

Removal of Phenol from hyper-saline wastewater using fluidized catalyst (catalytic?) -bed reactor

ABSTRACT

This paper discusses ~~the processes involved in the successful synthesis of~~ Cu/Mg/Al-chitosan ~~was synthesized successfully~~ and ~~its use in a~~ fluidized catalyst (catalytic?) - bed reactor ~~in order~~ to degrade phenol from hyper-saline wastewater. The results showed that ~~the~~ phenol ~~could~~ ~~can~~ be completely oxidized by Cu/Mg/Al-chitosan-H₂O₂ within 7 min at acidic pH. The influence of various variables ~~was investigated,~~ including solution pH, salinity concentration, H₂O₂ concentration, and Cu/Mg/Al-chitosan quantity ~~is investigated, to study their for their any effects~~ on phenol degradation in a synthetic saline wastewater. The maximum degradation of phenol ~~was iwas~~ achieved at pH 2 and 7 g Cu/Mg/Al-chitosan. ~~During this process, it is noted that~~ 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~~ efficiency ~~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

Comment [Editor1]: What is necessary? The process or the minerals and in what context?

oxidation techniques known ~~advances oxidation techniques~~, catalytic oxidation appears to be a promising field of study. It ~~has been reported to be~~ 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] pointed 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~~ received ~~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: $\text{CuM}^2\text{AlCO}_3$ ($\text{M}^2 = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Mg}^{2+}, \text{Zn}^{2+}, \text{and Fe}^{2+}$). ~~According to the literature, which has been recently reviewed by Nawrocki and Kasprzyk Hordern [4],~~ The catalysts' applicability ~~catalysts may be~~ affected [4] by several factors, including: leaching of metals into the liquid phase, high costs of production, and ~~the~~ availability of catalysts in solution (*i.e.* ~~needing to low~~ ~~dense density~~ supporting agents). These challenges technically, environmentally, and economically limit ~~their-most~~ full-scale applications of catalysts. ~~Thus~~ Therefore, the main concern ~~with regard to catalysts facing catalysts~~ ~~is~~ surrounds the development of a more environmental-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.

Comment [Editor2]: OK?

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-preferred~~ by other researchers [3, 4]. For example, Zhou *et al.* [3] used Cu/Ni/AlCO₃ for phenol degradation from aqueous solutions. 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

Comment [Editor3]: Please use the chemicals' names and then insert the acronyms in parentheses.

Comment [Editor4]: OK?

~~solution used as supporting. The e~~Chitosan has three functional groups, *i.e.* two hydroxyl groups (–OH) and one amino group (–NH₂), per glucosamine unit [5] ~~which for maintaining the catalysts, and~~ It is characterized by low densities ~~and~~ ~~s density is low for purpose of availability and covering the complete of solution.~~ In addition, ~~the~~ chitosan ~~that is~~ obtained from fishery-waste ~~is much more economical~~ ~~base is~~ ~~very cheaper~~ than activated carbon, ~~which is often used as a support agent, that usually used as supporting.~~

Comment [Editor5]: Please check for clarity

Comment [Editor6]: Please check for clarity

Although several works have ~~appeared~~ ~~been published so far on~~ ~~on the use of using~~ hydrotalcite-like compounds for the degradation of ~~different~~ pollutants, ~~it is seen that anno~~ investigation ~~of this catalyst into their catalyst's role as in terms of an agent to remove~~ ~~removal of~~ pollutants from ~~real~~ saline ~~real~~ wastewater; ~~is seen~~ ~~very rare.~~ ~~Based on our best literature review efforts, survey did not find,~~ except for a few reports ~~available~~ ~~on using~~ advanced oxidation processes for ~~the~~ removal of phenol from saline wastewaters [6,7], ~~any there was a marked absence of no~~ ~~investigations could be found~~ ~~on CMA~~ treatment of saline wastewaters containing high phenol concentrations. ~~An~~ ~~The~~ investigation ~~on of into the~~ TiO₂-photocatalytic process for the degradation of phenol in saline solution showed a significant inhibitory effect ~~for at~~ 50 g/L of NaCl ~~on the phenol degradation~~ [6]. ~~It was also stated that~~ The time required for ~~the~~ effective degradation of phenol increased ~~with as the~~ ~~increasing with increase in~~ NaCl content ~~increased.~~ ~~investigated by Maciel et al. [7] investigated.~~ The effectiveness of ~~the~~ Fenton and photo-Fenton processes on phenol degradation ~~from~~ ~~caused by~~ a saline effluent ~~was,~~ ~~investigated by Maciel et al. [7].~~ Their results ~~demonstrated~~ ~~show~~ that although both processes were effective ~~in for~~ phenol degradation, the high salt concentration inhibited the oxidation reaction considerably, ~~so that,~~ ~~and~~ only a 50% ~~removal~~ of TOC (*total organic carbon*) was ~~removed~~ ~~achieved~~ in the photo-Fenton process in the presence of 50 g/L NaCl, even after ~~a reaction time of~~ 100 min ~~reaction time~~. Moussavi *et al.* [8] reported an integrated system (catalytic ozonation/biological processes) ~~to for~~ ~~remove~~ phenol ~~removal~~ from a saline solution. Although, they ~~had~~ achieved ~~to~~ high efficiency ~~of removal,~~ ~~bulk of many of their materials and methods are prompted~~ ~~questionables~~ ~~on their~~ ~~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?

Comment [Editor9]: Do you mean to say 'no'? Or 'a'? Please check.

friendliness and safety, but many materials and methods were used, which some of them environmentally and safety point of view is concern.

Therefore, the present study represents the first application effort at using fishery waste-based agents as supporting supports of for the CMA to enable for complete removal of phenol from the hyper-saline wastewater using a fluidized bed reactor. The effects of the following basic variables like solution pH, CMA-chitosan quantity, types of salinity, and H₂O₂ concentration were evaluated in the tests on phenol degradation. For the latter (??), the efficiency of the CMA-catalyst-H₂O₂ was investigated to study in terms of its how effectiveness it was in the to remove of the removal of phenol from industrial hyper-saline wastewater under optimized conditions.

Comment [Editor10]: Ok?

Comment [Editor11]: Which one?

2. Materials and methods

2.1. Materials

The shrimp shell waste of the *Philocheras lowisi* was collected directly from the Persian Gulf, and the deacetylation was performed using a method similar to the method one reported by Novikov [9]. The 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 Na₂CO₃/NaOH. The preparation was performed in a 250-mL flask containing metal nitrates of Cu²⁺ (0.15–0.28 mol), Mg²⁺ (0.07–0.22 mol), and Al³⁺ (0.09–0.25 mol) to make achieve a the desired Cu:Mg:Al molar ratio. Specifically, 10 g of chitosan particles were added to this solution and then 250 mL base solutions with NaOH (0.8 mol) and Na₂CO₃ (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.~~

Comment [Editor12]: Do you mean a thermostat operated water bath?

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~~ 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~~ H₂O₂ (0.02-1.02 mol/L) was added at once, ~~and this which~~ initiating the reaction. Effluent was withdrawn continuously from the top of the reactor, and 5 mL aliquots were withdrawn ~~from their effluent~~ as sample at designated time intervals. ~~It was,~~ mixed with 0.1 g MnO₂ ~~for the purpose of to~~ eliminating residual H₂O₂ [3], and filtered ~~by means of using~~ 0.22- μ m membranes to analyze the reaction mixture. The ~~withdrawn point of the effluent was withdrawn is from a point about round~~ 3 cm above ~~that of~~ the circulation pump to avoid the carry over ~~effect~~ of CMA-~~chitosan.~~

Comment [Editor13]: Is this NHCl?

Comment [Editor14]: Ok?

Comment [Editor15]: Do you mean to say the level at which the effluent was withdrawn was about 3 cm above the level of the circulation pump. This was undertaken to avoid carrying over the CMA-chitosan?

2.4. Analysis

~~The p~~henol 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

Comment [Editor16]: Please be consistent with heading styles.

3.1. CMA-chitosan characterization

As shown in ~~Fig. ure 2,~~ ~~(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 (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 ~~—~~NH₂ 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 indicatesing a~~ weak interaction ~~of between the~~ chitosan ~~with and~~ the particle surface. ~~The e~~Complex formation between an amino group and CMA is most likely to take place in monodentate mode which ~~will expectedly~~ leaves more space on the surface of ~~the~~ CMA. ~~Although b~~Both ~~—~~NH₂ and ~~—~~OH groups of chitosan may be involved in ~~the~~ interactions with ~~the~~ CMA particle surface. ~~However, the~~ ~~—~~NH₂ groups² 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 evidences ~~is indicated show~~ that ~~CMA has modified~~ chitosan.

Comment [Editor17]: Please check for clarity

Comment [Editor18]: Complexity?

~~was has been modified by CMA.~~

Comment [Editor19]: Ok?

~~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 $2\theta = 6-45^\circ$, while no such peaks are visible ~~in the XRD of chitosan alone,~~ which ~~may occur~~ because ~~the of the trapping of chitosan is trapped by the~~ CMA ~~due to the trapping of CMA onto chitosan.~~

Comment [Editor20]: Ok?

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

The literature reviews have shown 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 the percentages of the byproducts 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 influenced the oxidation and the deep and catalytic activity of the catalyst. As shown in Table 2, increasing 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 the catalytic activity was could be enhanced by an increase in copper concentrations. In At low Al concentrations, i.e. Cu/Mg/Al molar ratio of 4:2:1, aluminum did does would not play any important role and therefore, Cu/Mg/Al had become a 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, probably may be explained by due 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; hence therefore, we selected the ratio 2:2.6:2 ratio for further experimentation.

Comment [Editor21]: Ok?

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Comment [Editor23]: What are the elements for this ratio?

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 as and the pathways and kinetics of the catalytic reactions, the solution pH was seen to playing an plays an important role in the overall performance of the CMA-chitosan-H₂O₂. Therefore, a series of experiments were carried out conducted 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 4 the 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. In order to better illustrate the effect of pH, the kinetics of phenol degradation was assessed for CMA-chitosan-H₂O₂. The resulting information data is has been summarized in Table 3, which indicates shows that the oxidation of phenol under the selected conditions was of pseudo-first order. As seen in Table 3, the reaction rate constant was 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. Attainment of The maximum phenol degradation at acidic pH can be attributed due to the complex interaction of between H₂O₂ and phenol molecules with the catalyst surface, which This will be discussed further later in the next section. The improvement of in the phenol degradation rate with decreasing pH might may be due attributed due to the acceleration of H₂O₂ mass transfer and H₂O₂ decomposition rates with pH [14]; this in turn is seen to have leads to the formation of highly reactive radicals, mainly [•]OH [15]. The A decreasing decrease in the pH, the higher would be is the leads to higher OH produced [•]OH and thus therefore, to be higher is the degradation rate. The solution pH had a negative effect on phenol degradation at values 8 and higher; i.e. the degradation rate of phenol was reduced under strong alkaline conditions (Table 3). This finding can may can be better interpreted by considering the taking into consideration both 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, is mostly dissociated into phenolate anions (pK_a= 9.9) at these basicity conditions [8]. Therefore, the affinity of CMA-chitosan for phenolate under strong alkaline conditions is restricted, and the surface catalyst reactions would are most likely to be probably be inhibited, leading to the reduction in phenol degradation rate. Moreover, the low phenol removal in alkaline solution is can be due attributed to the instability of H₂O₂ [3]. In alkaline pH, H₂O₂ immediately decomposes to produce H₂O and O₂, accordingly with a loss of in oxidizing ability loss. The degradation rate increased increases with decreasing pH, due to and this may be justified This can be justified by the fact that the decomposition of H₂O₂, which increases with decreasing pH, resulting in the formation of highly reactive [•]OH [3,16] with high oxidation potential of 1.8 V.

Comment [Editor24]: Was this found to be the lowest in an alkaline pH?

Comment [.25]: Some data might be helpful.

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For a better illustration of the catalytic role of the prepared CMA in CMA-chitosan-H₂O₂, an experiment was carried out in which a CMA-chitosan saturated with phenol was used instead of a fresh one (Figure 5). The results are shown in Figure 5. As can be observed in Figure 5, the percentage of phenol removed was about the same with both prepared and fresh did not deviate significantly from those obtained with the fresh CMA-chitosan-H₂O₂ under at the same similar experimental conditions. This suggests the catalytic role is the prevalent reaction in the CMA-chitosan-H₂O₂ rather than that of adsorption-oxidation one. It also indicates a synergistic role effect of CMA with H₂O₂ in degrading the phenol. According to Figure 5, 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 contact time. 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-H₂O₂ commenced at was started by 93.9% for during a contact time of a 7 min contact time and increased to 100% after a period of 70 min contact time. It is worth noting that the pH of the solution in the CMA-chitosan-H₂O₂ descended from an initial value of 6.5 to around 3.5 after a reaction time of 7 min reaction time. This is could be due to the formation of some acidic intermediates such as oxalic, acetic, and formic acids during the oxidation reaction [17]. Our studies are in agreement with This is was in accordance with Moussavi *et al.* [8] who, who have shown found a higher degradation of phenol in aqueous solutions employing using ozonation and with MgO.

To quantify the contribution of the prepared CMA-chitosan used in the CMA-chitosan-H₂O₂ in degrading phenol in saline wastewater was quantified by calculating its synergistic influence achieved from adding the CMA-chitosan to the reactor in the presence of H₂O₂ was calculated. It is quantified as follows:

$$\text{Synergistic influence} = \frac{\text{Phenol removed from CMA-chitosan-H}_2\text{O}_2 - (\text{sum of phenol removed by H}_2\text{O}_2 \text{ and adsorbed onto the CMA-chitosan})}{\text{sum of phenol removed by H}_2\text{O}_2 \text{ and adsorbed onto the CMA-chitosan}}$$

and the results are 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 in this figure here, combining the prepared CMA-chitosan with H_2O_2 had a significant synergistic influence (38% for in a 7--min contact time and 64% for in an 140--min reaction time) was attained from combining the prepared CMA-chitosan with H_2O_2 in phenol removal. This finding confirms/verifies the strong ability of the prepared CMA to catalyze the H_2O_2 reaction for in the degrading of phenol in saline wastewater. The high percentage in removal percentage of phenol by in the CMA-chitosan- H_2O_2 can may be accounted for/shows by the capability of CMA to decompose H_2O_2 and thereby enhance $\bullet OH$ generation [18]. Some researchers [e.g. 8, 19] have reported the synergistic effect in/for phenol removal.

3.4. Influence of CMA-chitosan and H_2O_2 concentration

The phenol removal experiments were conducted/performed at CMA-chitosan concentration (1-7 g) to determine the ideal/contributions of the catalyst-chitosan dosage for in phenol degradation. Results The Results showed (Fig. 6a) that the phenol degradation increased rapidly at higher with increasing CMA-chitosan concentrations. The higher the amounts of CMA-chitosan, the provide higher was the amounts of the catalyst formed/required?. Increase-An increase in the catalyst-catalyst dosage made/led to more surfaces becoming available for the reaction with H_2O_2 [10]; subsequently resulting in an increased phenol oxidation. Phenol removal is complete at -W, wherein, when the concentration of CMA-chitosan concentration of reached to between 5 and 7 g, the phenol could be removed completely. These Results demonstrates/showed that at in higher dosages of catalyst-related to the, greater availability number of catalyst surface active sites to react with the more/larger quantity of H_2O_2 ; these increases therefore enable enhanced generation of reactive radicals, mainly $\bullet OH$, resulting in improvement of the phenol removal efficiency.

Comment [Editor27]: Ok?

In another attempt, the effects of H_2O_2 concentration on phenol degradation were/was tested (and the results are were shown in Fig-ure 6b). When the concentration of H_2O_2 concentration increased from 0.02 to 0.06 mol/L, the phenol degradation percentages also increased correspondingly from 28% to 98.2%. The increase in H_2O_2 concentration in the solution leads to an increase in the formation of $\bullet OH$ [20].

Comment [Editor28]: Please check for clarity. Break the sentences into smaller parts for better comprehension

However, ~~when given at~~ higher H₂O₂ dosages, ~~the phenol removal was not further enhanced~~ ~~did not get~~ ~~enhanced further.~~ ~~On the contrary, it dropped down~~ ~~but dropped down~~. This ~~is~~ ~~was~~ because, at high H₂O₂ concentration, ~~both the substrate and H₂O₂ there is was a competition of for~~ ~~•OH consumption~~ ~~between the substrate and the H₂O₂.~~ ~~As reported by Mingee~~ Long *et al.* [21] ~~state that,~~ H₂O₂ ~~at~~ high concentration ~~could~~ ~~acts~~ as a scavenger of the highly potent •OH, and ~~recombine with~~ •OH ~~would~~ ~~recombine~~ to form H₂O and O₂. Therefore, it ~~would be~~ ~~is~~ necessary to select an optimal H₂O₂ concentration for catalytic reactions.

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3.5. Influence of salt type

~~The influence of~~ Some inorganic salts including NaCl, KCl, KNO₃, and Na₂SO₄ ~~influence~~ phenol conversion ~~is summarized in~~ (Table 4). ~~It is clear that the presence of salts and~~ affects the performance of CMA-chitosan-H₂O₂ ~~in~~ different ~~ways~~ ~~with respect to phenol oxidation.~~ ~~The presence of~~ NaNO₃ ~~markedly~~ decreased the conversion rate of phenol ~~markedly~~, whereas ~~the presence of~~ chlorides and sulfate ~~remarkably~~ increased the oxidation rate ~~remarkably~~. This ~~means that is meaning that~~ the NO₃⁻ ~~acted~~ as a radical scavengers to suppress the degradation of phenol, ~~in which their~~ ~~its~~ inhibitory effects ~~being~~ ~~as~~ attributed to a decrease in the rate of generation of hydroxyl radicals (•OH). As ~~it can be~~ seen from Table 4, ~~chloride ions increase the~~ phenol oxidation rate and ~~decrease~~ HRT ~~in the presence of chloride ions~~ ~~was~~ ~~increase and decrease, respectively, in comparison~~ ~~contrast~~ to ~~control, i.e. no~~ ~~absence of any salt, where~~ ~~the opposite is true~~ ~~(control condition)~~ ~~(???)~~ De Laet *et al.* [16] ~~previously~~ stated that the chloride ions ~~was~~ ~~were~~ ~~act~~ as radical scavengers ~~resulting in~~ ~~and~~ ~~caused~~ the formation of radicals such as •Cl₂⁻ that ~~were~~ less reactive than ~~the~~ •OH. Therefore, ~~this novel phenomenon requires~~ ~~more than just a cursory~~ ~~glance~~ ~~attention~~ ~~it deserves to pay much attention to the novel phenomenon.~~ Vione *et al.* [22] pointed out that phenol chlorination might occur in the presence of dissolved Fe³⁺, hydrogen peroxide, and chloride. Furthermore, ~~halogenated quinones also the~~ decomposition of H₂O₂ ~~could be promoted by halogenated~~ ~~quinones,~~ resulting in the formation of •OH [23]. ~~GC/MS confirm a~~ detectable amount of chlorinated quinones or other intermediate products ~~were confirmed~~ in our experiments ~~by~~ GC/MS.

Comment [Editor30]: Do you mean to say 'as compared to phenol oxidation'?

Comment [Editor31]: Do you mean to say 'increased and decreased, respectively when compared to the absence of any salts'?

Comment [Editor32]: What are these?

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 than ~~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 ~~was~~ added. ~~The e~~Efforts ~~was were conducted made~~ to detect ~~the~~ persulfate radical ($\text{S}_2\text{O}_8^{2-}$), and we successfully ~~found~~ ~~obtained~~ 4.8 mg/L of ~~persulfate radical~~. The sulfate ion under unclear mechanisms converted to persulfate radical ($2\text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_8^{2-}$). 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~~ efficiency 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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leaching of ~~the~~ catalytic active species or ~~the~~ poisoning of the active sites or ~~even the~~ fouling of the catalyst surface by intermediate reaction products.

~~Based on~~ The results of this study, ~~show that~~ di-valent magnesium and copper ~~can~~ could be released into ~~the~~ solution during the degradation of phenol by ~~the~~ CMA-chitosan-H₂O₂ system. Therefore, ~~we made an effort~~ was only made to identify the amounts of Cu²⁺ and Mg²⁺ ions during the experiments, ~~as because~~ the Al³⁺ ion ~~was proved~~ was undetectable in ~~the~~ effluents. ~~The results (are have been shown in~~ Fig-~~ure~~ 7). The relatively high levels of magnesium ion accumulation (more than the MCL of Mg²⁺ ion in drinking water) ~~was occurred, and this it results resulted in the formation of~~ in hard water. As ~~shown~~ depicted in Fig-~~ure~~ 7, the copper ion leached during the experiment was continually lower than the maximum contamination level of Cu²⁺ ion in drinking water. Lowering the leaching amount of metal ions ~~led to a~~ decreased ~~ing~~ the phenol removal ~~procedure by~~ capability of CMA-chitosan-H₂O₂.

3.7. Industrial wastewater treatment

The ~~next experiment was to study the~~ efficacy of CMA-chitosan-H₂O₂ in the removal of phenol from industrial wastewater ~~was subsequently evaluated. For this which, a~~ we obtained bulk wastewater sample ~~was obtained~~ from a petrochemical plant. The characteristics of the wastewater are presented in Table 5. The experiment was conducted at pH level as per ~~the~~ original wastewater with CMA-chitosan concentrations of 5 g, and HRT of 10 min. The main parameters of the wastewater sample before and after treatment with CMA-chitosan-H₂O₂ ~~are~~ have been presented in Table 5. ~~As seen in~~ The table ~~5 shows that~~ a very low quantity of CMA-chitosan at very short HRT (10 min) ~~could~~ completely removed phenol and improved some of ~~the~~ other characteristics of the treated wastewater. A point ~~to be noted that~~ can be derived from Table 5 is that ~~of the~~ TOC reduction during treatment. ~~The~~ CMA-chitosan-H₂O₂ ~~not only efficiently~~ degraded ~~the~~ phenol ~~efficiently, but~~ and also attained a high degree of TOC reduction ~~leading to and thus,~~ mineralization of the degradation intermediates. The oxidizing radical species attacked

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to the aromatic rings, and leading to its the degradation. Upon degradation of the of the phenol molecules, upon which, The degradation intermediates are then we are subjected to oxidized ation by the oxidizing radical agents including the hydrogen radical and other radical species, causing the a subsequent decrease in the TOC content further. These findings confirm the capability of the CMA-chitosan-H₂O₂ for the treatment of phenol-wastewater.

4. Conclusions

The CMA-chitosan-H₂O₂ process hasd an excellent runperformance in the process of the degraded ation of phenol frominfrom hyper-saline wastewater efficiently, and it whas found to have a higher catalytic capability in the presence of chloride and sulfate ions. The eOptimal values of operational parameters including CMA-chitosan quantity, H₂O₂ concentration, and solution pH werehave also been obtained. Furthermore, CMA-chitosan-H₂O₂ reduced the high concentration of phenol in industrial wastewater to levels around the designated standards for effluent discharge. It mayis thus proves be eoncluded that the CMA-chitosan-H₂O₂ process iwais a promising and economically viable processtechnology for the treatment of saline wastewater containing phenol.

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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-H₂O₂ (phenol concentration: 1000 mg/L, NaCl concentration: 55 g/L).

Fig. 5. Phenol removal by ~~the~~ H₂O₂, CMA-chitosan-H₂O₂, 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) H₂O₂ 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-H₂O₂ 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-H₂O₂ 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-H₂O₂ (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-H₂O₂.