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

**ABSTRACT**

This paper discusses the successful synthesis of Cu/Mg/Al-chitosan and its use in a fluidized catalyst (catalytic?) bed reactor to degrade phenol from hyper-saline wastewater. The results show that phenol can be completely oxidized by Cu/Mg/Al-chitosan-H2O2 within 7 min at acidic pH. The influence of various variables including solution pH, salinity concentration, H2O2 concentration, and Cu/Mg/Al-chitosan quantity is investigated to study their effect on phenol degradation in synthetic saline wastewater. The maximum degradation of phenol was achieved at pH 2 and 7 g Cu/Mg/Al-chitosan. During this process, chloride and sulfate ions have a synergistic effect on phenol removal, where the oxidation rate of phenol in the presence of sulfate ions is twice of that obtained under controlled conditions. Industrial wastewater containing phenol can 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 method demonstrates efficacy and holds promise as a simple and elegant method to eliminate phenol from wastewater.

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

**1. Introduction**

Chemical processes favor oxidation as an alternative method by which organic compounds may be oxidized and converted into simple minerals. The processes are useful [1] and have recently received significant attention. Amongst the various oxidation techniques known, catalytic oxidation appears to be a promising field of study. It is effective for the near-ambient degradation of pollutants as it holds promise of nearly complete degradation [2]. Zhou *et al.* [3] point out to the interest in the development of copper-based heterogeneous catalysts, especially hydrotalcite-like compounds. These compounds, referred to as layered double hydroxides, are classes of layered materials and have received increasing attention owing to diverse applications, especially in catalysis. These may be denoted by a general formula: CuM2AlCO3 (M2= Co2+, Ni2+, Cu2+, Mg2+, Zn2+, and Fe2+). The catalysts may be affected [4] by several factors including: leaching of metals into the liquid phase, high cost of production, and the availability of catalysts in solution (*i.e.* low-density supporting agents). These challenges technically, environmentally, and economically limit most full-scale applications of catalysts. Therefore, the main concern with regard to catalysts surrounds the development of a more environment-friendly catalyst entailing a simple and low-cost production method. In this regard, research is on to find novel materials with high catalytic activities that may be 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 compared to Ni, Pd, and Ag that were previously 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 apply Mg instead of Ni as magnesium is non-toxic, and does not pollute water when used as a leaching agent in the liquid to be treated. Moreover, the chitosan compound will be used as a supporting agent or as a catalyst in solution. Chitosan has three functional groups, *i.e.* two hydroxyl groups (–OH) and one amino group (–NH2), 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.

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. An investigation into the TiO2-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. investigatedthe 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-friendliness and safety.

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

**2. Materials and methods**

*2.1. Materials*

Shrimp shell waste of *Philocheras lowisi* was collected directly from the Persian Gulf and deacetylated using a method similar to Novikov [9]. Chitosan (is it shell waste?) was sieved in the size range 0.1–0.2 mm. Other chemicals and reagents used 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*

CMA–chitosan was synthesized by employing metal nitrates and Na2CO3/NaOH. The preparation was readied 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 achieve 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-wise into the flask and stirred vigorously with a magnetic stirrer and maintained for 4 h at 45°C using a thermostated water bath. It was then, cooled at room temperature and filtered. The solid was washed using double-distilled water until it became nitrate-free. This was then dried at 50°C for 7 h. Table 1 details the physical and chemical characteristics of CMA–chitosan.

*2.3. Experimental procedure*

The experiments were carried out in a fluidized bed reactor (FBR). As shown in Figure 1, a glass column 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 an upward flow of at least 50 m/h to fluidize 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 maintained at desired temperature (4–45°C). H2O2 (0.02–1.02 mol/L) was added at once initiating the reaction. Effluent was withdrawn continuously from the top of the reactor, and 5 mL aliquots were withdrawn as sample at designated time intervals. It was mixed with 0.1 g MnO2 to eliminate residual H2O2 [3], and filtered using 0.22-μm membranes to analyze the reaction mixture. The effluent was withdrawn from a point about 3 cm above the circulation pump to avoid the carry over effect of CMA–chitosan.

*2.4. Analysis*

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. TOC was measured by a Shimadzu TOC-5000 Analyzer (Shimadzu Co., Japan). The nature of CMA–chitosan was verified through Fourier transform infra-red analysis (FTIR) (Prestige, 21210045, Japan). Chitosan and CMA–chitosan samples were used before phenol removal. X-ray diffraction (XRD) patterns were determined on a Rigaku D/MAX 2200 (Tokyo, Japan) instrument.

**3. Results and discussion**

*3.1. CMA*–*chitosan characterization*

The FTIR spectroscopy (Figure 2) confirms the presence of CMA in our sample along with interaction between chitosan and catalyst crystal surfaces. The FTIR spectra show free chitosan and catalyst–chitosan particles. The resemblance of spectral features confirms the successful attachment of CMA to the surface of the chitosan particles. The absorption bands of –OH and –NH2 stretching modes at 3393 1/cm and 1647 1/cm undergo discernible shifts when compared chitosan on its own with the catalyst-chitosan which indicates a weak interaction between chitosan and the particle surface. Complex formation between an amino group and CMA is most likely to take place in monodentate mode which will expectedly leave more space on the surface of CMA. Both –NH2 and –OH groups of chitosan may be involved in interactions with the CMA particle surface. However, the –NH2 group behavior has more to do with particle stabilization characteristics derived from stronger binding strength with metals. These evidences show that CMA has modified chitosan.

XRD provided further evidence for the formation of CMA (Figure 3). 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 be because of the trapping of chitosan by CMA.

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

Literature search shows 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. Cu/Mg/Al molar ratio influences oxidation as also the deep and catalytic activity of the catalyst. Increasing Al concentrations 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 the catalytic activity. At low Al concentrations, *i.e.* Cu/Mg/Al molar ratio of 4:2:1, aluminum does not play any important role and therefore, Cu/Mg/Al becomes the bimetallic of Cu/Mg. In Cu/Mg bimetal, as stated in a previous study [12], rapid conversion of phenol takes place, probably due to mechanisms such as the formation of metal–hydride complexes with copper and dissociation of molecular hydrogen or other hydrogen sources on the surface of copper serving as a direct reductant for phenol. Deep degradation of phenol was our goal; hence, we selected the ratio 2:2.6:2 for further experimentation.

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

Given the effect of charge distribution on the catalysts’ surfaces [13], and the pathways and kinetics of the catalytic reactions, the solution pH is seen playing an important role in the overall performance of CMA-chitosan-H2O2. Therefore, a series of experiments were conducted to evaluate the catalytic ability of the prepared CMA-chitosan particles at different pHs in phenol degradation in saline wastewater. Figure 4 presents the time-course of phenol degradation at several solution pHs ranging from 2 to 10. As seen in the figure, phenol degrades the highest at a pH of 2 with 98.7% accuracy 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-H2O2. The data in Table 3 shows that the oxidation of phenol under select 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 H2O2 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 H2O2 mass transfer and decomposition rates with pH [14]; this in turn is seen to have led to the formation of highly reactive radicals, mainly •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 can be better interpreted by considering the speciation of phenol (pKa) and the surface charge of the CMA-chitosan with respect to solution pH and CMA-chitosan pHzpc. Since the pHzpc 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 (pKa= 9.9) at this basicity [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 H2O2 [3]. In alkaline pH, H2O2 immediately decomposes to H2O and O2 with a loss of oxidizing ability.

The degradation rate increases with decreasing pH due to 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.

For a better illustration of the catalytic role of the prepared CMA in CMA-chitosan-H2O2, 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, the percentage of phenol removed was about the same with both prepared and fresh CMA-chitosan-H2O2 under similar experimental conditions suggesting a catalytic role to CMA-chitosan-H2O2 rather than adsorption-oxidation 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-H2O2 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-H2O2 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.

The contribution of prepared CMA-chitosan used in CMA-chitosan-H2O2 in degrading phenol in saline wastewater was quantified by calculating its synergistic influence on the reactor in the presence of H2O2. It is quanitified as follows:

*Synergistic influence = Phenol removed from CMA-chitosan-H2O2−(Quantum of phenol removed by H2O2 and adsorbed onto the CMA-chitosan)*] (Figure 5).

As is evident here combining the prepared CMA-chitosan with H2O2 had a significant synergistic influence (38% in a 7-min contact time and 64% in a 140-min reaction time) on phenol removal. This finding confirms the strong ability of the prepared CMA to catalyze H2O2 in degrading phenol in saline wastewater. The high percentage in removal of phenol by CMA-chitosan-H2O2 shows the capability of CMA to decompose H2O2 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 H2O2 concentration*

Experiments were conducted to determine the ideal catalyst-chitosan dosage for phenol degradation. Results show (Fig. 6a) that phenol degraded rapidly at higher CMA-chitosan concentrations. Higher the amount of CMA-chitosan, the higher is the amount of catalyst formed/required?. An increase in the catalyst dosage made more surfaces available for reaction with H2O2 [10] subsequently resulting in increased phenol oxidation. Phenol removal is complete at a CMA–chitosan concentration of 5–7 g. Results show that at higher dosages of catalyst, greater number of catalyst surface active sites react with larger quantity of H2O2; these increases therefore enable enhanced generation of reactive radicals, mainly •OH, resulting in improvement in phenol removal efficiency.

In another attempt, the effect of H2O2 concentration on phenol degradation was tested (Figure 6b). When the concentration of H2O2 increased from 0.02 to 0.06 mol/L, phenol degradation percentages also increased correspondingly from 28% to 98.2% increasing the formation of •OH [20]. However, at higher H2O2 dosages, phenol removal did not enhance further. To the contrary, it dropped down. This is because, at high H2O2 concentration, both the substrate and H2O2 competed for •OH. Long *et al.* [21] state that H2O2 at high concentration could act as a scavenger of the highly potent •OH, and recombine with •OH to form H2O and O2. Therefore, it would be necessary to select an optimal H2O2 concentration for catalytic reactions.

*3.5. Influence of salt type*

Some inorganic salts including NaCl, KCl, KNO3, and Na2SO4 influence phenol conversion (Table 4) and affect the performance of CMA-chitosan-H2O2 in different ways NaNO3 decreased the conversion rate of phenol markedly, whereas chlorides and sulfate increased the oxidation rate remarkably. This means that NO3- acts as a radical scavenger to suppress the degradation of phenol, its inhibitory effect being 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. no salt, where the opposite is true.(???) De Laat *et al*. [16] state that the chloride ions act as radical scavengers resulting in the formation of radicals such as •Cl2− that are less reactive than •OH. Therefore, this novel phenomenon requires more than just a cursory glance. Vione *et al.* [22] point out that phenol chlorination might occur in the presence of dissolved Fe3+, hydrogen peroxide, and chloride. Further, halogenated quinones also decompose H2O2 resulting in the formation of •OH [23]. GC/MS confirm a detectable amount of chlorinated quinones or other intermediate products in our experiments.

Surprisingly, sulfate ions impact phenol oxidation rate significantly converting twice of that under controlled conditions implying of a possible role for some radicals containing sulfur in peroxide oxidation of phenol when sulfate ion is added. Efforts were made to detect the persulfate radical (•S2O82-) and we successfully obtained 4.8 mg/L of it. The sulfate ion under unclear mechanisms converted to persulfate radical (2SO42-→•S2O82-). The persulfate radical is known as a very strong oxidizer and is used for decontamination, given its oxidation potential, at 2.1 V, which is only slightly lesser than that of [ozone](http://en.citizendium.org/wiki/Ozone) (O32-, 2.2 V) but stronger than both [hydrogen peroxide](http://en.citizendium.org/wiki?title=Hydrogen_peroxide&action=edit&redlink=1) (H2O2, 1.8 V) and [permanganate](http://en.citizendium.org/wiki?title=Permanganate&action=edit&redlink=1) (MnO4, 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 CMA-chitosan in the oxidation of phenol, we used 5 g of CMA-chitosan in FBR with HRT of 7 min and determined it after every 7 min (Figure 7). As indicated, CMA-chitosan preserved its catalytic properties even after 5 h and until 7th h its efficacy was still good (>70%) probably due to the predominance of catalytic than adsorption–oxidation reactions or in-situ regeneration of chitosan [24]. A closer look at Figure 7 shows phenol removal accelerated slightly after 1 h, probably due to modifications to surface chemical properties (functional groups) and increase in BET and pore volumes of chitosan [24] but decreased significantly after 7 h probably due to the leaching of catalytic active species or the poisoning of the active sites or even the fouling of the catalyst surface by intermediate reaction products.

The results of this study show that di-valent magnesium and copper could be released into the solution during the degradation of phenol by the CMA-chitosan-H2O2 system. Therefore, we made an effort to identify the amounts of Cu2+ and Mg2+ ions during the experiments as the Al3+ ion was undetectable in the effluent (Figure 7). The relatively high levels of magnesium ion accumulation (more than the MCL of Mg2+ ion in drinking water) resulted in the formation of hard water. As shown in Figure 7, the copper ion leached during the experiment was continually lower than the maximum [contamination level](http://www.tcoek12.org/~stjusd/5305107.pdf) of Cu2+ ion in drinking water. Lowering the leaching amount of metal ions decreased the phenol removal 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 for which we obtained bulk wastewater sample 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 presented in Table 5. The table shows that a very low quantity of CMA-chitosan at very short HRT (10 min) completely removed phenol and improved some of the other characteristics of the treated wastewater. A point to be noted from Table 5 is that of the TOC reduction during treatment. CMA-chitosan-H2O2 degraded phenol efficiently and also attained a high degree of TOC reduction leading to mineralization of the degradation intermediates. The oxidizing radical species attack the aromatic rings and degrade phenol molecules. The degradation intermediates are oxidized by the oxidizing radical agents including the hydrogen radical and other radical species decreasing the TOC content further. These findings confirm the capability of CMA-chitosan-H2O2 for the treatment of phenol-wastewater.

**4. Conclusions**

The CMA-chitosan-H2O2 process has degraded phenol from hyper-saline wastewater efficiently and has a higher catalytic capability in the presence of chloride and sulfate ions. Optimal values of operational parameters including CMA-chitosan quantity, H2O2 concentration, and solution pH have also been obtained. Further, CMA-chitosan-H2O2 reduced the high concentration of phenol in industrial wastewater to levels around the designated standards for effluent discharge. It thus proves that the CMA-chitosan-H2O2 process is a promising and economically viable process 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 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 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 CMA-chitosan-H2O2.