

Comparing activated carbon and magnetic activated carbon in removal of linear alkylbenzene sulfonate from aqueous solution by heterogeneous catalytic ozonation process

Vahid Mohammadi^a, Masoumeh Tabatabaee^b, Abdolmajid Fadaei^{c,*}, Seyed Abolghasem Mirhoseini^a

^aDepartment of Environmental, School of Agriculture and natural resources, Islamic Azad University, Yazd, Iran.

^bDepartment of Chemistry, Yazd Branch, Islamic Azad University, Yazd, Iran.

^cDepartment of Environmental Health Engineering, School of Health, Shahrekord University of Medical Sciences, Shahrekord, Iran.

Received 6 March 2020; received in revised form 9 July 2020; accepted 18 July 2020

ABSTRACT

Activated carbon from pine cone (PCAC) was used as a precursor to prepare Fe₃O₄/magnetic activated carbon (MPCAC). Here, the removal of linear alkylbenzene sulfonate (LAS) was studied using catalytic ozonation process (COP) in exposure to MPCAC. Subsequently, it was compared with PCAC. Moreover, the effects of solution's initial pH, catalyst dosage, and the time of ozonation on the removal process were comparatively studied in reference to a sole ozonation process (SOP). According to the results of this study, compared with PCAC, degradability could be improved and initial concentration of LAS reduced by COP using MPCAC. Consequently, almost complete removal (>98%) of 25 mg/L of LAS was achieved under the optimum conditions (15 min ozonation time, 7 mg/min ozone flow, 0.3 g/L catalyst dosage and pH=10). Concluding, this nanocomposite is an effective active catalyst for mineralization and degradation of LAS in COP.

Keywords: Magnetic activated carbon, Heterogeneous catalytic ozonation process, LAS degradation, Aqueous solution.

1. Introduction

Because detergents are organic synthetic substances with high purifying and germicidal features, and they could be used to maintain health and control of communicable diseases, especially infectious diseases, the per capita consumption of detergents has increased. During the past decade, large quantities of detergents have entered the environment [1]. Surfactants are classified into four types on the basis of their ionic activity in water: anionic, cationic, non-anionic and amphoteric [2]. One of the surfactants that mostly are used in laundry detergents is anionic surfactants because of their excellent work to eliminate pollution including, filth, pus and some oily stains [3]. To illustrate, linear alkylbenzene sulfonate (LAS) is the most important anionic surfactant that has a hydrophobic chain and a polar head (Fig. S1).

Because of its considerable performance and inexpensiveness, it has been widely used in household detergents since the early 1960s [4]. According to the results of the study, LAS mean concentration in household wastewater is 3-21 mg/L [5], but it degrades extremely slowly and has potential to accumulate in aquatic environment. Therefore, the environmental impact of LAS could be considered as an important concern for many years.

Up to now, widely various catalysts have been used to remove organic pollutant such as azo dyes [6, 7]. It should be noted that new catalysts are included Ag [7], Pd [8], Cu [9, 10], Fe₃O₄ [11] and ZrO₂ [7] nanoparticles on various substrate such as graphene [12] and bentonite [6] which have been developed for treatment of wastewater and water processes. Recently, use of advanced oxidation processes (AOPs) has been a widespread technology to eliminate organic contamination. The AOPs are processes using highly active radicals including hydroxyl radicals ($\bullet HO$) as oxidants to remove the contaminant from water.

*Corresponding author.

E-mail address: ali2fadaei@yahoo.com (A. Fadaei)

Moreover, heterogeneous catalytic ozonation process (COP) is a novel type of AOP, which can enhance organic pollutants' degradation in exposure to solid catalysts. The COP, which is a useful and potent method of treatment, has been used to improve the ozonation process efficiency [13]. Many studies have reported that organic compounds mineralization could be enhanced by combination of ozonation with heterogeneous catalysts such as metal oxides, metals, mineral compounds such as activated carbon [14,15]. Accordingly, a variety of catalysts degrade ozone molecules into hydroxyl radicals ($\bullet HO$) that will react with organic substances in aqueous environments non-selectively [16]. To enhance COP efficiency in removing various contaminants, attempts have been aimed at designing and preparing novel catalysts [17]. Accordingly, the removal of various organic compounds has been investigated with this method. Also, compared to single ozonation process (SOP), better efficiency of heterogeneous catalytic ozonation has been reported [18-20].

Recently, there has been a principal focus on the activated carbons with highly developed surface area used in different applications, including water and wastewater treatment, as supporting substrate of catalytic materials [21]. Preparing activated carbons from natural materials has been proposed as a facile, inexpensive, and potentially fruitful technique towards the new environmentally friendly technologies for synthesizing carbonaceous substrates with a high surface area [22].

Additionally, magnetic nanoparticles have been widely synthesized and used as a suitable case to remove various organic compounds from wastewater and water. Therefore, the advantages of this materials are privileged magnetic properties, chemical stability, nontoxic synthesis, biocompatibility, low cost, easy separation from the aqueous solution [23].

In this research, pine cone derived from activated carbon (PCAC) was produced from pyrolysis of pine cone. Then, PCAC converted into magnetic activated carbon (MPCAC) by adding ferric chloride and iron sulfate solutions. Subsequently, this catalyst was characterized and used to remove LAS from aqueous environments in the COP. This study comparatively investigated the catalytic activity of powder activated carbon and pine cone-derived magnetic activated carbon to remove LAS from aqueous solution in the catalytic ozonation process. Both of these catalysts were utilized and compared with SOP. Moreover, the effect of some operating conditions including initial solution pH, catalyst dosage values and ozonation duration time were

systematically investigated to investigate the contribution of various factors.

2. Experimental

2.1. Chemicals

The semi-experimental study was conducted to investigate catalytic activity efficiency of MPCAC in removal LAS from the synthetic solutions in a laboratory-scale ozonation reactor. All chemicals and reagents in the present research, LAS and those used in LAS analysis and synthesis of Fe_3O_4/C nanocomposite, were of analytical grade. LAS, chloroform, NaH_2PO_4 , H_2O , H_3PO_4 (85 %), $FeCl_3$, $FeSO_4 \cdot 7H_2O$, $NaH_2PO_4 \cdot H_2O$, $Na_2B_4O_7 \cdot 10H_2O$, methylene blue and all of the other reagents and chemicals, which have been applied in our study, were purchased from Merck (Germany). The PCAC, as a precursor of the catalyst was used in the current study, as well as its characterization in comparison with the final catalyst MPCAC is presented in Table 1.

2.2. Preparation of synthetic solutions

Using standard methods for examining water and wastewater based on book No. 5540C [24], the experiment of synthetic solutions procedure is presented below:

Preparing LAS stock solutions: 1 mL of pure LAS was introduced in 1-liter flask, and one liter of distilled water was added to a final volume of one liter and the obtained solution was stored in the dark under the temperature of 4 °C.

The standard LAS solution: To prepare the solution, 10 mL of stock LAS solution was diluted to 1000 mL by adding water

Buffer solution sodium tetraborate 50 mM and pH=10.5.

Methylene blue reagent established at a slightly acid pH of g/L (3.13 mM): 0.1 g of methylene blue was dissolved in 100 ml of tetraborate buffer solution 10 mM, and the pH of the resulting solution was set at 5.0–6.0. This solution was stored in a topaz-colored flask.

Sodium tetraborate buffer, 50 mM at pH=10.5: 19 g of sodium dehydrated tetraborate ($Na_2B_4O_7 \cdot 10H_2O$) was dissolved in 850 ml of distilled water, and the pH was set at 10.5 and levelled to 1 L.

Phenolphthalein indicator: 1 g of phenolphthalein was dissolved in 50 ml of ethanol (C_2H_5OH , 95% v/v) and 50 ml of water was introduced while the solution was constantly being stirred. Any precipitate was removed through filtration.

The concentrations of LAS were measured by the standard methylene blue method. This method is based on the formation of an ionic pair between the anionic surfactants, AS, and the methylene blue gives an aqueous blue-colored solution (MBAS), according to the reaction on Fig. S2.

Calibration curve plotting: Preparing concentrations of 2.5, 5, 10, 15, 20, and 25 mg/L from the LAS standard solution using the formula $c_1V_1=c_2V_2$, Calibration curve was drawn to measure the removal of LAS (Fig. S3).

A methylene blue active substances (MBAS) assay was run to determine the amount of anionic surfactant (LAS). MBAS, transmit methylene blue cationic dye from an aqueous phase to the chloroform phase. It should be stated that this protocol is relatively convenient and accurate. It consists of three successive extractions from acid aqueous medium that contain excess methylene blue into chloroform (CHCl_3), and then an aqueous backwash and measuring the blue color in the CHCl_3 using spectrophotometry at 652 nm. Also, pH of the solution was monitored through adding sulfuric acid and sodium hydroxide.

2.3. Preparing activated carbon from pine cone (PCAC)

In order to prepare activated carbon, raw pine cone powder was obtained by crushing dry cones and sieve to obtain particle size of 45 to 90 μm . Then, 50 g of chopped dried pine cones were mixed in a glass with 250 ml solution of H_3PO_4 (85% v/v). Subsequently, the pine cones were dried in an oven at 105 $^\circ\text{C}$ for 12 h. Carbonizing dried pine cones was carried out as per the procedure below:

First, the dried samples were introduced into a stainless steel container that was placed in an electric furnace. The heating rate to reach the final carbonization temperature of 450 $^\circ\text{C}$ was 5 $^\circ\text{C}/\text{min}$ and the holding time was 2.5 h. After carbonizing, activated carbon was rinsed with distilled water and dried at 108 $^\circ\text{C}$ for 24 h [25].

2.4. Formation of magnetic activated carbon with Fe_3O_4 nanoparticles (MPCAC)

Based on the method suggested by Nakahira et al, MPCAC catalyst was prepared. The nanocomposite catalyst was prepared from PCAC by using ferric chloride and iron sulfate solutions. Afterwards, PCAC was suspended in 500 mL of distilled water. Next, a ferric chloride solution was freshly prepared by introducing 18 g FeCl_3 into 1300 mL of distilled water. Subsequently, a ferrous sulfate solution was prepared by adding 20 g FeSO_4 to 150 mL of distilled water. Both solutions were combined and vigorously stirred at 60-70 $^\circ\text{C}$. The resulting suspension was introduced into an aqueous suspension of activated carbon under room temperature and slowly stirred for 30 min. After stirring, aqueous solution of NaOH (10 M) was added drop by drop to the suspension to the pH of 10-11. Throughout addition of NaOH, the suspension appeared dark brown at pH~6 and then black at pH~10. After stirring for 60 min, the suspension was left under room temperature for 24 h and then repetitiously rinsed with distilled water and then ethanol and distilled water. The MPCAC was filtered and dried at 50 $^\circ\text{C}$ for 12 h in a hot air oven. The magnetic property of the MPCAC catalyst can be easily understood using a magnet (Fig. S4) [26].

2.5. Determining pH_{PZC}

The pH_{PZC} (point of zero charge) of PCAC and MPCAC were determined as follows: the 0.1 g of dried sample was poured into 6 glass Erlenmeyer flasks (100 mL) that contained 50 mL NaCl solution (0.1 N) with specified initial pH (2-12). The glass Erlenmeyer flasks were stirred at 25 $^\circ\text{C}$ for 2 days. Next, the contents of the flasks were separately filtered with 0.45 μm silicon filter and final pH was measured by pH meter (Hatch Sinsion1). Consequently, the pH_{pzc} was determined by drawing initial pH versus final pH [27]. Then, the pH_{pzc} of PCAC and MPCAC catalysts were measured 8.9 and 7.7, respectively (Fig. 1). In plots of pH final vs pH initial, its intersection with the curve bisector (plot of pH initial vs pH initial) shows the catalyst's pH_{pzc} [28].

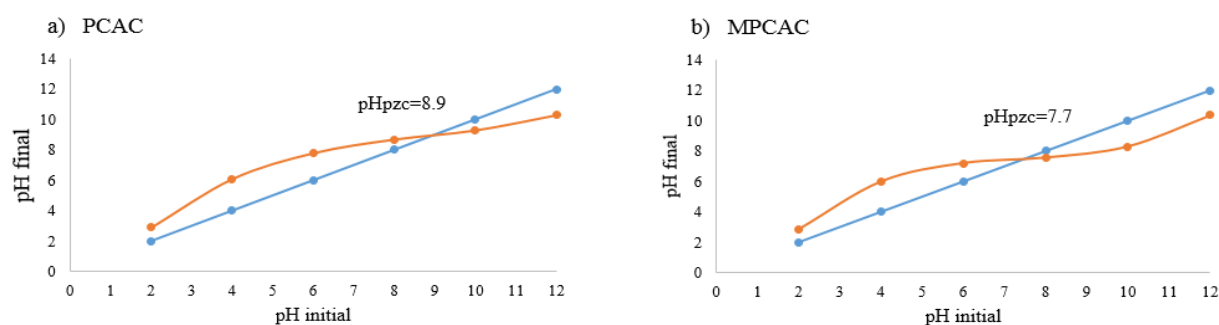


Fig. 1. Typical plot for the determination of pH_{pzc} of the PCAC (a) and MPCAC (b).

2.6 Reactor setup and operation

Catalytic ozonation was performed in a cylindrical glass column. Then, the ozone was produced from pure oxygen via corona discharge by mean of an ozone generator (ARDA, Model COG-1A) with 5 g O₃/h capacity (Fig. S5, a). To determine the capacity of ozone generator, the graph of ozone production in different inlet O₂ flow in ozone generator was drawn and used in this study (Fig. S5, b). The inlet O₂ flow to ozone generator was regulated and fixed on 1.5 L/min that led to generate 7 mg/min of ozone flow. Consequently, the ozone solution was measured by the standard potassium iodide (KI) absorption and finally destroyed in the off-gas stream of the reactor in a concentrated KI solution [20]. The ozone was regulated at a constant mass flow rate of 7 mg/min throughout the experiment.

In our study, PCAC and MPCAC was used as catalyst to oxidize LAS in the COP. In addition, the influence of some important parameters like initial solution pH (4, 6, 8 and 10), catalyst dosage (0.1, 0.2 and 0.3 g/L) and ozonation time (10, 15, 20, 25 and 30 min) as well as the impact of some important parameters like initial solution pH (4, 6, 8 and 10), catalyst dosage (0.1, 0.2 and 0.3 g/L) and ozonation time (10, 15, 20, 25 and 30 min) in LAS degradation were studied.

The experiments were done at room temperature (22±3 °C) in each run; catalysts were added to the reactor containing 1000 mL solution. Then, ozone was constantly bubbled from the bottom of the reactor into the solution (Scheme 1).

3. Results and discussion

3.1. Characterization of the Catalysts

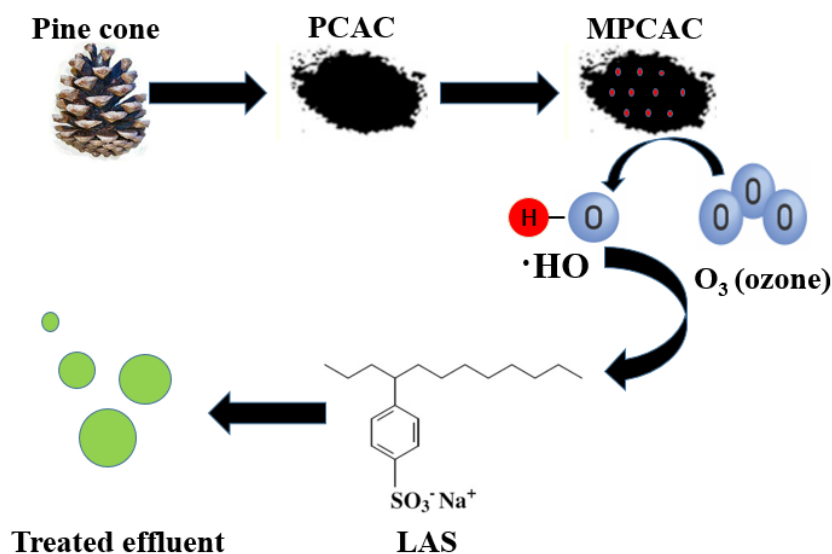
The characterizations of the catalysts were compared in Table 1. It reveals that magnetization processes affected the surface area and the value of microporous structure.

One of the most effective technologies which is used to identify the nature of crystalline materials is X-Rays Diffraction (XRD). The XRD pattern of PCAC (Fig. 2, a) exhibits three various Bragg angles (2 Theta, deg) that have maximum intensity for all samples (24-29) degrees and around (44) degrees corresponding to (002) and (100), (101) diffraction of the disordered stacking of the microstructures (JCPDS:00-001-0646). The MPCAC XRD pattern (Fig. 2, b), in addition to the hexagonal carbon peaks (JCPDS:00-001-0646), also shows peaks associated with Fe₃O₄ nanoparticles (JCPDS:01-075-0033). Using Debye-Scherrer equation (Eq. 1) on high intensity peak, the average crystallite size of particles was calculated to be 15.2 nm.

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where β represents the peak's width at half maximum, λ the radiation wavelength, and θ the Bragg angle [29].

Scanning electron microscopy (SEM) images of the PCAC and MPCAC in Fig. 3 indicated the SEM patterns of activated carbon samples before and after activation with ferric chloride and ferrous sulfate solutions. For both catalysts, images were recorded at magnifications of 2 μ and 200 nm. Moreover, the morphology of PCAC clearly indicates their homogeneous surface.



Scheme 1. The schematic representation for the fabrication of catalysts and their application in catalytic ozonation process in LAS degradation.

Table 1. Specification of magnetic carbonaceous nanocomposite and its precursor.

Parameters	PCAC	MPCAC
Specific surface area (m ² /g)	1040	868
Micro Pore volume (cm ³ /g)	0.42	0.26
pH _{pzc}	8.9	7.7
Average particle size	8 μm	15–21 nm
Color	Black	Black

It should also be mentioned that the SEM images of MPCAC illustrate the morphology of the nano-particles of Fe₃O₄ (average particle sizes of 17–21 nm) covered carbon substrate. In addition, SEM images illustrate the changes in morphology resulting from impregnation of iron oxide in the carbon matrix's pores. After impregnation of Fe₃O₄ nanoparticles, a spongy porous texture was formed that represents that well-dispersed iron oxide particles have formed covering PCAC.

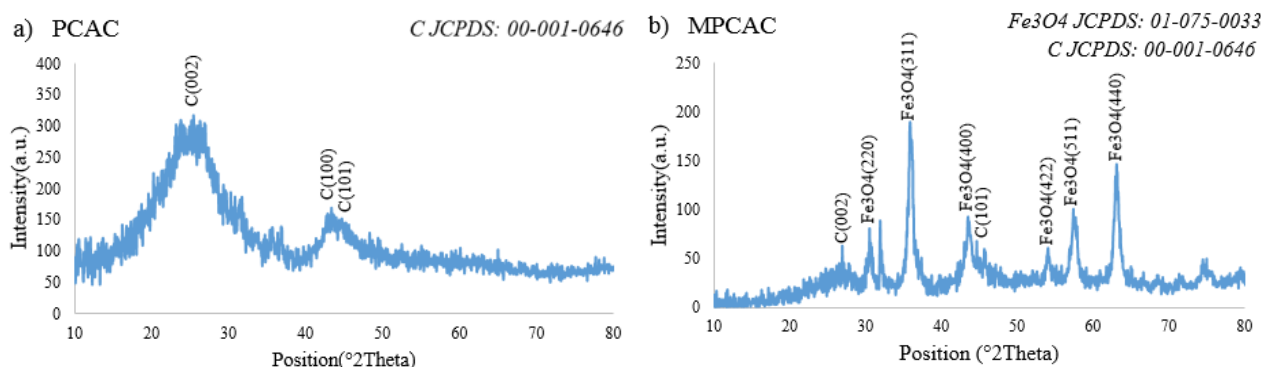
The surface area of PCAC and MPCAC were specified by BET surface area analyzer JW-BK132F and standard N₂ adsorption at 77 K. Because of some amount of pore blockage by dispersed iron-oxide particles, the surface area of MPCAC could be from 1040 m² g⁻¹ to 868 m² g⁻¹ (16.5% reduction) after iron impregnation. Accordingly, Fe₃O₄ nano-particles are bonded on the surface of activated carbon through hydroxyl groups. Moreover, the impacts on the surface area will be different for the carbon, and the iron oxide components of PCAC and MPCAC have a lower carbon weight fraction [30].

The Energy-dispersive X-ray spectroscopy (EDX) elemental analysis of PCAC (Fig. S6, a) and MPCAC (Fig. S6, b) supports the presence of the carbon and oxygen in PCAC and carbon, oxygen and ferrum in MPCAC catalyst. The EDX findings have further

ascertained the presence of Fe on the surface, and increase in oxygen percentage, supporting formation of the Fe₃O₄ nanoparticles on carbon matrix.

Transmission electron micrographs (TEM) of thin carbon sections exhibit greater shading in the pore sites as the electron beam passes through them, while pore walls appear black due to electron scattering. PCAC and MPCAC sizes and shapes are illustrated in Fig. 4 (a, b). The primary carbon particles were interconnected to shape networks. The iron oxide nanoparticles were adequately dispersed in MPCAC and the distribution size of the Fe₃O₄ nanoparticles in the MPCAC catalyst was obtained (Fig. 4), which has an average particle size of 20 nm.

Magnetic features of Fe₃O₄/PCAC catalyst was analyzed by a vibrating sample magnetometer in an operational magnetic field from -15 to 15 KOe under room temperature. As illustrated in Fig. 5, the catalyst has paramagnetic property which has no magnetic effect while removing the magnetic field. The magnetization saturation values of Fe₃O₄/PCAC is 42.50 emu/g. Paramagnetic characteristic of catalyst can be easily understood by a magnet. Indeed, when a magnet was placed near the outer wall of a glass container having a mixture of catalyst particles, the particles were completely absorbed by the magnet.

**Fig. 2.** The XRD patterns of PCAC (a) and MPCAC (b) catalysts.

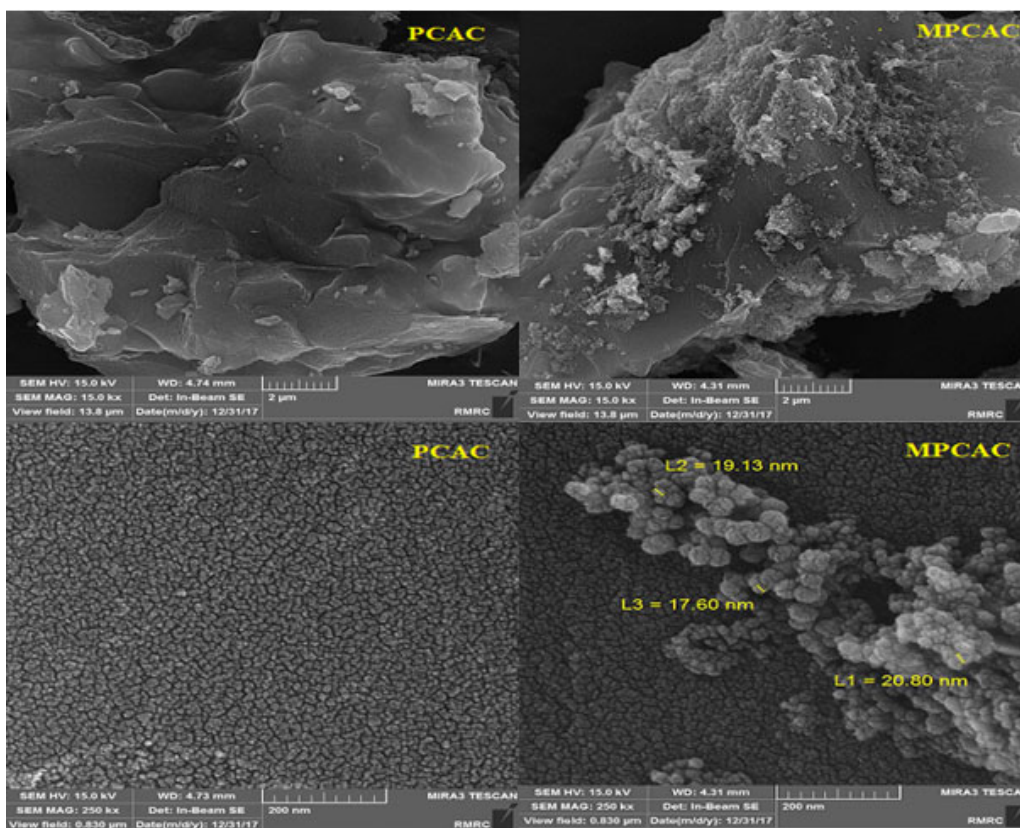


Fig. 3. The SEM images of PCAC and MPCAC.

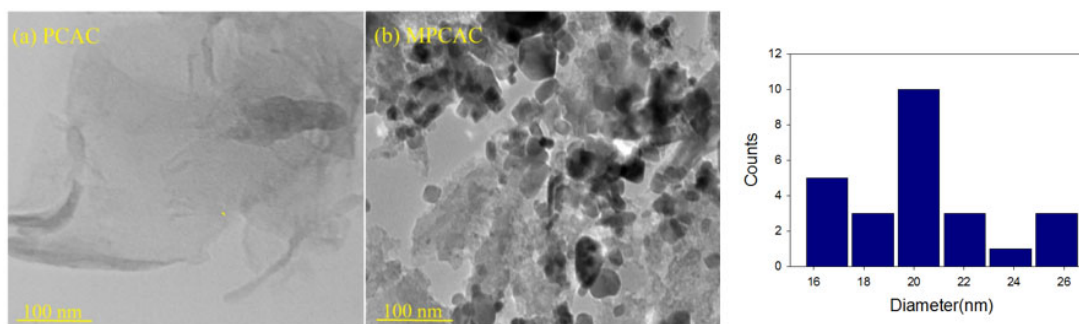


Fig. 4. The TEM images of PCAC (a), MPCAC (b) and Fe₃O₄ particles size distribution.

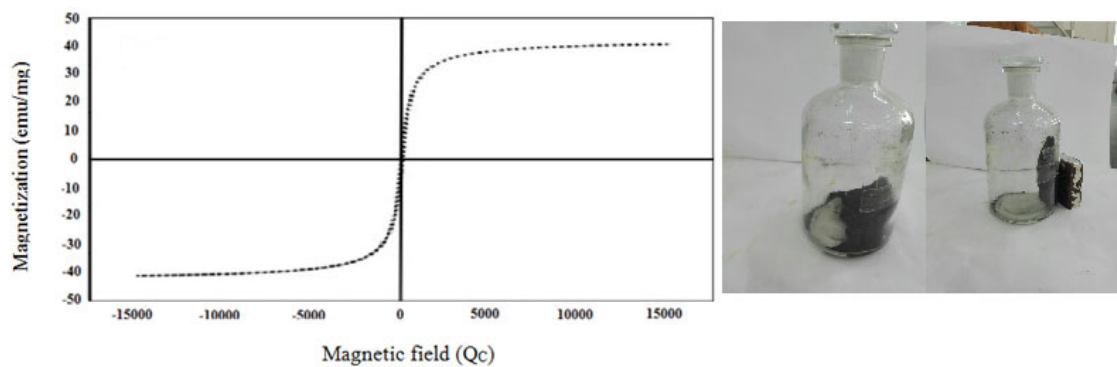


Fig. 5. Magnetic moment of magnetic activated carbon (MPCAC).

3.2. Influence of pH in removal LAS concentration

Since the solution's initial pH is one of the major influential variables in production of hydroxyl radical from O_3 decomposition [31], ozonation experiments were performed under different initial pHs (4, 6, 8, and 10). In Fig. 6, the impact of initial pH on the LAS degradation efficiency was shown in three processes including O_3 and $O_3/PCAC$ and $O_3/MPCAC$. Based on previous studies, the catalytic ozonation process is usually dependent on pH [32]. Moreover, solution pH is one of the important parameters which determine catalyst surface charge and ionic forms of pollutant present in the solution [33]. Given that the pka for LAS is less than 1, it could be observed in its anionic form in solution with pH greater than 1. Besides, the catalyst surface will be negatively charged when $pH > pHPzc$, positively charged when $pH < pHPzc$ and neutrally charged when $pH \approx pHPzc$ [34]. The results in Fig. 1 (a, b) shows the $pHPzc$ of the prepared PCAC and MPCAC. As revealed in Fig. 6, the maximum removal efficiency of LAS was attained at pH 10 in the COP and in presence of MPCAC, increasing pH from 4 to 10 leads to the removal efficiency from 91.3 % to 98.5 %, respectively, after 15 minute. As seen in the Fig. 1, $pHPzc$ of MPCAC was determined to be 7.7, thus at a pH above 7.7, the surface of the catalyst will have a negative charge and cannot absorb negatively charged LAS anions. LAS degradation rate was improved by increasing pH up to 10 due to accelerated ozone mass transfer and ozone decomposition at pH [35]. The maximum degradation was obtained at high pH conditions (where the rate of hydroxyl radical formation is higher) than at low pH values. In acidic conditions in which OH formation rate is slow, numerous organic pollutants are basically unreactive [36]. It should be stated that increasing pH leads to form highly reactive radicals, mainly $\bullet HO$ [37]. That is, the high presence of hydroxyl radicals at $pH=10$, rapidly decomposes LAS anions and does not require their presence at the catalyst surface. In addition, in the COP with using PCAC, increasing pH from 4 to 10 leads to the removal efficiency from 60.2 % to 69.2 %, respectively. However, in the absence of catalysts in the SOP, increasing the pH from 4 to 10 resulted in an increase of removal from 18% to 42% after 15 minutes of ozonation (Fig. 6). The enhancement of LAS degradation rate in the SOP with increasing pH can be explained by accelerating ozone mass transfer as well as ozone decomposition rates with increasing the pH, leading to the formation of highly reactive radicals, mostly $\bullet HO$, which has a higher oxidation potential than ozone molecules [38]. Therefore, LAS degradation in the SOP

in alkaline solution pHs was performed through indirect radical reactions.

Asgari et al. reported increased COP efficiency in pentachlorophenol (PCP) removal with increasing solution pH [39]. Also, Mousavi *et al.* compared furfural removal in SOP and COP, and reported that at pH 12, the removal percentage of furfural increased, which was reported to be 84% [40]. In a study, the color removal reactive black 5 efficiencies were higher in the COP than in SOP, and also the COP efficiency was enhanced with increasing pH [41]. Asgari et al. observed increased COP efficiency in pentachlorophenol (PCP) removal by increasing solution pH [39]. Also, Mousavi *et al.* compared furfural removal in SOP and COP, and reported that at pH 12, the removal percentage of furfural improved, which was reported to be 84% [40]. In a similar study, the color removal reactive black 5 efficiencies were higher in the COP than in SOP, and also the COP efficiency increased with increasing pH [41].

3.3. Effect of catalyst dosage

Given the purpose of determining the impact of the catalyst dosage on the degradation of LAS through heterogeneous ozonation process, experiments were carried out at various catalyst dosages.

As seen in Fig. 7 (a), the impact of catalyst dosage in 0.1–0.3 g/L on LAS removal was studied in the COP at solution volume of 1000 ml and reaction time of 15 min. It can be obviously noticed that the removal of LAS, as a function of catalyst dosage, shows a significant enhancement effect of catalyst dosage on the ozonation process, especially in the first 15 min of the reaction time. For instance, at a reaction time of 15 min, the degradation of LAS reached from 42% in the absence of catalyst to 98.5% and in exposure to 0.3 g/L of MPCAC catalyst.

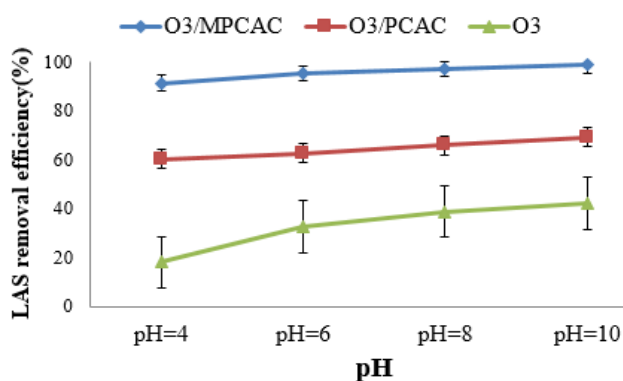


Fig. 6. Effect of initial pH on removal efficiency of LAS (Concentration= 25 mg/L; Catalyst dosage= 0.3 g/L; reaction time: 15min, ozone flow rate =7 mg/min).

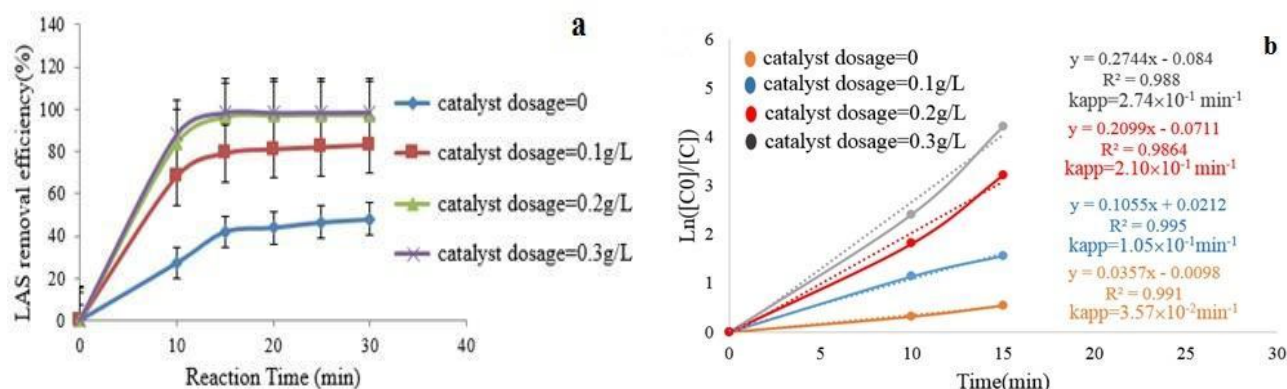


Fig. 7. (a) Effect of catalyst dosage on LAS Removal efficiency in SOP (catalyst dosage=0) and COP with MPCAC (Concentration= 25 mg/L, ozone flow rate =7 mg/min, pH=10) and (b) the pseudo-first-order rate constants of LAS degradation in COP at different catalyst dosage of MPCAC.

Although the optimum dosage of catalyst in COP is mainly dependent on the catalyst type, the reaction conditions, the target compound, and desired performance [39], the value of 0.3 g/L was obtained as the optimum dosage of MPCAC in the present research that was compared with PCAC under similar selective conditions. These results appear to indicate that an increase in LAS degradation can be attributed to the (O₃/MPCAC) ratio and the availability of more active sites in the process of ozone transformation into •HO radicals [42, 43], resulting in improvement of the LAS removal.

In general, the dependence of the degradation rates on the concentration of organic pollutants has been explained appropriately by the Langmuir–Hinshelwood (L–H) kinetic model (Eq. 2). The modified L–H equation is given by:

$$r = -dC/dt = k_r\theta = k_rKC/1 + KC \quad (2)$$

where k_r represents the reaction rate constant, K is the reactant adsorption constant, θ is the fraction of catalyst surface coverage and C is the substrate concentration at time t . Throughout catalytic degradation, intermediates are formed and may interfere in determining kinetics due to competitive degradation. Within a short time, interval, changes like intermediates impacts could be neglected. The catalytic degradation rate can be presented as a function of concentration based on Eq. 3.

$$r_0 = k_rKC/1 + KC \quad (3)$$

where r_0 represents the initial rate of catalytic degradation of LAS and C_0 is the initial concentration. When the substrate concentration is sufficiently low (less than 0.3 g/L in this study) and no catalyst saturation occurs, catalytic disappearance with PCAC or MPCAC, can comply with apparent first-order kinetics. Here,

Equation can be simplified to a pseudo-first order kinetic model (Eq. 4).

$$\ln([C_0]/[C]) = k_rKt = k_{app}t \quad (4)$$

where $k_{app} = k_rK$. The plot of $\ln([C_0]/[C])$ versus time in Fig. 7 (b) shows straight lines, according to which linear variations slope equals to the pseudo first order rate constant, k_{app} which was calculated to be $3.57 \times 10^{-2} \text{ min}^{-1}$, $1.05 \times 10^{-1} \text{ min}^{-1}$, $2.10 \times 10^{-1} \text{ min}^{-1}$, and $2.74 \times 10^{-1} \text{ min}^{-1}$ for catalyst dosage of 0, 0.1, 0.2 and 0.3 g/L, respectively. These results clearly show that the degradation rate increased on the basis of improving the dosage of the MPCAC catalyst, which lead to a more efficient removal of the LAS [44].

Asgari et al. proposed that the ozone decomposition rate increased with granular activated carbon dosage as a catalytic in the ozonation process [22]. Moreover, the findings of studies done by Moussavi and Khosravi were in line with these results [45]. Shahamat et al. investigated the catalytic features of a carbon nanocomposite in DNP catalytic ozonation, concluding that the nanocomposite is an active and efficient catalyst in DNP degradation and mineralization in COP [20].

3.4. Influence of ozonation time

The reaction time plays an important role during the heterogeneous catalytic ozonation process.

In this part of the study, the effect of O₃/MPCAC and O₃/PCAC on the LAS removal rate was then compared with the single ozonation process (SOP). Fig. 8 (a) depicts the O₃ exposure at the different times considered in the three treatment systems (O₃, O₃/PCAC and O₃/MPCAC) under the same experimental conditions.

The LAS removal percentage was increased with improving ozonation time in the SOP (O₃), COP_{PCAC} (O₃/PCAC) and COP_{MPCAC} (O₃/MPCAC). As illustrated

earlier, the LAS removal rate was considerably greater in O₃/MPCAC system.

Increasing ozonation time from 10 to 30 min could lead to improve removal efficiency of LAS from 88% to 98.7% in the O₃/MPCAC. Whereas in the O₃/PCAC, the corresponding removal efficiency were obtained 60% to 72%, respectively. Also, in SOP, the LAS removal percentage were increased from 27.2% to 48%. As it is observed, the impact of reaction time on the performance of COP is more marked than SOP. The gaseous ozone concentration raised the equilibrium ozone concentration in the aqueous phase and enhanced the mass transfer driving force and could lead to mass transfer of ozone into the liquid phase and also increased volumetric mass transfer coefficient of ozone [46]. According to the results, the percentage of LAS removal did not change significantly after 15 min. Nevertheless, further increases of contact time to 30 min, did not influence the degraded LAS percentage. Therefore, optimal time for O₃/MPCAC in the COP was determined 15 min.

LAS removal kinetics in SOP and COP in exposure to PCAC and MPCAC similar to Fig. 7 were investigated and compared (Fig. 8, b). These results showed that the rate constant (k_{app}) of elimination of LAS in the COP and MPCAC catalyst is higher than two other processes.

3.5. Catalyst durability

One advantage of the proposed nano-catalyst is easily separating from aqueous solution and reusing it by magnet without centrifugation or filtration. For this purpose, individually amount of 0.3 g PCAC and MPCAC in 1000 mL solution of LAS with 25 mg/L concentration was used for LAS removal in optimum conditions. After catalytic ozonation process, the catalysts easily were separated, then recovered by

washing with diluted HCl solution. The catalytic activity of the recovered catalysts in the COP were evaluated for 4 runs. On the basis of the results shown in (Fig. S7), this magnetic catalyst preserved its magnetic and catalytic features following 5 runs and reused. It should be mentioned that the decrease in LAS removal was extremely slight (only 8 %). After the first use, the catalytic activity of MPCAC was 98.7%, and after 5 cycles it was decreased to 90.7 %. Although, the catalytic activity capacity is decreased by recycling, this decreases is not so significant. While the catalytic activity of the PCAC was 72 %, and after 5 cycles, it was reduced to 52 %. The results showed that compared to MPCAC, PCAC catalytic activity capacity has decreased significantly. According to low-cost, nontoxic and ease of preparation, Fe/activated carbon catalyst could be a good catalyst for the COP. This can be of the catalytic properties [47]. In accordance with some studies, ozonation decreases activated carbon's catalytic features by decreasing basic groups and increasing oxygenated surface functional groups like hydroxyl [48]. However, others have indicated that, use of functional chemical groups like Fe₃O₄, on the surface of catalysts increased pore volume and specific surface area [20].

4. Conclusions

COP was investigated for removal of LAS from synthetic solution in the presence of MPCAC. Catalyst dosage showed a substantial improving impact on the ozonation process. Besides, our results displayed that the exposure to Fe₃O₄ nanoparticles on the activated carbon matrix has the synergistic effect and promote the catalytic activity of MPCAC, which causes ozone decomposition and increase radical hydroxyl production at its surface leads to more and faster removal of LAS.

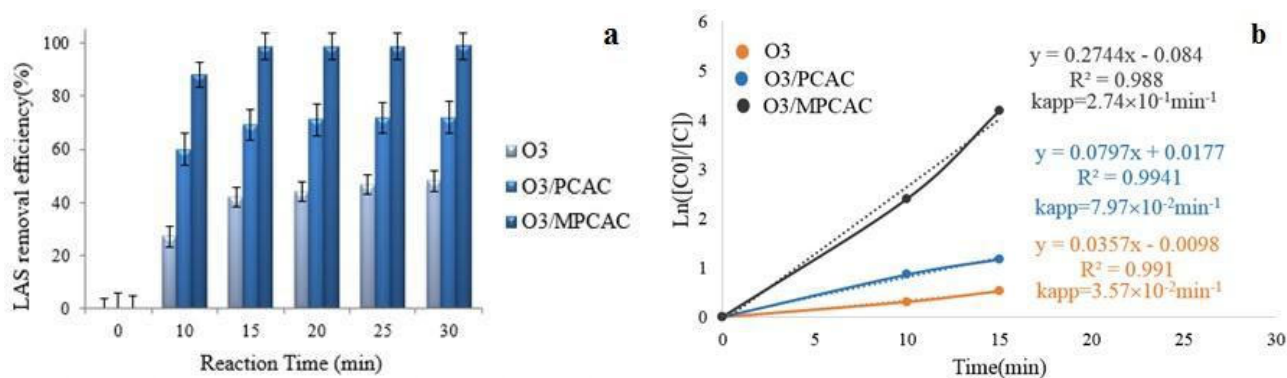


Fig. 8. (a) Effect of reaction time on LAS degradation efficiency in COP and comparison with SOP. (Concentration= 25 mg/L, ozone flow rate =7 mg/min, pH=10, catalyst dosage=0.3g/L) and (b) the pseudo-first-order rate constants of LAS degradation in O₃, O₃/PCAC and O₃/MPCAC.

Also, at alkaline pH, the efficiency of MPCAC was better in LAS removal than PCAC. Based on the results, almost complete removal LAS was achieved under the optimum conditions. The LAS removal percentage increases with improving ozonation time in COP (O_3 /MPCAC and O_3 /PCAC) and SOP (O_3). The findings evidently showed that compared to the PCAC, COP could enhance the degradability and decrease the initial dosage using MPCAC. Concluding, this nanocomposite is an effective active catalyst for mineralization and degradation of LAS in COP. Based on our results, a mechanism was suggested for removal of LAS.

Acknowledgments

The authors would like to thank the Yazd Branch, Islamic Azad University, Yazd, for its partial support of this study.

References

- [1] M. Dehghani, A. Najafpoor, K. Azam, *Desalination* 250 (2010) 82-86.
- [2] M. Ghoochani, S. Shekoohiyan, A.H. Mahvi, *J. Agric. Environ. Sci.* 10 (2011) 464-469.
- [3] S. Sirisattha, Y. Momose, E. Kitagawa, H. Iwahashi, *Water Res.* 38 (2004) 61-70.
- [4] Z. Wang, B. Xiao, X. Wu, X. Tu, Y. Wang, X. Sun, *Environ. Monit. Assess.* 171 (2010) 501-512.
- [5] A. Mahvi, N.A. Nakhjavan, K. Naddafi, *Horiz. Med. Sci.* 10 (2004) 36-41.
- [6] A. Rostami-Vartooni, L. Rostami, M. Bagherzadeh, *J. Mater. Sci.: Mater. Electron.* 30 (2019) 21377-21387.
- [7] A. Rostami-Vartooni, A. Moradi-Saadatmand, M. Bagherzadeh, M. Mahdavi, *Iran. J. Catal.* 9 (2019) 27-35.
- [8] M. Nasrollahzadeh, S.M. Sajadi, A. Rostami-Vartooni, M. Alizadeh, M. Bagherzadeh, *J. Colloid Interface Sci.* 466 (2016) 360-368.
- [9] A. Rostami-Vartooni, M. Alizadeh, M. Bagherzadeh, *Beilstein J. Nanotechnol.* 6 (2015) 2300-2309.
- [10] M. Nasrollahzadeh, S.M. Sajadi, A. Rostami-Vartooni, M. Bagherzadeh, R. Safari, *J. Mol. Catal. A: Chem.* 400 (2015) 22-30.
- [11] F. Riahi, M. Bagherzadeh, Z. Hadizadeh, *RSC Adv.* 5 (2015) 72058-72068.
- [12] M. Nasrollahzadeh, M. Maham, A. Rostami-Vartooni, M. Bagherzadeh, S.M. Sajadi, *RSC Adv.* 5 (2015) 64769-64780.
- [13] H. Zhao, Y. Dong, G. Wang, P. Jiang, J. Zhang, *Chem. Eng. J.* 219 (2013) 295-302.
- [14] M. Sui, S. Xing, L. Sheng, S. Huang, H. Guo, *J. Hazard. Mater.* 227 (2012) 227-236.
- [15] B. Kasprzyk-Hordern, M. Ziółek, J. Nawrocki, *Appl. Catal. B Environ.* 46 (2003) 639-669.
- [16] J. Nawrocki, B. Kasprzyk-Hordern, *Appl. Catal. B Environ.* 99 (2010) 27-42.
- [17] G. Moussavi, A. Khavanin, R. Alizadeh, *J. Hazard. Mater.* 171 (2009) 175-181.
- [18] Y. Dadban-Shahamat, M. Sadeghi, *Desalin. Water Treat.* 57 (2016) 20447-20456.
- [19] C. Ni, J. Chen, *Water Sci. Techn.* 43 (2) (2001) 213-220.
- [20] Y. Dadban-Shahamat, M. Farzadkia, S. Nasser, *J. Environ. Health Sci. Eng.* 12 (2014) 50.
- [21] K. Yang, J. Peng, C. Srinivasakannan, L. Zhang, *Biores. Techn.* 101 (2010) 6163-6169.
- [22] A.C. Lua, T. Yang, *J. Colloid Interface Sci.* 290 (2005) 505-513.
- [23] J. Zolgharnein, Z. Choghaei, M. Bagtash, *Desalin. Water Treat.* 57 (2016) 27672-27685.
- [24] T. Razavi, A. Fadaei, M. Sadeghi, S. Shahsavan markadeh, *Desalin. Water Treat.* 57 (2016) 28755-28761.
- [25] L. Niazi, A. Lashanizadegan, H. Sharififard, *J. Cleaner Prod.* 185 (2018) 554-561.
- [26] D. Mohan, A. Sarswat, V.K. Singh, *Chem. Eng. J.* 172 (2011) 1111-1125.
- [27] H. Sharififard, M. Soleimani, F.Z. Ashtiani, *J. Taiwan Inst. Chem. Eng.* 43 (2012) 696-703.
- [28] S. Senobari, A. Nezamzadeh-Ejhi, *J. Photochem. Photobiol. A* 394 (2020) 112455.
- [29] S. Aghdasi, M. Shokri, *Iran. J. Catal.* 6 (2016) 481-487.
- [30] L.C.A. Oliveira, R.V.R.A. Rios, J.D. Fabris, V. Garg, K. Sapag, *Carbon* 40 (2002) 2177-2183.
- [31] B. Divband, A. Jodaei, M. Khatamian, *Iran. J. Catal.* 9 (2019) 63-70.
- [32] S. Ghattavi, A. Nezamzadeh-Ejhi, *Desalin. Water Treat.* 166 (2019) 92-104.
- [33] S. Dianat, *Iran. J. Catal.* 8 (2018) 121-132.
- [34] A. Eslami, A. Oghazyan, M. Sarafraz, *Iran. J. Catal.* 8 (2018) 95-102.
- [35] P.M. Alvarez, J.F. Garcia-Araya, F.J. Beltran, I. Giraldez, *Carbon* 44 (2006) 3102-3112.
- [36] J. Fernández, J. Riu, E. García-Calvo, A. Rodríguez, A.R. Fernández-Alba, D. Barceló, *Talanta* 64 (2004) 69-79.
- [37] Y.F. Rao, H.J. Luo, C.H. Wei, L.F. Luo, *J. Cent. South Univ. Technol.* 17 (2010) 300-306.
- [38] Y.H. Han, K. Ichikawa, H. Utsumi, *Water Sci. Techn.* 50 (2004) 97-102.
- [39] G. Asgari, F. Samiee, M. Ahmadian, *Appl. Water Sci.* 7 (2017) 393-400.
- [40] M. Leili, S.R. Mousavi, K. Naddafi, M. Ghaffari, *J. Sabzevar. Uni. Med. Sci.* (2013) 51-61.
- [41] G. Asgari, E. Hoseinzadeh, M. Taghavi, J. Jafari, *Jundishapur J. Health. Sci.* (2012) 21-30.
- [42] X. Liu, Z. Zhou, G. Jing, J. Fang, *Sep. Purif. Technol.* 115 (2013) 129-135.
- [43] M. Muruganandham, J. Wu, *Catal. Commun.* 8 (2007) 668-672.
- [44] N. Omrani, A. Nezamzadeh-Ejhi, M. Alizadeh, *Desalin. Water Treat.* 162 (2019) 290-302.
- [45] G. Moussavi, R. Khosravi, *Bioresour. Technol.* 119 (2012) 66-71.
- [46] J. Wu, H. Gao, S. Yao, L. Chen, Y. Gao, H. Zhang, *Sep. Purif. Technol.* 147 (2015) 179-185.
- [47] X. Qu, J. Zheng, Y. Zhang, *J. Colloid Interface Sci.* 309 (2007) 429-434.
- [48] J. Rivera-Utrilla, M. Sanchez-Polo, *J. Hazard. Mater.* 187 (2011) 1-23.