



Waste sludge from shipping docks as a catalyst to remove amoxicillin in water with hydrogen peroxide and ultrasound

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ABSTRACT

The waste sludge from shipping docks contains important elements that can be used as a catalyst after proper processing. The purpose of this study was to remove of amoxicillin (AMX) from the aquatic environment using waste sludge from shipping docks as catalyst in the presence of hydrogen peroxide/ultrasound waves. The catalyst was produced by treating waste sludge at 400 °C for 2 h. N₂ adsorption, SEM, XRD, XRF, and FTIR techniques characterized the structural and physical properties of the catalyst. The BET-specific surface area of the catalyst reduced after AMX removal from 4.4 m²/g to 3.6 m²/g. To determine the optimal removal conditions, the parameters of the design of experiments were pH (5–9), contaminant concentration (5–100 mg/L), catalyst dosage (0.5–6 g/L), and concentration of hydrogen peroxide (10–100 mM). The maximum removal of AMX (98%) was obtained in the catalyst/hydrogen peroxide/ultrasound system at pH 5, catalyst dose of 4.5 g/L, H₂O₂ concentration of 50 mM, AMX concentration of 5 mg/L, and contact time of 60 min. The kinetics of removal of AMX from urine ($k = 0.026$ 1/min), hospital wastewater ($k = 0.021$ 1/min), and distilled water ($k = 0.067$ 1/min) followed a first-order kinetic model ($R^2 > 0.91$). The catalyst was reused up to 8 times and the AMX removal decreased to 45% in the last use. The byproducts and reaction pathway of AMX degradation were also investigated. The results clearly show that to achieve high pollutant removal rate the H₂O₂/ultrasound and catalyst/ultrasound synergy plays a key role.

1. Introduction

Antibiotics are a significant group of pharmaceuticals that prevent human and animal infections. They have also been widely used as feed additives to promote growth and weight gain in livestock [1]. Antibiotics are a diverse group of chemicals that can be divided into different subgroups, such as β -lactams, tetracyclines, aminopenicillins, and others [2]. Amoxicillin (AMX) is a semi-synthetic penicillin belonging to the β -lactam family [3]. This compound has the lowest metabolism among drugs so that after consumption, about 80–90% is excreted unchanged in the urine and feces [4]. Accordingly, their presence in the aquatic environment gradually increases, leading to

enhanced resistance [5,6]. Therefore, a powerful and efficient method needs to be developed to eliminate this recalcitrant substance from contaminated water sources.

AMX is difficult to decompose or mineralize using conventional treatment systems and the literature data on its removal efficiency is limited [1,2,7–9]. In the last decade, advanced oxidation processes (AOPs) have been used not only to reduce pharmaceutical pollution in waters but also to completely degrade (mineralize) pollutants into benign products such as H₂O and CO₂ [10]. The main mechanism of the advanced oxidation processes is based on the production of radicals such as hydroxyl radicals (OH[•]) [11,12].

There are several AOPs that can degrade AMX, to a different extent

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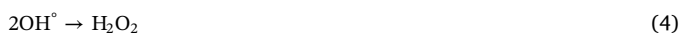
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basing on operating conditions. Recently, microwave-assisted Fenton's oxidized AMX at a faster rate compared to Fenton's process only, where AMX (450 µg/L) degraded completely in less than 5 min. Ozonation degrades over 90% AMX, with a total organic carbon (TOC) decrease of 18% in 20 min [13,14]. Elmolla and co-authors degraded 100% AMX (100 mg/L) by photocatalytic Fenton in 50 min [15]. Always Elmolla et al. performed UV photocatalysis to degrade AMX up to 60% with TiO₂ in 300 min. When they added H₂O₂, the degradation reached 100% [16].

Recent literature reports the oxidation of AMX with ultrasound and ozone alone or in tandem. With ultrasound only (75 W) they degraded 99%, but mineralized only 10% [17]. Khani et al. recently describe the sonophotocatalytic degradation of AMX over Mn-TiO₂ systems synthesized with the aid of ultrasound to tune the band-gap, which degraded only 50% pollutant in 200 min [5]. Some research groups, remove AMX by adsorption only. For instance, Kerkez-Kuyumcu et al. synthesized magnetically modified graphene nano-platelets to remove AMX from water just by simple adsorption and achieved 84% removal in 1.5 h [18]. Abazari et al. synthesized nanostructured pillar MOF with ultrasound to remove antibiotics from water by adsorption. The adsorption capacity was up to 90% AMX in 4 h [19]. Stucchi et al. synthesized Mn-TiO₂ catalytic systems with the aid of US. These catalysts carried higher surface area and adsorbed up to three times more AMX compared to the samples prepared with samples synthesized with traditional techniques and TiO₂ P25 [6].

In the recent years, the sonochemical treatment (an AOP) has shown to be efficient to remediate pharmaceutical compounds from polluted water [5]. Sonochemistry is based on a cyclical sequence where micro-bubbles form and grow until reaching a critical size; then, they collapse violently in a process called acoustic cavitation, which is induced by the interaction between ultrasonic waves and dissolved gases in aqueous solutions [20]. The collapse of the micro-bubbles generates small hot spots with singular conditions of pressure (up to 1000 atm) and temperature (up to 5000 K) [21]. Several literature works proved that the removal efficiency of organic pollutants with AOPs such as photocatalysis and ultrasound (US) increases with the addition of reactive oxidant species (ROS), i.e. a substance capable of producing hydroxyl radicals [22–24]. Hydrogen peroxide can be one of these oxidants. In the case of US, the synergy of US/H₂O₂ is as follows in Eqs. (1–5) [25].



The removal of antibiotics using ultrasonic waves and H₂O₂ with heterogeneous catalysts has already been reported in the scientific literature [26–28]. However, in this study, we propose a highly original catalyst as we obtained it from waste sludge shipping docks. As far as we know, waste sludge (sea sediments in the shipping docks) has never been reported as a catalyst precursor. Depending on their activity, shipping ports remove waste sludge to keep efficient traffic routes and in the meantime is left to accumulate. In Europe, dredging activities generate ~200 million m³/year of waste sludge (sediment) [29]. Waste sediments contain a variety of organic and above all inorganic compounds, which can be active components in a catalyst.

The overall objective of this study was to remove AMX from aqueous solutions using a catalyst made from sea sediment in combination with hydrogen peroxide and US. The system can potentially be applied for the treatment of hospital and pharmaceutical wastewater. We discuss the influence of operating parameters, the kinetics of antibiotic removal in three solutions (distilled water, urine, and hospital wastewater), the synergistic effect of studied system components, and the

catalyst reuse potential.

2. Materials and methods

2.1. Chemicals

H₂O₂ was obtained from Merck Company (Germany). The amoxicillin (AMX) powder (purity: 99.5%, molecular weight: 365.4 g/mol, molecular formula: C₁₆H₁₉N₃O₅S, solubility in water: 3430 mg/L at 25 °C) was bought from the Kosar Pharmaceutical Company. Double distillation water was used to make the solutions. All products were used without further purification.

2.2. Preparation of catalyst from waste sludge (sea sediment)

The waste sludge (sea sediment) was collected as a catalyst precursor from Bushehr port pier, washed with distilled water for 1 h and dried at 105 °C for 24 h. It was milled and then sieved with a 40-mesh sieve to produce uniform particles. To investigate the pretreatment temperature and find the optimal one, the particles were treated in an electric furnace at different temperatures (300, 350, 400, 500 °C) and residence time in the furnace for 1, 2, 3, 4 h, either with or without the presence of oxygen.

2.3. Amoxicillin (AMX) degradation experiments

0.1 g AMX powder was dissolved in 100 mL deionized water to give a stock solution of 1000 mg/L. The stock solution was prepared weekly. All oxidation experiments were performed indoors and inside a 100 mL flask containing 75 mL of working solution. The operating factors and their levels were AMX concentration (5, 25, 50, 75, 100 mg/L), catalysts mass concentration (0.5, 1.5, 3, 4.5, 6 g/L), pH (5, 6, 7, 8, 9), hydrogen peroxide concentration (10, 25, 50, 75, 100 mM), and contact times (5, 10, 20, 40, 60 min). For testing, the samples were first placed in the flask and then in a water sonication bath (Model S30H, Elma) with 2.75 L capacity and the frequency of 37 kHz. The maximum peak power of the bath was 320 W, with an effective power of 80 W. The value of electrical energy coming into the reaction solution from the ultrasonic tool was calculated as 5.04 kJ [22]. After a pre-established time, the reaction mixture was passed through a Whatman® - Grade 42 filter paper. The residual AMX concentration was measured by a Waters 2695 HPLC analyser equipped with a (Waters Alliance 2998-PDA (λ = 270 nm)) detector. A mixture of formic acid (0.1%) and methanol (25:75 v/v) (with a pH value of 2.5) at a flow rate of 1.0 mL/min was used as a mobile liquid phase.

In this study, the temperature was constant and equal to the ambient temperature (25 ± 1 °C). The experiments were repeated three times and their mean was reported as the final result. The final AMX removal efficiency was determined by mass balance. At the end of each run, the catalyst samples were collected from the reaction solution using Whatman filter paper (No. 42). To reuse the catalyst, the used samples were separated and rinsed with distilled water and then dried at 105 °C.

2.4. Catalyst characterization

To determine the zero-charge potential (pH_{ZPC}), 100 mL of sodium chloride (0.05 mM) was added to the flask. The pH of the solution was then adjusted to the 3 to 11 range by hydrochloric acid (0.1 mM) and sodium hydroxide (0.1 mM). In the next step, 0.5 g of the catalyst was added and placed in a shaker incubator at 200 rpm for 18 h. The initial pH was plotted against the difference between the initial and final pH, and the X-axis intersection point was marked as pH_{ZPC}.

In this study, the catalyst characterization including the pore volume and the specific surface area were determined by the BET (N₂ adsorption-desorption isotherms) method using a particle analyzer

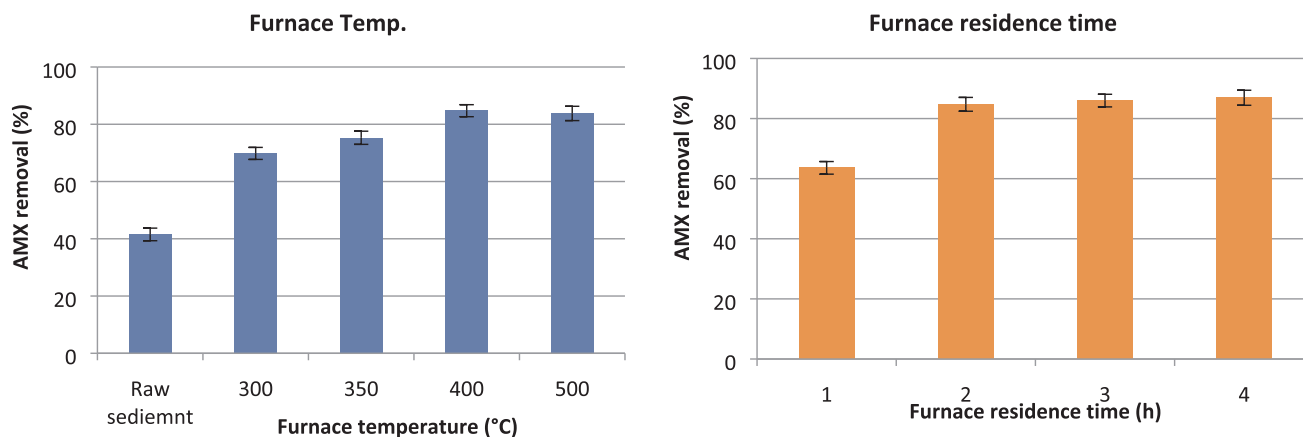


Fig. 1. The effect of furnace temperature and residence time in the furnace on AMX (AMX) removal (pH: 7, catalyst dose: 3 g/L, H₂O₂ content: 50 mM, reaction time: 40 min, AMX concentration: 50 mg/L).

(ASAP 2000 model). X-ray diffraction (XRD) determined the crystalline phase of the catalyst and XRF analysis was applied to determine the elemental oxides of the sea sediment catalyst. To determine the functional groups in the catalyst, an FTIR instrument (Prestige, 212100405, Japan) was used. The surface morphology of the catalyst before and after the catalytic tests was determined by scanning electron microscopy (SEM, JSM-6700F, Hitachi, Japan). ICP-OES was used to measure the content of metals in the sea sediment as the precursor of the catalyst.

3. Results and discussion

3.1. Optimization of temperature and residence time in the furnace to prepare the catalyst

To determine the optimum temperature for catalyst preparation, experiments were performed at different temperatures (raw sediment, 300, 350, 400, 500 °C) and residence time in the furnace of 2 h. As shown in Fig. 1, the removal of amoxicillin (AMX) increased with increasing temperature to 400 °C and remained almost constant afterward. The highest removal rate of AMX (85%) was obtained with the catalyst precursor pretreated at 400 °C (Fig. 1). Therefore, this temperature was chosen as the optimum temperature. The reason for this is that calcined temperatures below 400 °C lead to the formation of weak crystals, i.e. crystals that still contain molecularly bound water, which made them unstable and in turn affected the catalytic activity in the removal process. Similar findings have been reported by Kanakaraju et al [30]. On the other end, high temperatures cause the aggregation of particles and increase the size of the crystals, leading to decomposition and finally pyrolysis beyond a certain temperature [31].

To determine the optimum residence time in the furnace to yield the most active catalyst, the raw sea sediment was placed in the furnace at 400 °C at various times (1 to 4 h). As shown in Fig. 1, the highest removal rate of AMX (82%) was at 2 h. After 3 and 4 h times, the removal efficiencies were similar to that at 2 h, therefore the one at 2 h was retained from an economic and energy-saving point of view [32].

3.2. Catalyst characterization

3.2.1. Sea sediment characterization

The percentage of important chemical constituents in the raw sediment sample used in this study as the catalyst precursor is given in Table S1. The total oxides were above 77%, the sea sediment is a combination of different materials. The compounds present in sea sedimentation included CaO > Al₂O₃ > Fe₂O₃ > Na₂O > MgO > K₂O >

SO₃. Metal oxides such as magnesium oxide and iron oxide are active catalysts for the removal of water pollutants in combination with different AOPs [8,31,33]. Therefore, we speculate that these oxides are the active catalyst components in the removal of AMX.

The metals concentration in the raw sea sediment (waste sludge) was measured by ICP-OES (Table 1). There are different metals in the sea sediments. Some metals, such as titanium, magnesium, manganese, copper, and zinc oxidize after thermal treatment, which will produce catalytically active metal oxides. Some other metals (such as arsenic, chromium, and cadmium) are water contaminants. However, after calcination, we exclude that these metals would leak from the catalyst structure and disperse in water.

3.2.2. Catalyst surface properties

The specific surface area (SSA) of the catalyst was calculated by the BET method using N₂ adsorption–desorption (Fig. 2). The isotherm has two major parts (P/P° less than 0.4 and P/P° > 0.4). The SSA of the sea sediment catalyst was 4.4 m²/g. After the catalyst was used for AMX removal, the BET surface decreased to 3.6m²/g. Also, the volume of the catalyst pores decreased from 0.0127 g/cm³ to 0.0120 g/cm³. This is probably due to a partial collapse of the catalyst structure after being used in a liquid medium for too long [34]. In a similar study, Zn-Fe-

Table 1
Metals in sea raw sediment (waste sludge) measured by the ICP-OES.

Element	Wavelength	Value (µg/g)
Al	396.152	7479.8
As	188.98	4.97
Ca	318.127	201063.8
Ce	418.659	7.41
Co	228.615	1.87
Cr	267.716	46.2
Cu	324.754	5.03
Fe	259.94	5160.66
La	408.671	2.87
Li	670.783	2.99
Mg	280.27	9657.36
Mn	260.568	128.23
Na	568.821	4479.04
Ni	231.604	8.59
Pb	220.353	0.91
Sr	460.733	1205
Ti	334.188	1124.69
V	292.401	14.59
Y	360.074	2.61
Zn	334.502	4.07
Zr	349.619	2.19

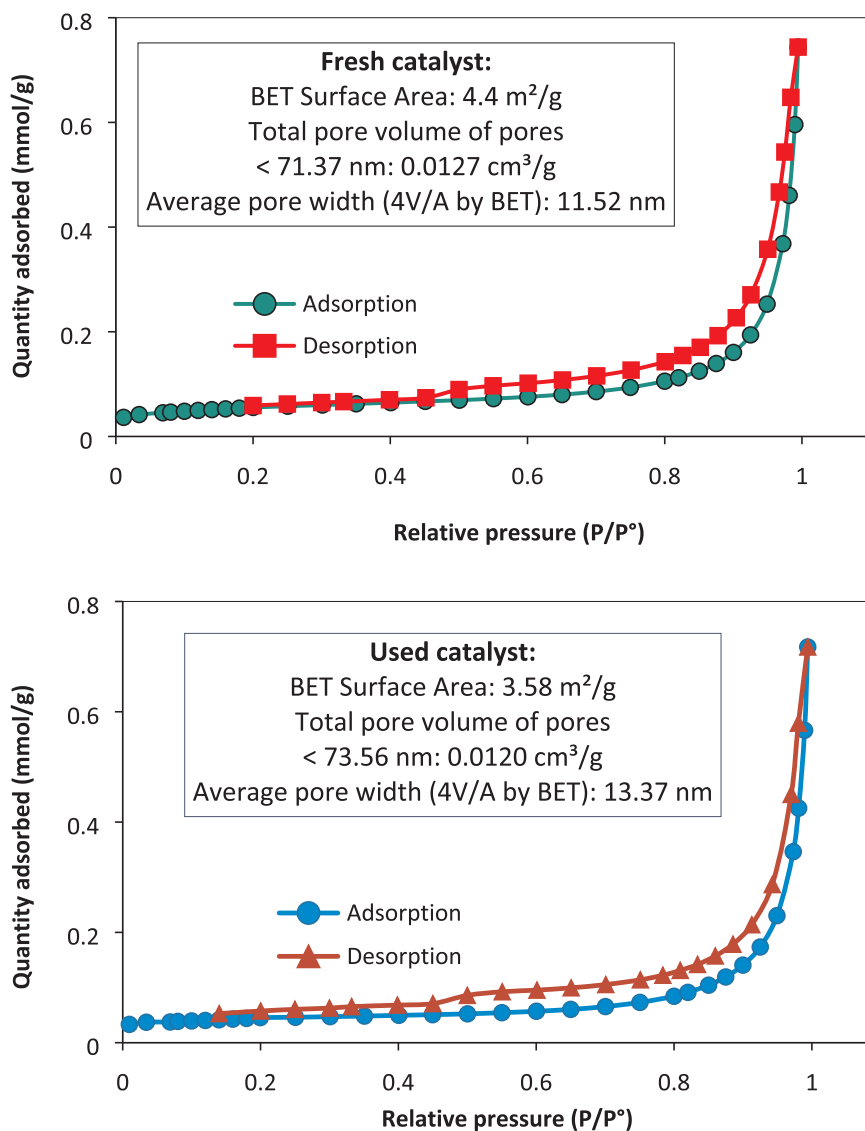


Fig. 2. N₂ adsorption-desorption isotherms for fresh (top) and used (bottom) catalyst.

CNTs was used as a catalyst to remove sulfamethoxazole and had an SSA of 51.7 m²/g which is higher than the catalyst in this study [35]. The fly ash used to remove AMX had a surface area of 23m²/g, which is also higher than the catalyst of this study [9]. Since the pore diameter is between 2 and 50 nm, this catalyst is classified as a mesoporous one, which corresponds to a group III IUPAC classification [36]. The hysteresis loops of the catalyst sample can be classified as an H3 type. The shape of the cavities for this type is slit-shaped pores [22].

3.2.3. FTIR

The functional groups present in the sea sediment (waste sludge) catalyst are shown in Fig. S1. The absorption peak at 3407 cm⁻¹ is related to -OH groups [7]. The wavenumbers of 2871 cm⁻¹ and 2930cm⁻¹ indicate the asymmetric C-H traction [37]. The peaks in the 400–700 cm⁻¹ range are related to the Al-O group [9]. Peaks at 869 cm⁻¹ and 792 cm⁻¹ belong to the Mg-O group and quartz (SiO₂) [7,38]. Fig. S1 shows the FTIR of the used catalyst. In this figure, the wavenumbers have changed, indicating that the catalyst has changed its properties after either its catalytic activity in the water, or by the action of the ultrasound waves.

3.2.4. XRD

Fig. 3 shows the XRD patterns for the sea sediment catalyst before and after the application in AMX removal in the 2θ range of 5–80°. The peaks at 2θ equal to 29.5° (the highest intensity), 44°, 57°, 58°, 61°, 62° correspond to MgO [39]. Also, the peak at a 2θ angle of 24° and 50° is related to quartz [40]. The ZnO peak is detectable at 2θ diffraction angles of 32°, 40°, 68° [35]. The Fe₂O₃ peaks were found at 2θ angles of 27°, 31°, 40°, 60° [8,41]. The peak at 2θ equals to 22°, 25°, 47.48° is attributed to TiO₂ [4]. A comparison of the two XRD spectra fresh and used catalyst shows that the intensity of the crystalline peaks decreased after the AMX removal process. This decrease in the crystal peak intensity after being used in the catalytic process may be due to the formation of a coating of the organic molecules on the catalyst surface. The Scherrer equation was used to calculate the magnesium oxide crystal size (D, nm) [42].

$$D = \frac{K \cdot \lambda}{B \cdot \cos\theta} \quad (6)$$

In this equation, the λ denotes the X-ray wavelength (1.54 Å...), the k denotes the shaped factor (approximately 0.9), B denotes the peak width at half-height, and θ denotes the peak locations.

The average crystallite size for the fresh and used catalyst samples

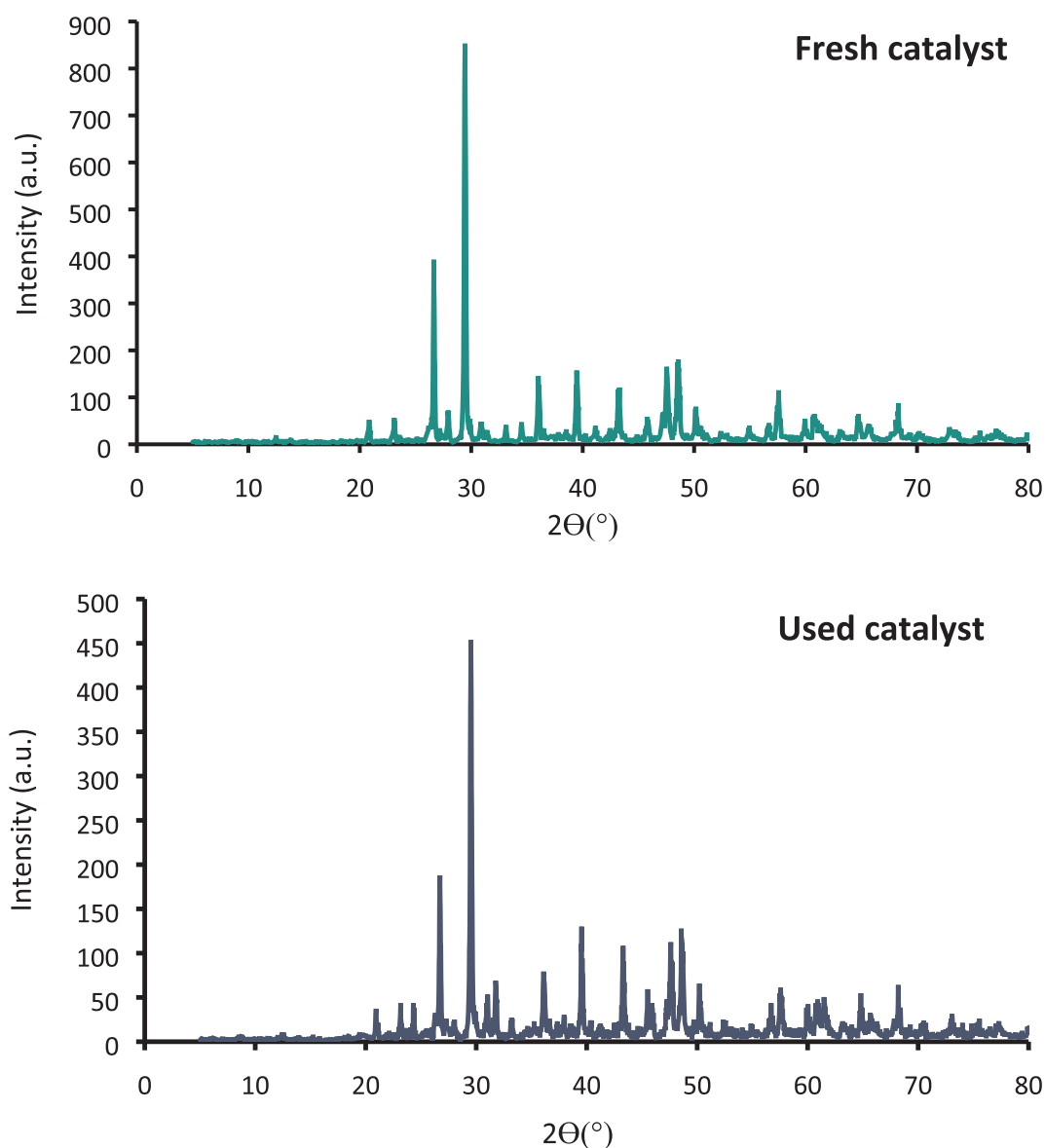


Fig. 3. XRD pattern for the catalyst before and after use in the AMX removal.

was computed to be 80.32 nm and 80.44 nm, respectively. The proximity of these two values indicates no significant effect of drug adsorption on the catalyst structure.

3.2.5. XRF

The XRF analysis results for the catalyst provided by waste sludge are shown in Table 2. Among the compounds detected by XRF, the highest weight (wt.%) composition of the catalyst corresponds to SiO_2 followed by MgO , CaO , and Al_2O_3 .

3.2.6. SEM-mapping

The surface morphology and elemental content of the sea sediment catalyst before and after the AMX removal are shown in Fig. 4. After thermal treatment, the sea sediment structure exhibits particles of different sizes and shapes, clustered among each other, and separated by fractures (Fig. 4, Fresh catalyst). The used catalyst has a smoother surface, but above it, some irregular shape particles are still present as individual entities. This finding is consistent with the decrease of the BET surface catalyst after the removal of AMX, which corresponds to a partial collapse of the structure and to the formation of oxide layers

after the permanence of the catalyst in the oxidant aquatic environment during the degradation of AMX [8]. We performed as well the EDX analysis on both fresh and used catalyst to confirm elemental distribution and element content (Fig. 4). EDX analysis confirmed the presence of O, Mg, Al, and Si in the catalyst structure. The maximum intensities were observed for O and then by Mg, Si, and Al followed. For the used catalyst, the values of Mg and Si decrease, while O increases, accordingly with the formation of oxides in water. The imaging results also support this finding, as after oxidation in water, the particles appear as dense and clumped masses.

3.2.7. Zero charge potential (pH_{zpc})

As shown in Fig. 5, the pH_{zpc} of the sea sediment catalyst was determined to be 8.92. At a pH below pH_{zpc} the catalyst surface is positively charged and is suitable for anion adsorption or cation exchange. At low pHs, the carboxyl groups ($-\text{COOH}$) in the structure of AMX changes to carboxylate ($-\text{COO}^-$). The electrostatic attraction between the AMX anion and the positively charged catalyst increases therefore at lower pH, thus removing more AMX [43].

Table 2
XRF analysis results for fresh sea sediment catalyst.

Compound	Concentration (w/w%)
Na ₂ O	6.38
MgO	16.86
Al ₂ O ₃	11.37
SiO ₂	19.94
P ₂ O ₅	5.93
SO ₃	6.39
Cl	4.45
K ₂ O	4.44
CaO	13.97
TiO ₂	0.89
Cr ₂ O ₃	0.06
MnO ₂	2.23
Fe ₂ O ₃	5.21
SrO	0.44
CuO	0.29
ZnO	0.37
NiO	0.05
V ₂ O ₅	0.08
ZrO ₂	0.62
BaO	0.03

3.3. Influence of operating variables on amoxicillin (AMX) removal by sea sediment–Hydrogen peroxide–sonication

3.3.1. The initial concentration of AMX

The influence of the initial concentration of AMX (5, 25, 50, 75, 100 mg/L) on its removal efficiency was explored at fixed conditions of pH: 7, catalyst dose: 3 g, concentration of hydrogen peroxide: 50 mM, and reaction time: 40 min, and in the ultrasonic bath. The results are shown in Fig. 6a and display that the removal rate of AMX decreased with increasing concentration. Samples containing lower concentrations of AMX had a higher rate of decomposition than higher concentrations ones. Studies by other researchers, such as Su et al. [28] and Liu et al. [35], showed that increasing antibiotic concentration reduced its removal. We ascribe this to the insufficient amount of radicals generated by hydrogen peroxide and ultrasound to completely remove the pollutant as the concentration increases.

3.3.2. Solution pH

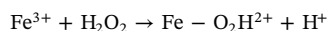
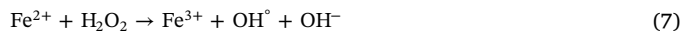
The effect of pH (5 to 9) on the removal efficiency of AMX was measured at fixed operating conditions of initial AMX concentration: 50 mg/L, catalyst dose: 3 g/L, H₂O₂ concentration: 50 mM, reaction time: 40 min and in the ultrasound bath (Fig. 6B). The results showed that the removal efficiency decreased with increasing pH. Therefore, pH 5 was considered as the optimum pH. AMX molecules have three decomposition constants for the functional groups of carboxyl (pka = 4.2), amine (pka = 7.4), and phenol (pka = 9.6). So, AMX molecules can be cationic, neutral, and anionic at different pHs [30]. The AMX pka of 4.2 can be one of the reasons for its removal at acidic pH. At acidic pHs, the catalyst of the sea sediment is positively charged and attracts more AMX molecules, as explained in the section concerning the zero charge potential. This increases the adsorption of the model pollutant on the catalyst and the synergy with the other two AOPs, i.e. oxidation by hydrogen peroxide and ultrasonically-generated radicals. Increasing the hydroxyl radicals production in the acidic medium, thereby further decomposes AMX. Matta et al. report similar results with persulfate oxidants as oxidation initiators [3].

3.3.3. Synergy between ultrasound and catalyst

The effect of dosage of sea sediment catalyst (0.5, 1.5, 3, 4.5, 6 g/L) on the AMX removal efficiency was investigated at fixed operating conditions of pH: 5, AMX concentration: 50 mg/L, H₂O₂ concentration: 50 mM, reaction time: 40 min and in the ultrasound bath. The results showed that by increasing the catalyst dose up to 4.5 g/L, the removal

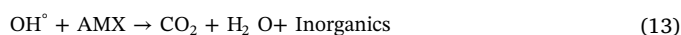
rate of AMX increased and then stabilized, so this dose was considered as the optimal (Fig. 6C). The percentage of AMX removal increased with increasing catalyst dose due to the increase in the available surface area for the production of hydroxyl radicals.

Also, Fe₂O₃ present in sea sediment is a catalytic compound that can produce Fe³⁺ in acidic solutions. reacts with H₂O₂ to produce intermediate compounds. According to the following reactions, these compounds can produce hydroxyl radicals and react with pollutants [9].

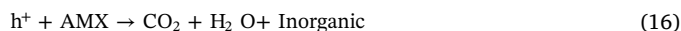


According to the catalyst composition data, there are other compounds in the catalyst structure besides FE such as magnesium oxide (MgO) and zinc oxide (ZnO). Ultrasound (and H₂O₂) acts synergistically with these compounds to form active radicals that degrade AMX.

Possible synergistic mechanisms between MgO and ultrasound (and H₂O₂) are as follows [44].



Possible synergistic mechanisms between ZnO and ultrasound (and H₂O₂) are as follows [45].



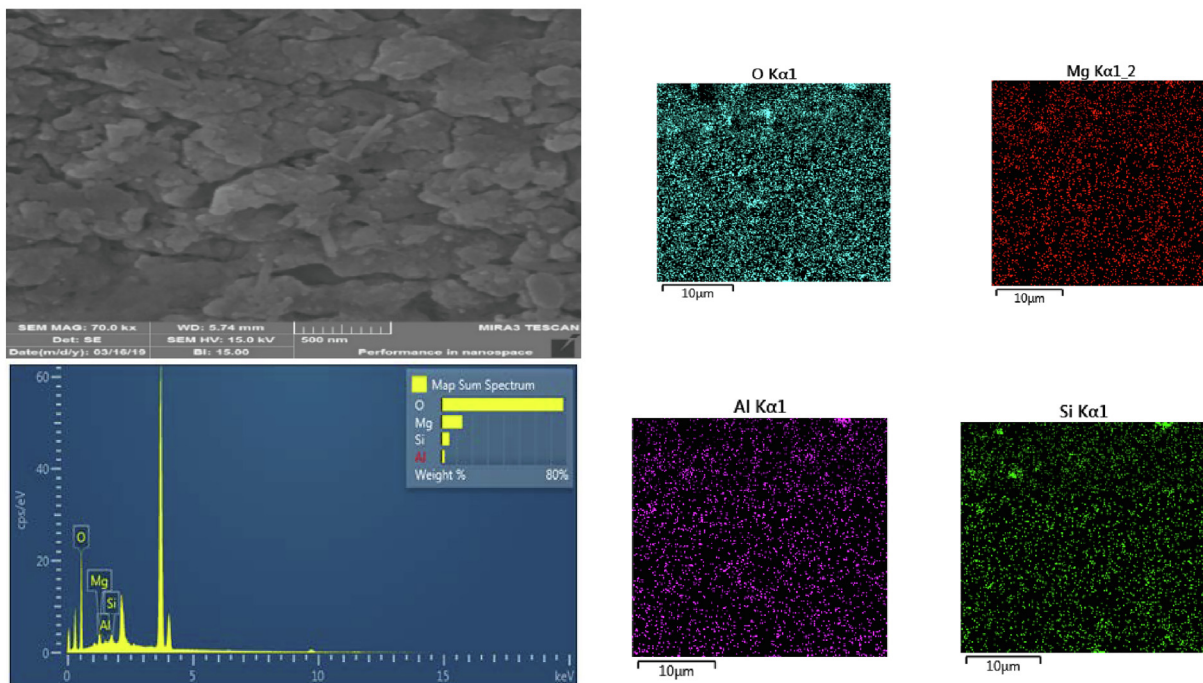
3.3.4. Synergy between ultrasound and hydrogen peroxide

In this step, the effect of different concentrations of hydrogen peroxide (10, 25, 50, 75, 100 mM) on the removal efficiency of AMX was tested at fixed operating variables of pH: 5, AMX concentration: 50 mg/L, catalyst dosage: 4.5 g/L, and reaction time: 40 min and in the ultrasonic bath (Fig. 6). The results showed that by increasing the concentration of hydrogen peroxide up to 50 mM the removal of AMX increased and then there was no significant change, and the removal efficiency remained fairly constant. Thus, if excess hydrogen peroxide is present in the media, the hydrogen peroxide itself acts as an effective hydroxyl radical receptor, decomposing into water and oxygen, reducing the overall hydroxyl radical in the media. Chen et al. [46] and Elmolla et al. [16] confirmed this result. This also applies when ultrasound is present and produces both hydroxyl (OH[°]) and perhydroxyl (°OH₂) radicals. Indeed, the ultrasound operating conditions was the same throughout the tests as both the power and power density were the same as the ultrasound bath employed did not allow to change these parameters. More radicals could have been produced with an increase in ultrasound power up to an optimum amount able to generate maximum radical concentration, either alone or in synergy with H₂O₂ [47].

3.3.5. Reaction time and kinetics of amoxicillin removal in distilled water, urine, and real wastewater

The effect of reaction time (5, 20, 40, 60 min) on the removal of AMX was studied at fixed conditions of pH: 5, AMX concentration: 50 mg/L, catalyst dose: 4.5 g/L, and H₂O₂ concentration: 50 mM. The results are shown in Fig. 7. The removal percentage increased with increasing reaction time as expected [45,48]. The decomposition rate of AMX in aqueous matrices (wastewater, urine, and distilled water) is shown in Fig. 7. As it can be seen, the removal of AMX from distilled water is significantly greater than in other environments (urine and

(Fresh catalyst)



(Used catalyst)

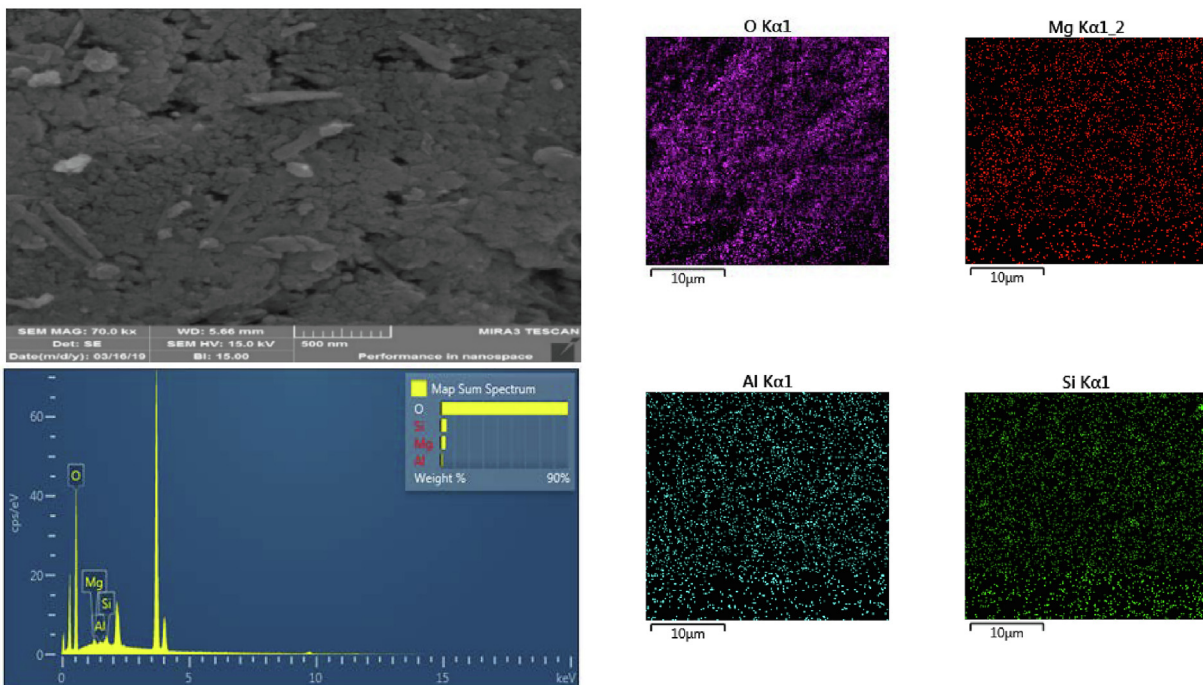


Fig. 4. SEM-EDX images and mapping of the four major elements in the catalyst before and after AMX removal.

hospital wastewater). A possible reason for this is the absence of competitors and radical scavengers in distilled water [6].

The AMX removal kinetics was tested by a first-order model (Eq. (17)):

$$-L_n \frac{C}{C_0} = kt \tag{17}$$

where C_0 is the initial concentration of AMX and C is the real-time

concentration of AMX. If $L_n \frac{C}{C_0}$ is plotted against time t , a line is obtained whose slope equals the reaction rate constant (k).

The kinetic of AMX decomposition from hospital wastewater, urine, and distilled water was investigated in the sea sediment catalyst – hydrogen peroxide–sonication system and the R^2 values were 0.9195, 0.9305, and 0.9299, respectively. The reaction rate constant (k) for hospital wastewater, urine, and distilled water was 0.021 1/min, 0.026 1/min, and 0.067 1/min, respectively. On the other hand, AMX

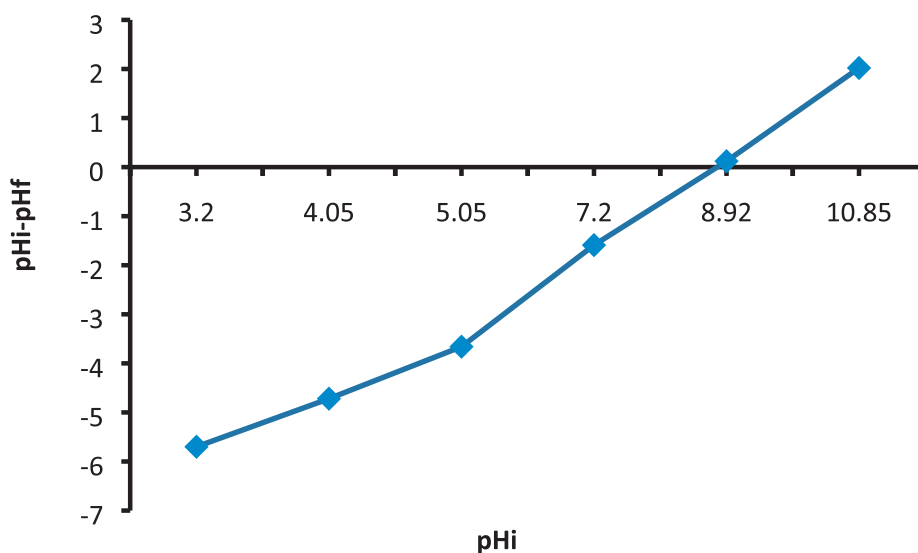


Fig. 5. pH_i vs. pH_i-pH_f to determine the pH_{zpc} for the sea sediment catalyst.

oxidation rates are lower in-hospital wastewater due to the presence of radical consumers [49]. The characteristics of this wastewater are presented in Table 3. As it is depicted in this table, the wastewater contains organic and inorganic substances that can scavenge hydroxyl radicals.

A reaction rate constant of 0.067 1/min (for distilled water) was obtained using the seawater catalytic process in synergy with hydrogen peroxide and ultrasound. This value is higher than other studied

systems to remove AMX. For example, the reaction rate constant obtained using magnetic and ultrasonic adsorbents to remove AMX was reported to be 0.030 1/min [41]. The rate constant for the removal of AMX in the US/O₃ system in distilled water was 0.064 1/min [17]. In a study, to remove AMX in distilled water with a ZnO/UV system, the reaction rate constant was 0.018 1/min. The results showed that the studied system has better efficiency for the removal of AMX [15].

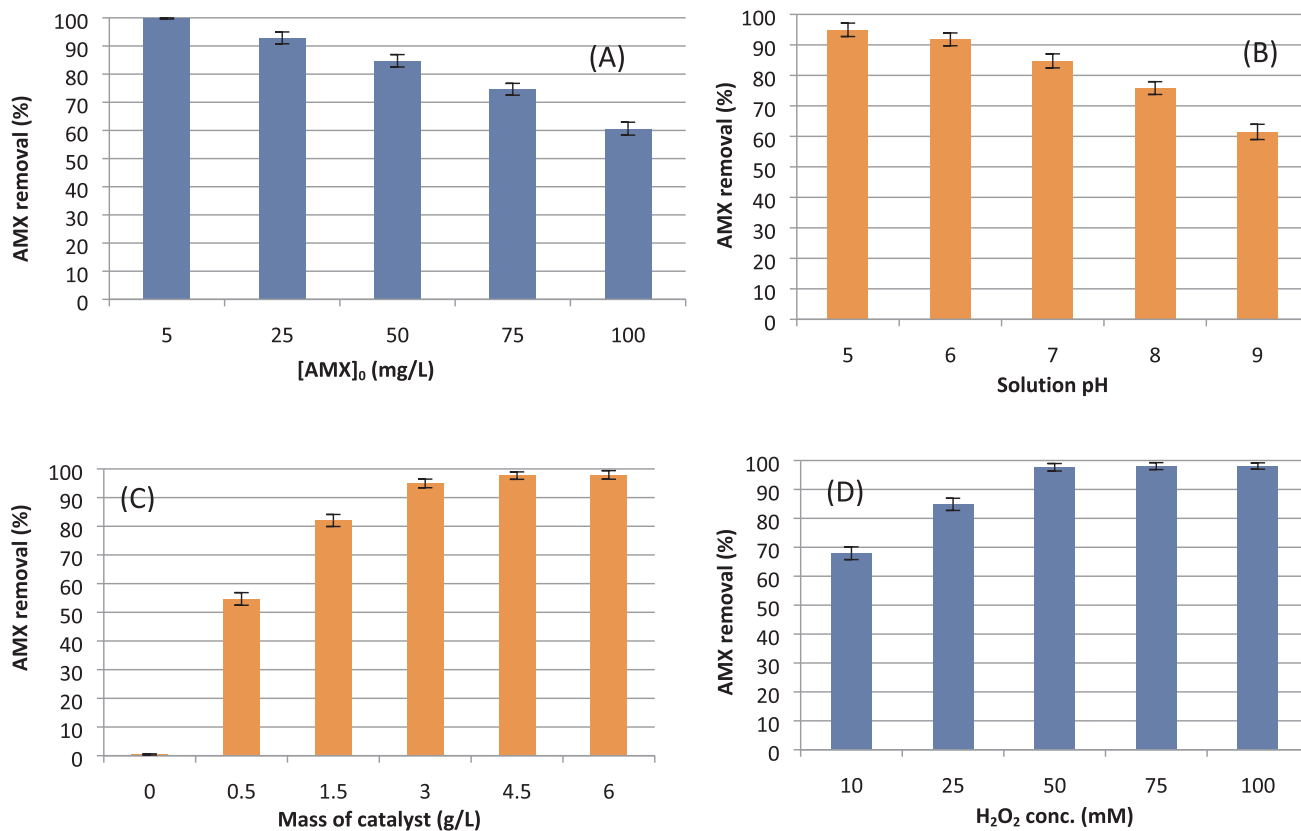


Fig. 6. The effect of different parameters on the removal rate of AMX over a sea sediment catalyst and hydrogen peroxide –sonication, (A) initial contaminant concentration, (B) solution pH, (C) catalyst concentration, and (D) H₂O₂ concentration.

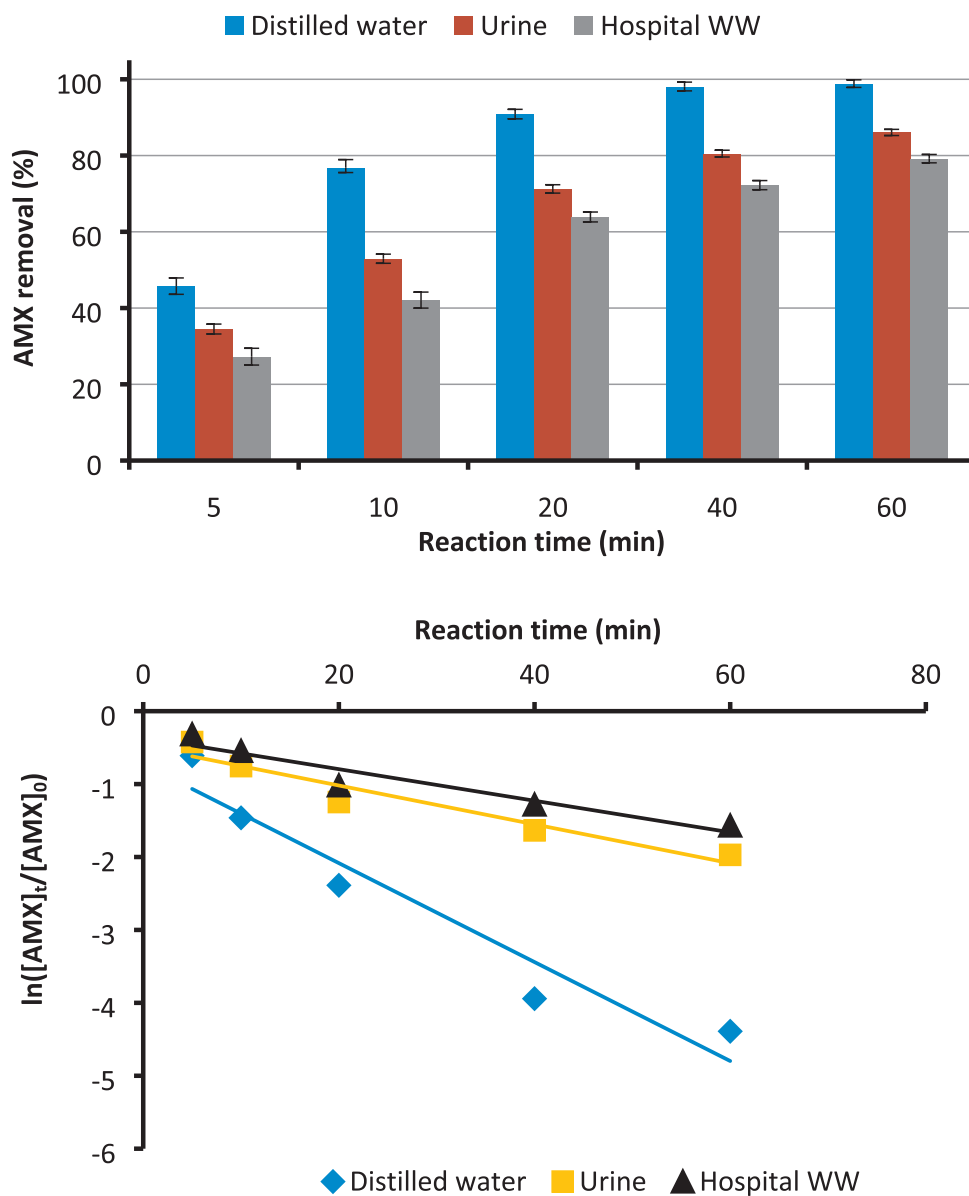


Fig. 7. Influence of reaction time on the removal of AMX from distilled water, urine and hospital wastewater by ultrasound/hydrogen peroxide/sea sediment catalyst and their first-order kinetics.

Table 3

Characteristics of the studied hospital wastewater.

Parameter	pH	Turbidity (NTU)	BOD ₅ (mg/L)	COD (mg/L)	TOC (mg/L)	TDS (mg/L)
value	6.9 ± 0.2	402 ± 17	305 ± 22	620 ± 14	285 ± 26	1129 ± 75

3.4. Overall synergy of the sea sediment catalyst –hydrogen peroxide and ultrasound

The effect of the sea sediment catalyst, hydrogen peroxide, and ultrasound was evaluated separately and compared with the integrated process to observe the effect of the combination of the processes on the AMX removal. The pollutant removal in contact with ultrasonic waves alone, sea sediment catalyst alone, hydrogen peroxide alone, and binary combinations of these components were investigated at the optimum conditions reported above. The results of these experiments are shown in Fig. 8. The results show that in the absence of any ultrasonic waves,

the performance of hydrogen peroxide or sea sediment catalyst alone, even under acidic conditions was significantly low. This difference in the performance can be seen by comparing the removal values for H₂O₂-US and catalyst-H₂O₂-US. This indicates the importance of the presence of sea sediment catalyst in increasing the efficiency of the system. The absence of a seawater catalyst, which is a suitable source of electrons for hydrogen peroxide and radical hydroxyl production, disrupts the system and reduces the efficiency of AMX removal. On the other hand, the presence of ultrasonic waves, not only is capable of generating more radicals in the synergy with the catalyst and hydrogen peroxide as highlighted in the section above but also introduces a better

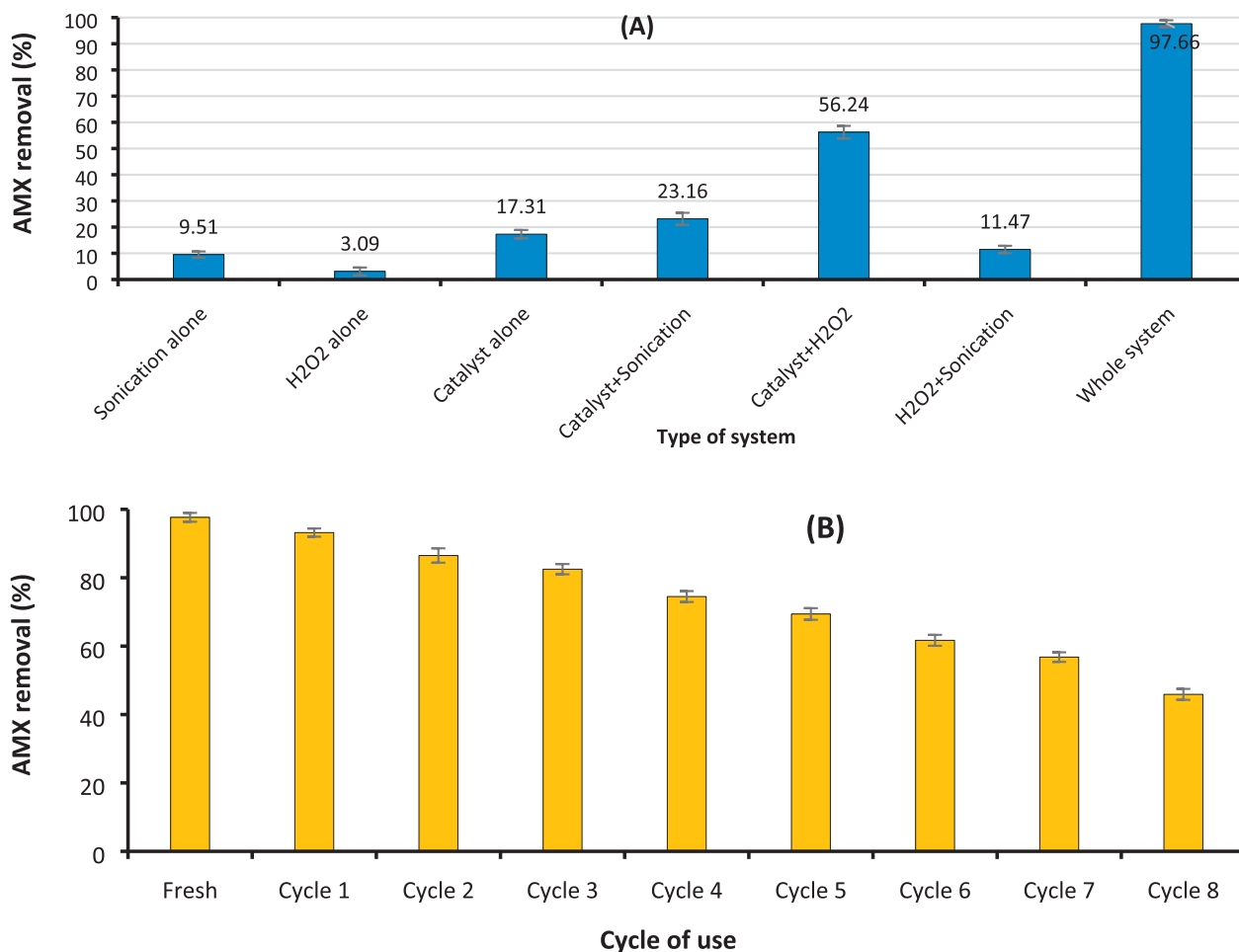


Fig. 8. (A) Influence of studied system components on AMX removal and (B) the removal efficiency of AMX by the recovered catalyst.

mixing of the entire system. radicals. Also, ultrasonic waves, by creating small bubbles (cavitation), increase the level of catalyst contact with hydrogen peroxide and favours the transport of radicals (increase mass transfer) [44]. The absence of hydrogen peroxide in the environment partly eliminates the source of hydroxyl radicals as only the ones generated by the interaction with ultrasound with water and metal oxides on the catalyst are present. Although ultrasonic waves are capable of producing some hydroxyl radicals from water molecules, the amount of hydroxyl radical produced will not be sufficient. It can be concluded that the presence of each of the factors used in the process (ultrasonic waves, hydrogen peroxide, and sea sediment catalyst) is necessary.

3.5. Comparison of systems reported in the literature with the system developed in this study

The results of AMX removal by the ultrasound/H₂O₂/catalyst system have been compared with the methods reported in the articles in Table 4. As it can be seen, the efficiency of AMX removal in the studied system occurs in a relatively short time and milder conditions than other processes. Despite the catalyst loading being overall higher than other literature data, our catalyst was derived by a waste precursors, which makes it inherently expensive in comparison to other catalytic systems reported. Therefore, it can be concluded that the system presented in this work has a high potential to remove amoxicillin from water and it is worth it to investigate it for the removal of other aqueous pollutants, singularly or in a matrix.

3.6. Recovery and reuse of sea sediment catalyst

The reuse of the sea sediment catalyst for the degradation of AMX is shown in Fig. 8. The catalyst activity at each step did not decrease significantly compared to the previous step. The new catalyst was able to remove about 98% of AMX at a concentration of 25 mg/L. When the test reached cycle 9, the degradation efficiency was reduced to less than 50%. Sheydaei et al. [53] reported a reduction in the activity of less than 30% after 4 times the use of a catalyst to remove norfloxacin. Kanakaraju et al. [30] reported a reduction in the efficacy of less than 30% after 3 times the reuse of zeolite/TiO₂ to remove AMX. We ascribe the loss of catalyst's activity to the loss of active components from the catalyst due to leaching in the aqueous phase.

3.7. AMX decomposition pathways with sea sediment catalyst- hydrogen peroxide-ultrasound

AMX decomposition by-products created in the sea sediment catalyst- hydrogen peroxide-sonication system were identified by GC-MS (Fig. S2). It is expected that hydroxyl radicals obtained by hydrogen peroxide generated by the presence of catalyst promote the AMX degradation reaction [32]. Molecular structures resulting from the breakdown of AMX were analyzed based on *m/z* obtained from the mass spectrum by ChemDraw software. The proposed intermediates and the degradation pathways by the loss of amine groups [54], ring-opening, oxidation of methyl groups [55] disruption of bonding between pentagonal and hexagonal rings [56] are shown in Fig. 9. Also,

Table 4
Comparison the reported methods in the literature with the system developed in this work to remove amoxicillin.

Maximal AMX degradation (%)	Technique	Reaction conditions	Reference
COD: 93.4%	Sulphate radicals under ultrasound irradiation	[amoxicillin]: 0.119 mmol/L, [oxone]: 5 mmol/L, [Co ²⁺]: 0.025 mmol/L, T: 24 °C, ultrasound: 20 kHz, 200 W, pH: 3, reaction time: 60 min.	[28]
AMX: 90%	Heterogeneous sonocatalytic/ZnO@Fe ₃ O ₄ magnetic nanocomposite	[amoxicillin]: 10 mg/L, [ZnO@Fe ₃ O ₄]: 0.8 g/L, ultrasound: 6 kHz, 60 W, pH: 3, reaction time: 120 min.	[50]
AMX: 98%	Sulfate radicals/ultrasound	[amoxicillin]: 0.11 mmol/L, [Ag]: 1.45 mmol/L, [PS]: 152.3 mmol/L, ultrasound: 200 W, pH: 7, reaction time: 60 min.	[51]
AMX: 36.1%	Fly ash/UV/H ₂ O ₂	[amoxicillin]: 50 ppm, [Fly ash]: 1 g/L, [H ₂ O ₂]: 10 mM, pH: 7.1, reaction time: 4 h.	[9]
AMX: 94%	Clay supported bimetallic Fe/Ni nanoparticles	[amoxicillin]: 60 mg/L, [B-Fe/Ni]: 4 g/L, pH: 6.05, reaction time: 60 min.	[38]
AMX: 84.1%	Magnesium oxide nanocatalyst/ultrasound	[amoxicillin]: 11 mg/L, [MgO]: 1.8 g/L, ultrasound: 37 kHz, 370 W, pH: 7, reaction time: 80 min.	[44]
AMX: 98.2%	Heterogeneous electro-Fenton process by Nano-Fe ₃ O ₄	[amoxicillin]: 20 mg/L, [Fe ₃ O ₄]: 10 g/L, pH: 6.05, Applied current: 60 mA, reaction time: 60 min.	[52]
COD: 27%	UV/H ₂ O ₂ /TiO ₂	[amoxicillin]: 104 mg/L, [TiO ₂]: 1 g/L, [H ₂ O ₂]: 100 mg/L, pH: 11, reaction time: 300 min.	[16]
AMX: 98%	Waste sludge from shipping docks as the catalyst/H ₂ O ₂ /ultrasound	[amoxicillin]: 5 mg/L, catalyst dose: 4.5 g/L, [H ₂ O ₂]: 50 mM, ultrasound: 37 kHz, pH: 5, reaction time: 60 min.	This study

the existence of smaller fragments with molecular masses of 206, 195, etc. has been proved by the studies of Tan et al. [57].

4. Conclusion

In this study, we produced by simple thermal treatment a new catalyst from sea sediment (sludge waste) obtained from shipping docks. We tested the catalyst in the presence of hydrogen peroxide and

ultrasound waves to remove AMX. The catalyst obtained at 400 °C for 2 h had the best performance in the AMX elimination. The results showed that at low AMX concentrations, acidic environment, 4.5 g/L catalyst concentration, and 50 mM hydrogen peroxide were the best conditions to remove nearly 100% of AMX in only 60 min. However, only after 20 min, the removal was already over 80%. The removal of AMX followed the first-order kinetics, with a reaction rate constant of 0.067 1/min (in distilled water), which is higher than the ones reported

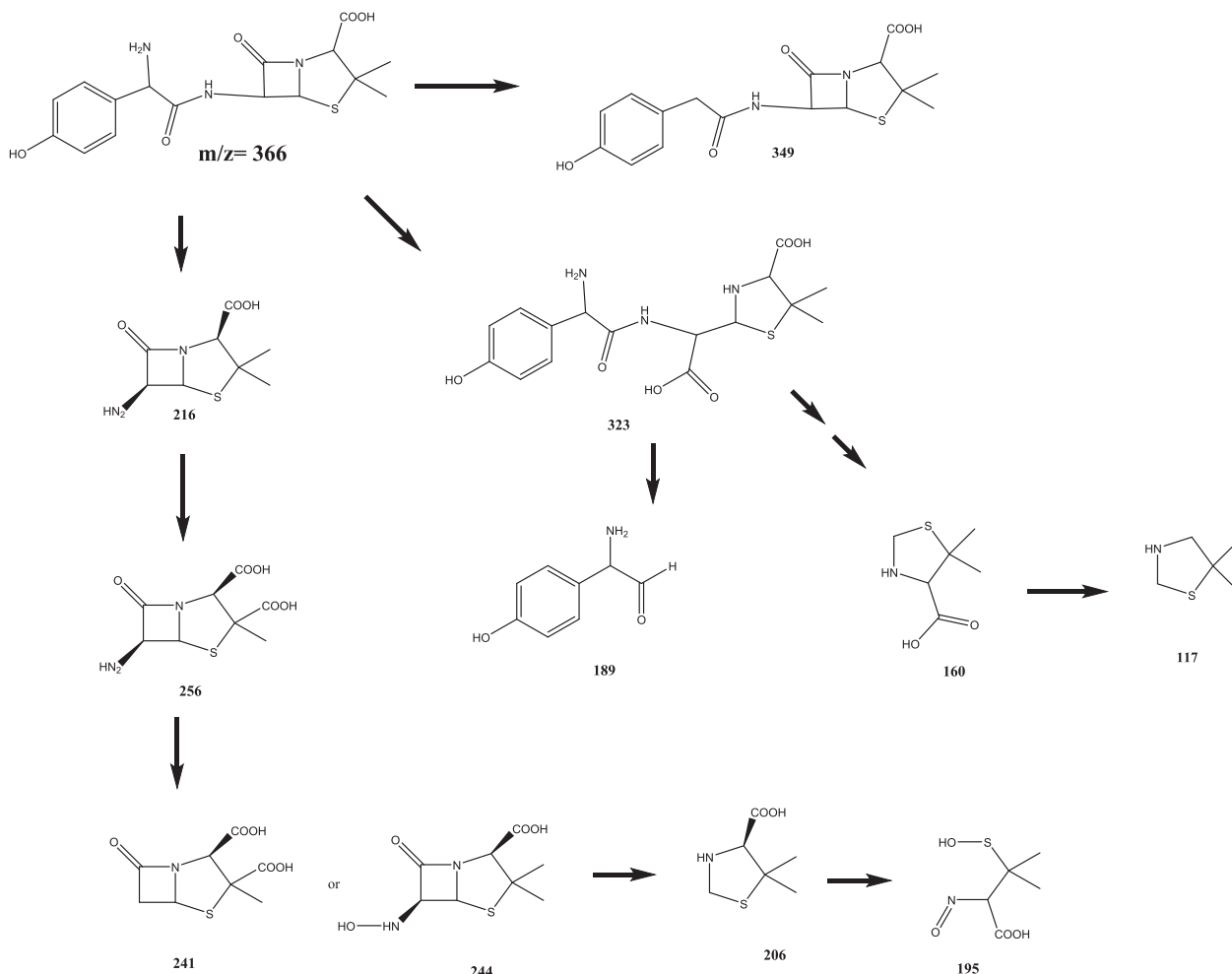


Fig. 9. AMX degradation pathway in the ultrasound/hydrogen peroxide/catalyst system.

in the literature for similar systems. In hospital wastewater and urine, the reaction rate was about 1/3 of the one in distilled water. The results clearly show that the synergy between ultrasound and hydrogen peroxide and ultrasound/H₂O₂/catalyst is key to achieve the high removal rate. After nine uses the catalyst lost over 50% of its activity, however, the results achieved in the single removal tests are unprecedented.

CRedit authorship contribution statement

Fatemeh Damiri: Formal analysis, Writing - original draft. **Sina Dobaradaran:** Methodology, Validation. **Seyedenayat Hashemi:** Methodology, Conceptualization. **Rauf Foroutan:** Methodology. **Mehdi Vosoughi:** Methodology. **Soleyman Sahebi:** Methodology, Conceptualization. **Bahman Ramavandi:** Supervision, Writing - review & editing. **Daria Camilla Boffito:** Supervision, Writing - review & editing.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ultsonch.2020.105187>.

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