.2	90.88	31	0.96	
	6	89.4	81.94	40	1.28	
	8	92.99	81.94	39	1.04	
	11	89.52	81.94	42	1.29	
Current Intensity (A)	0.5	83.8	85.4	49.1 (for 85% removal)	0.77	1
	0.8	87.6	93.1	30.30 (for 85% removal)	0.53	
	1	91	93.4	19 (for 85% removal)	0.45	
	1.2	92.5	90.2	25 (for 85% removal)	0.64	
	1.5	89.2	82.9	36 (for 85% removal)	1.04	

The current intensity is the other important variable that significantly affects the electrochemical processes [30]. Generally, due to the increase in the production of Fe^{3+} ions on the anode, SDBS removal rate depends directly on the electric current [31]. In high amounts of current, high number of coagulants and production of gas on electrode surface enhances the mixing and floating processes [26, 32]. According to the results, the current intensity of 1A was chosen as the optimum amount.

Photocatalytic System Results

Effect of Initial SDBS Concentration

In order to investigate the effect of SDBS concentration, experiments were carried out at different initial concentrations. The results are shown in Figs. 1 (a) and (b). As indicated, the increase in initial SDBS concentration led to a decrease in removal efficiency. Thus, at the initial concentrations of 150, 300 and 700 mg/L (COD equal to 200, 500 and 900 mg/L), after 24 h, SDBS removal efficiencies were reached to 97.6, 84.15 and

52.28% and COD removal efficiencies were 82.93, 72.04 and 0.0%, respectively.

As it is observed, with SDBS concentration increase, the removal efficiency reduces, due to the decrease in UV penetration and OH^\bullet production. Thus, at high concentrations of SDBS (700 mg/L), after 24 h, no significant amount of SDBS and COD were removed. Since less pollutant removal time cannot be a deterministic criterion in choosing an optimal concentration, energy consumption at the same removal efficiency was calculated. According to Figs. 2(a) and (b), at concentrations of 150, 300 and 700 mg/L, the amounts of energy consumption for 50% of SDBS removal, were 57.1, 43.1 and 57.1 KWh, respectively. According to the results, the concentration of 300 mg/L (COD of 500 mg/L) was selected as the optimal concentration for further investigations.

Effect of pH

One of the effective parameters in photocatalytic reactions is the initial pH. It significantly affects the surface charge, oxidation and reduction potential

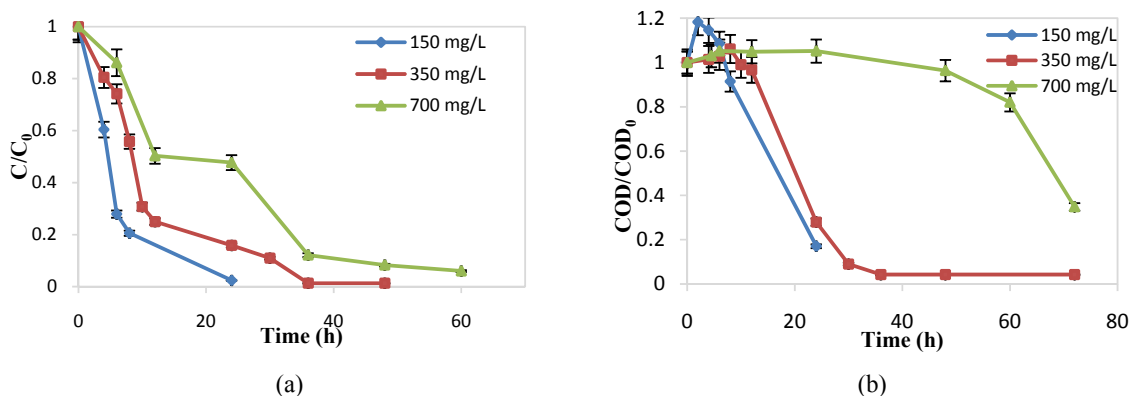


Fig. 1. (a) SDBS concentration to initial SDBS concentration ratio vs. time (b) COD/COD_0 vs. time in various initial SDBS concentrations ($[TiO_2] = 0.5$ mg/L, $pH=8$)

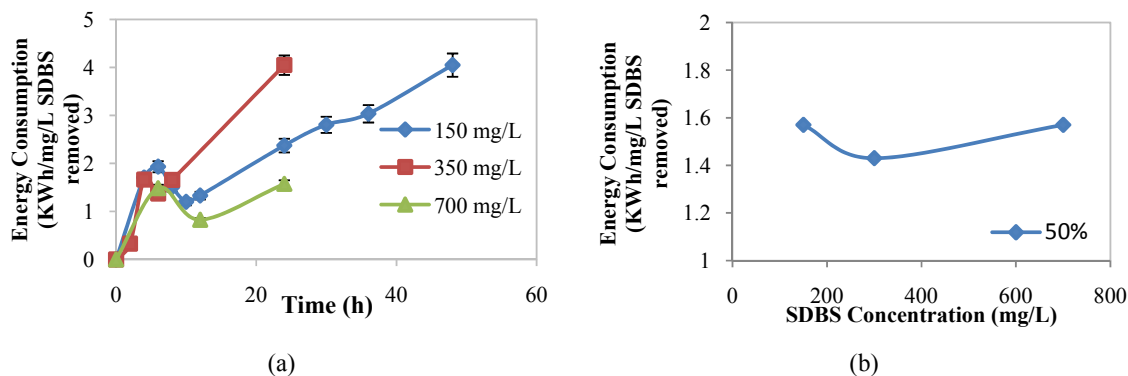


Fig. 2. (a) Energy consumption vs. time (b). Energy consumption vs. SDBS concentration at 50% removal efficiency ($[TiO_2] = 0.5$ mg/L, $pH=8$)

and position of energy bands. According to Figs. 3 (a) and (b), after 48 h at pHs of 6, 8, and 11, SDBS removal efficiencies were 99.3, 98.7 and 99%, and COD removal efficiency were 96, 95.8 and 55%, respectively.

Since the point of zero charges (pH_{pzc}) of TiO_2 nanoparticle is between pH 6.25 and 7.5, if pH is higher than pH_{pzc} , the particles have a negative charge, and they have a positive charge when pH value is lower than pH_{pzc} . Maximum removal efficiency happens in the pHs between solution pH and the photo-catalyst pH_{pzc} because, in this range, the solution and photocatalyst have non-similar charges, which causes particles to be absorbed into the photocatalyst. Since SDBS is an anionic surfactant, when pH value is higher than pH_{pzc} , the nanoparticles and SDBS have similar charges. Thus, the particles and photocatalyst repelled each other and the system efficiency will reduce [33]. Consequently, while the initial pH was in its natural amount (about 8), the removal rate was higher than the other pHs. Moreover, at this pH, no

chemicals are required to adjust the initial pH for starting up the system. Therefore, natural pH of 8 was considered as the optimum level.

Effect of Initial TiO_2 Concentration

SDBS and COD removal efficiencies are shown in Figs. 4(a) and (b). As observed, after 24 h, when TiO_2 concentrations were 0.3, 0.5, 0.8 and 1.2 g/L, SDBS removal efficiencies were 93.9, 84.1, 96.9 and 78.1% and the COD removal rates were 87, 95, 95, and 45%, respectively. Also, after 48 h, for the above-mentioned TiO_2 concentrations, SDBS removal efficiencies were 98.4, 98.7, 99.8 and 98.1%, and COD removal efficiencies were 87, 95, 95.3 and 95%, respectively.

The results indicate that by increasing the amount of catalyst, SDBS removal efficiency also increases, as also reported by the other researchers [34]. As it can be observed, by increasing nanoparticles to more than 0.5 mg/L due to an increase in turbidity, a descending trend was observed in removal efficiency [35]. Therefore, initial TiO_2 particles

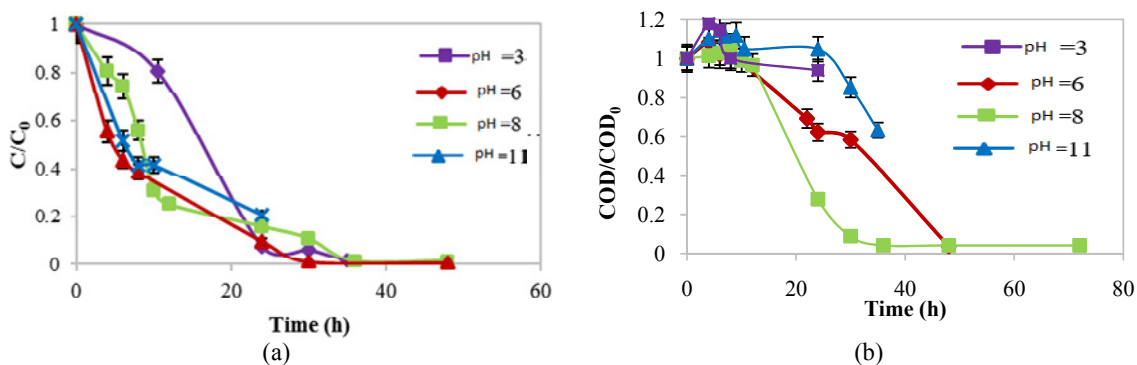


Fig. 3. (a) SDBS concentration to initial SDBS concentration ratio vs. time in various initial pH levels (b) COD/COD_0 vs. time in various initial pH levels ($[TiO_2] = 0.5 \text{ mg/L}$, $[SDBS] = 300 \text{ mg/L}$)

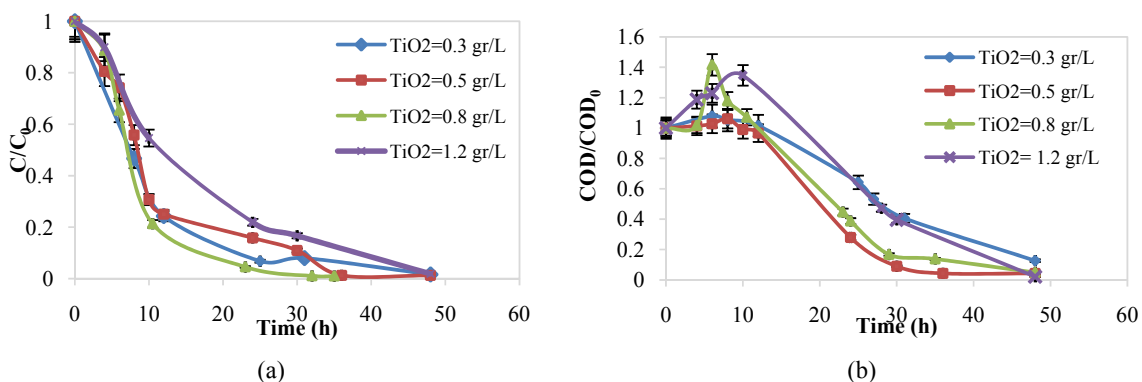


Fig. 4. (a) SDBS concentration to initial SDBS concentration ratio vs. time in various TiO_2 concentrations (b) COD/COD_0 vs. time in various TiO_2 concentrations ($pH=8$, $[SDBS] = 300 \text{ mg/L}$)

concentration of 0.5 gr/L was considered as the optimum value.

Hybrid System

In order to evaluate the removal efficiency of the hybrid system, the optimum conditions in each system were considered. First synthetic wastewater was treated, with the optimum conditions of electrocoagulation/flotation system ([SDBS] =750 mg/L, COD=1000 mg/L, pH=8), until the characteristics of output wastewater met the optimum conditions of photocatalytic system ([SDBS] = 300 mg/L, COD=500mg/L, pH=8). After that, wastewater was entered the second system. The results of SDBS and COD removal efficiencies are shown in Figs. 5(a) and (b). As it is observed, after 12 minutes, SDBS concentration reached from 750 to 329 mg/L. Afterward, it entered the second system with the SDBS concentration of 329 mg/L (COD= 300 mg/L, pH=8, TiO_2 = 0.5 mg/L). According to Fig. 5 (a), COD removal efficiencies after 6, 12, 24 and 48 h in the singular photocatalytic system are 0, 3.3, 72 and 95.7%, respectively but in the hybrid system, the efficiencies are 71.83, 75, 77 and 96.27%, respectively. As shown in Fig. 5 (b), SDBS removal efficiencies after 6, 12, 24 and 48 h in the singular photocatalytic system are 25, 74.96, 84 and 98.5%, respectively, and in the hybrid system are 72.5, 80.61, 83.01 and 99.6 %, respectively. Compared to the single systems, by using the hybrid system, the removal efficiencies were improved.

LC-MS Test Result

In the electrocoagulation/flotation system, in the presence of chlorine ions, chlorine oxidation compounds are formed, which can

break down the contaminating molecules. Also, in the photocatalytic system, the pollutant is broken down by the above-mentioned reactions. Therefore, the more accurate investigation was required on the production and accumulation of intermediate compounds, during and after the processes. The results of LC-Mass experiments on the initial sample of photocatalytic system (initial concentration=350 mg/L), final sample of the photocatalytic system (initial concentration=350 mg/L) and final sample of electrocoagulation/flotation system (initial concentration=750 mg/L) are shown in Figs. 6 (a) to (c).

As observed, in the initial sample, the first peak with 360 m/z refers to the molecular weight of sodium dodecylbenzene sulfonate, which is indicated by letter M. The rest of the numbers are related to other existing combinations. The numbers of 154, 248 and 180 could be related to $M-SO_3-Na$, $M-C_{12}H_{25}-Na$, and $M-C_{12}H_{25}$ that are lighter than SDBS and are created by some of the bonds being broken in the surfactant structure.

In the main sample of the photocatalytic system in Fig. 6 (b), most of the peaks have come down in the initial sample. This indicates that, after the reaction, compounds concentrations have reduced. The new peaks are formed at the number of 321 that is related to M-Na. As indicated in Fig. 6 (c), in the electrocoagulation/flotation system, the treated water also contains lower concentrations of heavy compounds than the initial sample. Also, due to the high molecular weight of the surfactant used in the electrocoagulation/flotation system, the substance became a lighter compound. Finally, it can be concluded that both methods are effective to remove the anionic surfactant of sodium dodecylbenzene

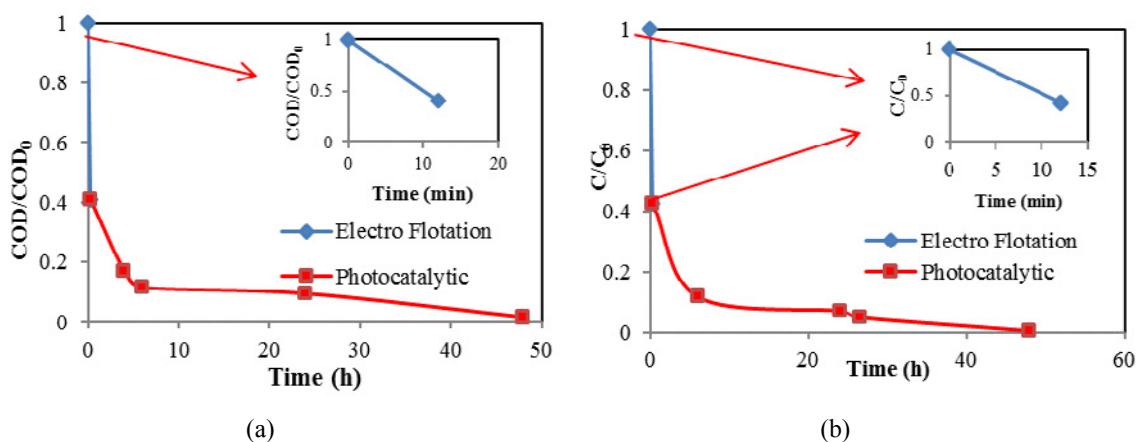


Fig 5. (a) SDBS concentration to initial SDBS concentration ratio) vs. time (b) COD/COD₀ vs. time in a hybrid system

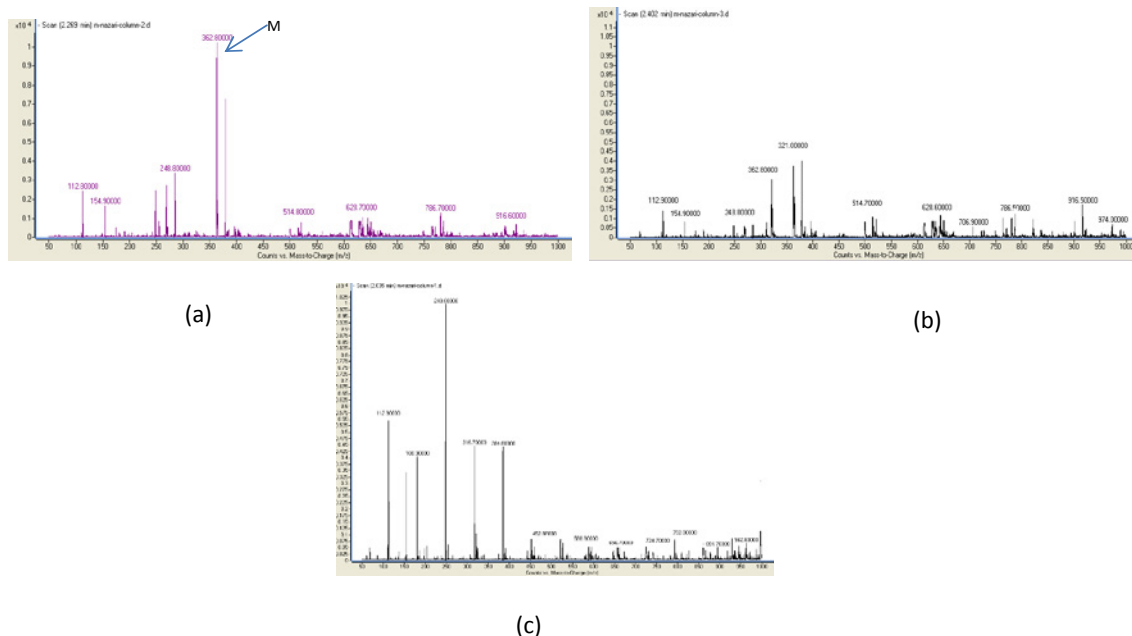


Fig 6. (a) LC-mass spectrometry test of SDBS in the initial sample of photocatalytic system (b) LC-mass spectrometry test of SDBS in final sample of photocatalytic system (c) LC-mass spectrometry test of SDBS in final sample of electrocoagulation/flotation system

sulfonate and other similar compounds.

As observed, the advantages of using electrocoagulation/flotation as a pretreatment system are:

- Reduction of sludge production and energy consumption due to the reduction of retention time from 60 minutes to 12 minutes.
- Increase in the removal rate in the photocatalytic system of the hybrid system
- Ability to remove high contaminant concentrations in the hybrid system. Because the photocatalytic system alone cannot remove high concentrations.

CONCLUSION

According to the drawn results, electrocoagulation/flotation, photocatalytic and hybrid systems have high SDBS and COD removal efficiencies. In the electrocoagulation/flotation system, while pH was 8, the distance between electrodes was 1 cm. After 60 minutes, the initial SDBS concentration was 750 mg/L, and SDBS and COD removal efficiencies were 93.54 and 90%, respectively. In the photocatalytic system, SDBS and COD removal efficiencies were achieved to be 98.7 and 95%, respectively. After 48 h, while the pH was around 8, the initial SDBS concentration was 300 mg/L, and nano TiO₂ particles concentration was 0.5 mg/L. In the hybrid system, SDBS and COD removal efficiencies were

obtained to be 99 and 96.27%, respectively. Results indicated that due to the reduction of retention time and energy consumption and generated sludge in electrocoagulation/flotation system, as a pretreatment for the photocatalytic system, it can be used as a safe and flexible method for industrial wastewater treatment, in high contaminant concentrations.

CONFLICTS OF INTEREST

There are no conflicts to declare.

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