Removal of ~~P~~phenol ~~removal~~ from hyper-saline wastewater using fluidized catalyst (catalytic?) ~~-~~bed reactor

ABSTRACT

Th~~is paper discusses~~ ~~the processes involved in~~ the successful synthesis of ~~a~~ Cu/Mg/Al-chitosan ~~was synthesized successfully~~ and its use in a ~~used in a~~ fluidized catalyst (catalytic?) bed reactor ~~in ord~~ to degrade phenol from hyper-saline wastewater. The results showed that ~~the~~ phenol ~~could~~ can be completely oxidized by Cu/Mg/Al-chitosan-H_2O_2 within 7 min at acidic pH. The influence of various variables ~~was investigated,~~ including solution pH, salinity concentration, H_2O_2 concentration, and Cu/Mg/Al-chitosan quantity is investigated, to study their ~~for their any~~ effect~~s~~ on phenol degradation in ~~a~~ synthetic saline wastewater. The maximum degradation of phenol ~~was~~ was achieved at pH 2 and 7 g Cu/Mg/Al-chitosan. During this process, ~~it is noted that C~~chloride and sulfate ions ~~had~~ have a synergistic effect on phenol removal, where the ~~phenol~~ oxidation rate of phenol in the presence of sulfate ions is ~~seen to be~~ twice ~~o times more than~~ of that ~~e oxidation rate~~ obtained ~~in~~ under controlled conditions. ~~Finally, it is found that an i~~Industrial wastewater containing phenol, ~~may~~can be ~~could be~~ effectively treated using a relatively low concentration of Cu/Mg/Al-chitosan, 5 g, and in a short hydraulic retention time of 7 min. Overall, the ~~presented~~ method ~~demonstrated~~ demonstrates effic~~ien~~acy and holds promise ~~a promising~~ as a simple and elegant method to eliminate ~~the~~ phenol from wastewater.

Keywords: Phenol, Degradation, Cu/Mg/Al-chitosan, Catalyst, Hyper-saline wastewater.

1. Introduction

~~Using~~ Chemical processes ~~(and their use)~~ ~~chemical processes in particular advances~~ favor oxidation as an alternative method by which organic compounds may be oxidized ~~for oxidation of organic compounds~~ and ~~converting~~ converted~~those products~~ into simple ~~and~~ minerals. These processes are ~~highly~~ useful ~~necessary~~ [1] and have recently received ~~been the subject of~~ significant attention. Amongst the various

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oxidation techniques known ~~advances oxidation techniques~~, catalytic oxidation appears to be a promising field of study. It ~~has been reported to be~~ is effective for the ~~near~~ near-ambient degradation of pollutants~~,~~ ~~because~~ as it ~~can provide~~ holds promise of ~~a~~ nearly- complete degradation [2]. Zhou *et al.* [3] point~~ed~~ out ~~that in recent years,~~ to ~~there is a considerable~~ the interest ~~has been expressed~~ in the development of copper-based heterogeneous catalysts~~,~~ especially hydrotalcite-like compounds ~~in recent years~~. ~~Hydrotalcite like~~ These compounds, referred ~~to~~ as layered double hydroxides, are ~~a~~ classes of layered materials ~~and have~~ receiv~~ed~~ing ~~an increasing~~ increasing attention ~~in recent years~~ owing to ~~their~~ diverse applications, especially in catalysis. ~~and has~~ These may be denoted by a general formula ~~of~~: CuM^2AlCO_3 (M^2= Co^{2+}, Ni^{2+}, Cu^{2+}, Mg^{2+}, Zn^{2+}, and Fe^{2+}). ~~According to the literature, which has been recently reviewed by Nawrocki and Kasprzyk Hordern [4], t~~ The ~~catalysts' applicability~~ catalysts may be affected [4] by several factors~~,~~ including: leaching of metals into the liquid phase, high cost~~s~~ of production, and the availability of catalyst~~s~~ in solution (*i.e.* ~~needing to~~ low- ~~dense~~ density supporting agent~~s~~). These challenges technically, environmentally, and economically limit ~~their~~ most full-scale application~~s~~ of catalysts. ~~Thus~~ Therefore, the main concern with regard to catalysts ~~facing catalysts is~~ surrounds the development of a more environment~~al~~ friendly catalyst ~~with~~ entailing a simple and low-cost production method. In this regard, ~~ongoing~~ research is on ~~has been Accordingly, research is ongoing to~~ attempting to find novel materials with ~~the~~ high catalytic activities that ~~are also~~ may be ~~easy and cheap~~ economical and easy to produce.

Therefore, in the present study, we focus on Cu/Mg/Al (CMA) as the catalyst, because all elements in this compound are routinely used in waterworks systems and are easily available ~~rather than~~ compared to Ni, Pd, and Ag that ~~may have been~~ were previously ~~applied~~ pre~~of~~ferred by other researchers [3, 4]. For example, Zhou *et al.* [3] used $Cu/Ni/AlCO_3$ for phenol degradation from aqueous solution~~s~~. But in this study, we ~~shall applied~~ apply Mg instead of Ni ~~because given~~ as if magnesium ~~being~~ is non-toxic, and does not pollute water when used as a leaching agent in the ~~leached into the~~ liquid to be treated. ~~under treatment is not toxic and would not cause water pollution.~~ Moreover, ~~for purpose of availability of catalyst in solution~~ the chitosan compound ~~was~~ will be used as a supporting agent or as a ~~the~~ catalyst in

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solution. Chitosan has three functional groups, *i.e.* two hydroxyl groups (–OH) and one amino group (–NH$_2$), per glucosamine unit [5] which maintain the catalysts. It is characterized by low densities. In addition, chitosan obtained from fishery-waste is much more economical than activated carbon, which is often used as a support agent.

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Although several works have appeared on the use of hydrotalcite-like compounds for the degradation of pollutants, no investigation into the catalyst's role as an agent to remove pollutants from real saline wastewater is seen. Literature survey did not find, except for a few reports on advanced oxidation processes for the removal of phenol from saline wastewaters [6,7], any investigations on CMA treatment of saline wastewater containing high phenol concentrations. The investigation into the TiO$_2$-photocatalytic process for the degradation of phenol in saline solution showed a significant inhibitory effect at 50 g/L of NaCl [6]. The time required for the effective degradation of phenol increased with increase in NaCl content. Maciel *et al.* [7] investigated the effectiveness of Fenton and photo-Fenton processes on phenol degradation caused by a saline effluent. Their results show that although both processes were effective in phenol degradation, the high salt concentration inhibited the oxidation reaction considerably, and only 50% of TOC (total organic carbon) was removed in the photo-Fenton process in the presence of 50 g/L NaCl, even after a reaction time of 100 min. Moussavi *et al.* [8] reported an integrated system (catalytic ozonation/biological processes) to remove phenol from a saline solution. Although, they had achieved high efficiency, bulk of their materials and methods are questionable from the perspectives of environment-

Comment [Editor7]: Please use full forms and acronyms together during the first usage. Subsequently, you may use only the acronyms.

Comment [Editor8]: The inhibitory effect showed when the NaCl reacted on phenol?

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3

friendliness and safety. ~~but many material and methods was used which some of them environmentally and safety point of view is concern.~~

Therefore, the present study represents the first ~~application~~ effort at using ~~of~~ fishery waste-based agents as ~~supporting~~ supports ~~of~~ for the CMA ~~to enable~~ for complete removal of ~~for removal of~~ phenol from ~~the~~ hyper-saline wastewater using a fluidized bed reactor. ~~Effects~~ The effects of ~~the following se~~ basic variables like ~~were evaluated in the tests on phenol degradation; :~~ solution pH, CMA-chitosan quantity, types of salinity, and H_2O_2 concentration, were evaluated ~~in the tests on phenol degradation~~. For the latter (???), the efficiency of ~~the~~ CMA-catalyst-H_2O_2 was investigated to study ~~in terms of~~ its ~~how~~ effectiveness ~~it was in the~~ to remove ~~al of the removal of~~ phenol from industrial hyper-saline wastewater under optimized conditions.

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2. Materials and methods

2.1. Materials

~~The s~~Shrimp shell waste of ~~the~~ *Philocheras lowisi* was collected directly from the Persian Gulf. ~~and The~~ deacetylat~~ed~~ion ~~was performed~~ using a method similar to ~~the method one reported by~~ Novikov [9]. ~~The e~~Chitosan (is it shell waste?) was ~~finally~~ sieved in the size range 0.1–0.2 mm. Other chemicals and reagents used ~~in this work~~ were of analytical grade and applied without further purification. Double-distilled water was used to prepare all solutions.

2.2. Preparation of the CMA-chitosan

~~The~~ CMA-chitosan was synthesized by employing metal nitrates and Na_2CO_3/NaOH. The preparation was ~~performed~~ readied in a 250-mL flask containing metal nitrates of Cu^{2+} (0.15–0.28 mol), Mg^{2+} (0.07–0.22 mol), and Al^{3+} (0.09–0.25 mol) to ~~make~~ achieve ~~a~~ the desired Cu:Mg:Al molar ratio. Specifically, 10 g of chitosan particles ~~was~~ were added to this solution and then, 250 mL base solutions with NaOH (0.8 mol) and Na_2CO_3 (0.05 mol) were added ~~drop~~ drop-wise into the flask ~~which was~~ and stirred vigorously with a magnetic stirrer and ~~was kept~~ maintained for 4 h at 45-°C using a thermostated water

bath. ~~After that, the mixture was continuously stirred and kept at 45 °C for 4 h,~~ . It was then ~~was~~, cooled at room temperature and filtered. The ~~achieved~~ solid was washed using double--distilled water until it became nitrate-free~~,~~. This was~~and then~~, dried at 50-°C for 7 h. Table 1 ~~he~~ details ~~of~~ the physical and chemical characteristics of CMA--chitosan ~~are presented in Table 1~~.

2.3. Experimental procedure

The experiments were carried out in a fluidized bed reactor (FBR). As shown in Fig.-ure 1, a glass column ~~with having~~with a diameter of 20 mm and length of 250 mm was employed as the reactor. The total volume of the reactor was 78 ml. A circulation pump was installed to maintain the~~an~~ ~~for maintaining the~~ upward flow ~~velocity~~ of at least 50 m/h to fluidize ~~the~~ CMA-chitosan. The hydraulic retention time (HRT) was changed by varying the flow rate of the influent and effluent pumps. The solution pH was adjusted to the designated values by adding 0.1 N HCl and NaOH solutions to the reservoir of raw wastewater. The reservoir was magnetically stirred and ~~kept~~ maintained at ~~the~~ desired temperature (4--45 °C). ~~and The~~ H_2O_2 (0.02--1.02 mol/L) was added at once, ~~and this~~which initiat~~ing~~ed the reaction. Effluent was withdrawn continuously from the top of the reactor, and 5 mL aliquots were withdrawn ~~from thein effluent~~ as sample at designated time intervals. It was, mixed with 0.1 g MnO_2 ~~for the purpose of~~to eliminat~~eing~~ residual H_2O_2 [3], and filtered ~~by means of~~using 0.22--μm membranes to analyze the reaction mixture. The ~~withdrawn point of the~~ effluent was withdrawn ~~is~~ from a point a~~bout round~~ 3 cm above ~~that of~~ the circulation pump to avoid the carry over effect of CMA--chitosan.

2.4. Analysis

~~The p~~Phenol concentration in the supernatant was determined using DIONEX Ultimate 3000 high-performance liquid chromatography (HPLC). The intermediate compounds were monitored by UV--Vis spectroscopy and HPLC. ~~In addition, the total organic carbon (~~TOC~~)~~ was measured by a Shimadzu TOC-5000 Analyzer (Shimadzu Co., Japan). The nature of ~~the~~ CMA--chitosan ~~nature~~ was verified through Fourier transform infra-red analysis (FTIR) (Prestige, 21210045, Japan). ~~The~~ Chitosan and CMA--

chitosan samples were used before ~~the process of~~ phenol removal. ~~was undertaken. The~~ X-ray diffraction (XRD) patterns were ~~also~~ determined on a Rigaku D/MAX 2200 (Tokyo, Japan) instrument.

3. Results and discussion

3.1. CMA ~~-~~ chitosan characterization

~~As shown in Figu. re 2, t~~The FTIR spectroscopy (Figure 2) confirms the presence of CMA in our sample ~~and~~ along with ~~the~~ interaction between ~~the~~ chitosan and catalyst crystal surfaces. ~~Fig. ure 2 depicts t~~The FTIR spectra ~~show of~~ free chitosan and catalyst ~~-~~ chitosan particles. The resemblance ~~in between the~~ of ~~the~~ spectral features ~~confirmed~~ confirms the successful attachment of CMA ~~onto~~ to the surface of the chitosan particles. The absorption bands of ~~the ——~~ OH and ~~——~~ NH$_2$ stretching modes at 3393 1/cm and 1647 1/cm ~~are seen to~~ undergo discernible shifts ~~when we comparing~~ compared ~~the~~ chitosan ~~alone~~ on its own with the catalyst-chitosan~~,~~ which indicat~~esing~~ a weak interaction ~~of~~ between ~~the~~ chitosan ~~with~~ and the particle surface. ~~The cC~~Complex formation between an amino group and CMA is most likely to take place in monodentate mode which will expectedly leave~~s~~ more space on the surface of ~~the~~ CMA. ~~Although bB~~Both ~~——~~NH$_2$ and ~~——~~OH groups of chitosan may be involved in ~~the~~ interactions with the CMA particle surface~~.~~, However, the ~~——~~NH$_2$ group~~s'~~ behavior has more to do with ~~should be attributed more to the~~ particle stabilization characteristics ~~that are~~ derived ~~because of~~ from ~~their~~ stronger binding strength with metals. These evidence~~ss~~ ~~indicated~~ show that CMA has modified chitosan. ~~was has been modified by CMA.~~

~~F~~XRD provided further evidence for the formation of CMA ~~was obtained by through the use of XRD (as demonstrated in~~ Fig. ~~ure~~ 3). ~~The~~ CMA ~~-~~ chitosan in its crystalline form exhibits many sharp diffraction peaks between 2Ө = 6–45°, while no such peaks are visible in the XRD of chitosan alone~~,~~ which may ~~occur~~be because ~~the~~of the trapping of chitosan ~~is trapped~~ by ~~the~~ CMA ~~due to the trapping of CMA onto chitosan~~.

3.2. Influence of Cu:Mg:Al molar ratio on phenol degradation

6

The lLiteratures reviews havesearch showed showsn that the predominant products of catalytic phenol degradation are hydroquinone, p-benzoquinone, formic acid, acetic acid, and fumaric acid [3, 10]. Several byproducts were formed (Table 2) during the degradation of phenol. Table 2 showed shows the percentages of the by-products of phenol degradation by achieved by resorting to putting the CMA-chitosan in the FBR reactor along with the determined HRT. It was found that the Cu/Mg/Al molar ratio influencesd the oxidation and theas also refore, the deep and catalytic activity of the catalyst. As shown in Table 2, iIncreasing Al concentrations could significantly enhance (Table 2) the deep oxidation of phenol into smaller molecules such as, formic acid, acetic acid, and fumaric acid owing to the presence of more surface oxygen species [11], while increased copper concentrations enhance , whereas tthe catalystic activity was could be enhanced by an increase in copper concentrations. InAt low Al concentrations, i.e. Cu/Mg/Al molar ratio of 4:2:1, aluminum did doeswould not play any important role and therefore, Cu/Mg/Al had becoeoames a the bimetallic of Cu/Mg. In the Cu/Mg bimetal, as stated in our a previous study [12], the rapid phenol conversion of phenol takes place, probablymay be explained bydue to mechanisms such as; the formation of metal--hydride complexes with the copper and the dissociation of molecular hydrogen or other hydrogen sources on the surface of copper serving as a direct reductant for phenol. Deeply degradation of phenol was of our goal; hencetherefore, we selected the ratio 2:2.6:2 ratio for further experimentation.

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3.3. Influence of pH and synergy of CMA, H₂O₂, and chitosan

Given the effect of Due to affecting the charge distribution on the catalysts' surfaces [13], as well asand the pathways and kinetics of the catalytic reactions, the solution pH wais seen to playing an plays an important role in the overall performance of the CMA-chitosan-H₂O₂. Therefore, a series of experiments were carried outconducted to evaluate the catalytic ability of the prepared CMA-chitosan particles at different pHs in phenol degradation in saline wastewater. Fig. ure 4 presents the time-course of phenol degradation at several solution pHs ranging from 2 to 10. As seen in Fig. ure 4the figure, phenol the degrades ation of phenol was the highest at a pH of 2, with here 98.7% accuracy of phenol was removed

after a 7-min retention time, and the lowest at alkaline pH. To better illustrate the effect of pH, the kinetics of phenol degradation was assessed for CMA-chitosan-H_2O_2. The data is summarized in Table 3, which shows that the oxidation of phenol under selected conditions was of pseudo-first-order. The reaction rate constant decreased progressively from 0.028 to 0.012 l/min (corresponding to maximum degradation of phenol from 100 to 56.5%) when the pH was increased from 2 to 10. The maximum phenol degradation at acidic pH may be due to complex interaction between H_2O_2 and phenol molecules with the catalyst surface. This will be discussed later.

The improvement in phenol degradation rate with decreasing pH may be due to the acceleration of H_2O_2 mass transfer and decomposition rates with pH [14]; this in turn is seen to have led to the formation of highly reactive radicals, mainly $^{\bullet}OH$ [15]. A decrease in pH leads to higher OH and therefore to higher degradation rate. The solution pH had a negative effect on phenol degradation at values 8 and higher; *i.e.* the degradation rate of phenol reduced under strong alkaline conditions (Table 3). This finding may be better interpreted by considering the speciation of phenol (pK_a) and the surface charge of the CMA-chitosan with respect to solution pH and CMA-chitosan pH_{zpc}. Since the pH_{zpc} of CMA-chitosan is 7.8, a negative charge is developed on its surface at these pHs (8 and 10). Phenol, on the other hand, mostly dissociated into phenolate anions (pK_a= 9.9) at these basic conditions [8]. Therefore, the affinity of CMA-chitosan for phenolate under strong alkaline conditions is restricted, and the surface catalyst reactions are most likely to be inhibited, leading to reduction in phenol degradation rate. Moreover, the low phenol removal in alkaline solution can be attributed to the instability of H_2O_2 [3]. In alkaline pH, H_2O_2 immediately decomposes to H_2O and O_2, with a loss of oxidizing ability.

The degradation rate increases with decreasing pH due to the decomposition of H_2O_2, which increases with decreasing pH, resulting in the formation of highly reactive •OH [3,16] with high oxidation potential of 1.8 V.

For a better illustration of the catalytic role of the prepared CMA in CMA-chitosan-H_2O_2, an experiment was carried out in which CMA-chitosan saturated with phenol was used instead of a fresh one (Figure 5). As can be observed here, the percentage of phenol removal was about the same with both prepared and fresh CMA-chitosan-H_2O_2 under the similar experimental conditions. This suggests a catalytic role to CMA-chitosan-H_2O_2 rather than adsorption-oxidation. It as also a synergistic role. Around 25% of the phenol was adsorbed onto the CMA-chitosan during a short retention time of 7 min (Figure 5); thereafter, the adsorption percentage remained almost unchanged up to a contact time of 105-min. This reveals the low capacity and rapid adsorption properties of phenol on CMA-chitosan particles and thus the saturation of the catalyst. The degradation of phenol in CMA-chitosan-H_2O_2 commenced at 93.9% during a contact time of 7-min and increased to 100% after a period of 70-min. It is worth noting that the pH of the solution in the CMA-chitosan-H_2O_2 descended from an initial value of 6.5 to around 3.5 after a reaction time of 7-min. This could be due to the formation of some acidic intermediates such as oxalic, acetic, and formic acids during oxidation [17]. Our studies are in agreement with Moussavi *et al.* [8] who have shown higher degradation of phenol in aqueous solutions employing ozonation and MgO.

To the contribution of prepared CMA-chitosan used in CMA-chitosan-H_2O_2 in degrading phenol in saline wastewater was quantified by calculating its synergistic influence on the reactor in the presence of H_2O_2. It is quanitified as follows:

Synergistic influence = Phenol removed from CMA-chitosan-H_2O_2 − (Quantum of phenol removed by H_2O_2 and adsorbed onto the CMA-chitosan), and the results were plotted in (Figure 5).

> **Comment [Editor26]:** Do you mean to say that 'Moussavi et al. found that phenol degradation was higher in aqueous solutions when ozonized with MgO'?

As is evident here, combining the prepared CMA-chitosan with H_2O_2 had a significant synergistic influence (38% in a 7-min contact time and 64% in an 140-min reaction time) on phenol removal. This finding confirms the strong ability of the prepared CMA to catalyze H_2O_2 in degrading phenol in saline wastewater. The high percentage in removal of phenol by CMA-chitosan-H_2O_2 shows the capability of CMA to decompose H_2O_2 and thereby enhance •OH generation [18]. Some researchers [*e.g.* 8, 19] have reported the synergistic effect in phenol removal.

3.4. Influence of CMA-chitosan and H_2O_2 concentration

Experiments were conducted to determine the ideal catalyst-chitosan dosage for phenol degradation. The Results showed (Fig. 6a) that phenol degraded rapidly at higher CMA-chitosan concentration. Higher the amount of CMA-chitosan, higher the amounts of catalyst formed/required?. An increase in the catalyst dosage made more surfaces available for reaction with H_2O_2 [10] subsequently resulting in increased phenol oxidation. Phenol removal is complete at. wherein, when the CMA-chitosan concentration of 5-7 g. Results showed that at higher dosages of catalyst, greater number of catalyst surface active sites react with larger quantity of H_2O_2; these increases therefore enable enhanced generation of reactive radicals, mainly •OH, resulting in improvement in phenol removal efficiency.

In another attempt, the effect of H_2O_2 concentration on phenol degradation was tested (and the results were shown in Fig. 6b). When the concentration of H_2O_2 increased from 0.02 to 0.06 mol/L, phenol degradation percentages also increased correspondingly from 28% to 98.2%. increasing in H_2O_2 the formation of •OH [20].

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However, at higher H_2O_2 dosages, phenol removal did not get enhanced further. To the contrary, it dropped down. This was because, at high H_2O_2 concentration, both the substrate and H_2O_2 competed for •OH. Long *et al.* [21] state that H_2O_2 in high concentration could act as a scavenger of the highly potent •OH, and recombine with •OH to form H_2O and O_2. Therefore, it would be necessary to select an optimal H_2O_2 concentration for catalytic reactions.

3.5. Influence of salt type

Some inorganic salts including NaCl, KCl, KNO_3, and Na_2SO_4 influence phenol conversion (Table 4). It is clear that salts affect the performance of CMA-chitosan-H_2O_2 in different ways. $NaNO_3$ decreased the conversion rate of phenol markedly, whereas chlorides and sulfate increased the oxidation rate remarkably. This means that the NO_3^- acted as a radical scavenger to suppress the degradation of phenol, its inhibitory effect was attributed to a decrease in the rate of generation of hydroxyl radicals (•OH). As seen from Table 4, chloride ions increase phenol oxidation rate and decrease HRT in contrast to control, i.e. absence of any salt, where the opposite is true. (???) De Laat *et al.* [16] stated that the chloride ions act as radical scavengers resulting in the formation of radicals such as •Cl_2^- that are less reactive than •OH. Therefore, this novel phenomenon requires more than just a cursory glance. Vione *et al.* [22] pointed out that phenol chlorination might occur in the presence of dissolved Fe^{3+}, hydrogen peroxide, and chloride. Furthermore, halogenated quinones also decompose H_2O_2, resulting in the formation of •OH [23]. GC/MS confirm a detectable amount of chlorinated quinones or other intermediate products in our experiments.

Surprisingly, ~~we found~~ that ~~a significant impact of~~ sulfate ions impacted ~~significantly~~ ~~on the~~ phenol oxidation rate significantly ~~.~~ ~~The phenol oxidation rate in the presence of sulfate ions was seen to be~~converting twice of ~~two times more~~ that~~n the oxidation rate obtained in~~ under controlled conditions~~.~~ ~~This probably means~~ implying ~~of~~ a possible role for ~~ies that~~ some radicals containing sulfur ~~could played an important role~~ in ~~promoting the~~ peroxide oxidation of phenol when ~~the~~ sulfate ion ~~wa~~is added. ~~The e~~Efforts ~~was~~ were ~~conducted~~ made to detect ~~the~~ persulfate radical ($^{\bullet}S_2O_8^{2-}$)~~,~~ and we successfully ~~found~~ obtained 4.8 mg/L of ~~persulfate radical~~it. The sulfate ion under unclear mechanisms converted to persulfate radical ($2SO_4^{2-} \rightarrow {}^{\bullet}S_2O_8^{2-}$). The persulfate radical is known as a very strong oxidizer and is used for ~~purposes of for~~ decontamination ~~purpose~~, ~~as~~ given its oxidation potential, at 2.1 V, which is only slightly ~~weaker~~ lesser than that of ozone (O_3^{2-}, 2.2 V) but stronger than both~~:~~ hydrogen peroxide (H_2O_2, 1.8 V) and permanganate (MnO_4, 1.7 V).

3.6. Durability and leaching the catalyst metals

An important characteristic of a catalyst, from a practical point of view, is its deactivation or durability potential. To evaluate the durability of ~~the~~ CMA-chitosan in the oxidation of phenol, ~~the~~ we used 5 g of CMA-chitosan ~~was used~~ in FBR with HRT of 7 min~~. The phenol oxidation efficiency was~~ and determined it after every ~~each~~ 7 min~~, and results are~~ have been ~~plotted in~~ (Fig.~~ure~~ 7). As indicated, ~~the~~ CMA-chitosan preserved its catalytic properties even after 5 h and ~~after that~~ until 7th h~~.~~ ~~it was noticed that the~~its effic~~iac~~yency was still good ~~acceptable~~ (>70%)~~.~~ probably~~This~~ ~~can~~ ~~may be described~~ due~~either~~ ~~by~~ to the predominance of catalytic ~~reactions rather~~ than adsorption~~-~~ ~~-~~oxidation reactions ~~in the CMA-chitosan,~~ or ~~to~~ as the in~~-~~-situ regeneration of chitosan [24]. A closer look at Fig.~~ure~~ 7 shows~~reveals~~ ~~that the procedure of~~ phenol removal accelerated ~~has~~ ~~improved~~ ~~been~~ slightly~~ improved~~ after 1 h, probably due to~~ the~~ modifications~~ of~~to surface chemical properties (functional groups) and ~~the~~ increase ~~of~~in BET and pore volumes of chitosan [24] but decreased~~. However,~~ significantly after ~~the~~ 7 h ~~operation, the phenol removal process~~was ~~significantly decreased. This~~ probably due ~~may~~ ~~was attributed~~ to the ~~be due to~~

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~~to~~ the aromatic rings~~,~~ and ~~leading to its~~ the degrad~~eation~~. ~~Upon degradation of the~~ of the phenol molecules~~.,~~ ~~upon which, t~~The degradation intermediates ~~are then~~we~~are subjected to~~ oxid~~ized~~ ~~ation~~ by the oxidizing radical agents including the hydrogen radical and other radical species~~,~~ ~~causing the~~ a ~~subsequent~~ decreas~~inge~~ ~~in~~the TOC content further. These findings confirm the capability of ~~the~~ CMA-chitosan-H_2O_2 for the treatment of phenol--wastewater.

4. Conclusions

The CMA-chitosan-H_2O_2 process ha~~sd~~ ~~an excellent run~~performance ~~in the process of the~~ degrad~~ed~~ ~~ation~~ ~~of~~ phenol ~~from~~in~~from~~ hyper-saline wastewater efficiently~~,~~ and ~~it w~~has ~~found to have~~ a higher catalytic capability in the presence of chloride and sulfate ions. ~~The o~~Optimal values of operational parameters including CMA-chitosan quantity, H_2O_2 concentration, and solution pH ~~were~~have also been obtained. Further~~more~~, CMA-chitosan-H_2O_2 reduced the high concentration of phenol in industrial wastewater to levels around the designated standards for effluent discharge. It ~~may~~is thus proves ~~be concluded~~ that the CMA-chitosan-H_2O_2 process i~~wa~~is a promising and economically viable process~~technology~~ for the treatment of saline wastewater containing phenol.

Acknowledgements

We appreciate the financial assistance and access to instrument~~s related assistance provided~~ by the Bushehr University of Medical Sciences in conducting this work.

Fig. 1. Schematic of experimental apparatus used for catalytic degradation of phenol.

Fig. 2. FTIR spectra of chitosan (a) and CMA--chitosan (b).

Fig. 3. XRD patterns of chitosan (a) and CMA-chitosan (b).

Fig. 4. The influence of pH on phenol degradation from saline wastewater in the CMA-chitosan-H_2O_2 (phenol concentration: 1000 mg/L, NaCl concentration: 55 g/L).

Fig. 5. Phenol removal by ~~the~~ H_2O_2, CMA-chitosan-H_2O_2, and adsorption onto CMA-chitosan particles (phenol concentration: 1000 mg/L, NaCl concentration: 55 g/L).

Fig. 6. (a) Influence of CMA-chitosan amount and (b) H_2O_2 amount on phenol degradation (phenol concentration: 1000 mg/L, NaCl concentration: 55 g/L).

Fig. 7. The durability of ~~the~~ CMA-chitosan in oxidation of phenol by CMA-chitosan-H_2O_2 and leaching of metal catalysts (phenol concentration: 1000 mg/L, NaCl concentration: 55 g/L).

Table 1. The physical and chemical characteristics of CMA-chitosan.

Table 2. Reaction rate constants of phenol degradation in the CMA-chitosan-H_2O_2 at various pHs (phenol concentration: 1000 mg/L, NaCl concentration: 55 g/L).

Table 3. Influence of Cu/Mg/Al molar ratio on phenol conversion and phenol oxidation intermediates (pH: 6, phenol concentration: 1000 mg/L, NaCl concentration: 55 g/L).

Table 4. Influence of inorganic salts on phenol conversion by CMA-chitosan-H_2O_2 (pH: 6.1, phenol concentration: 1000 mg/L, NaCl concentration: 55 g/L).

Table 5. The quality of petrochemical wastewater before and after treatment with ~~the~~ CMA-chitosan-H_2O_2.