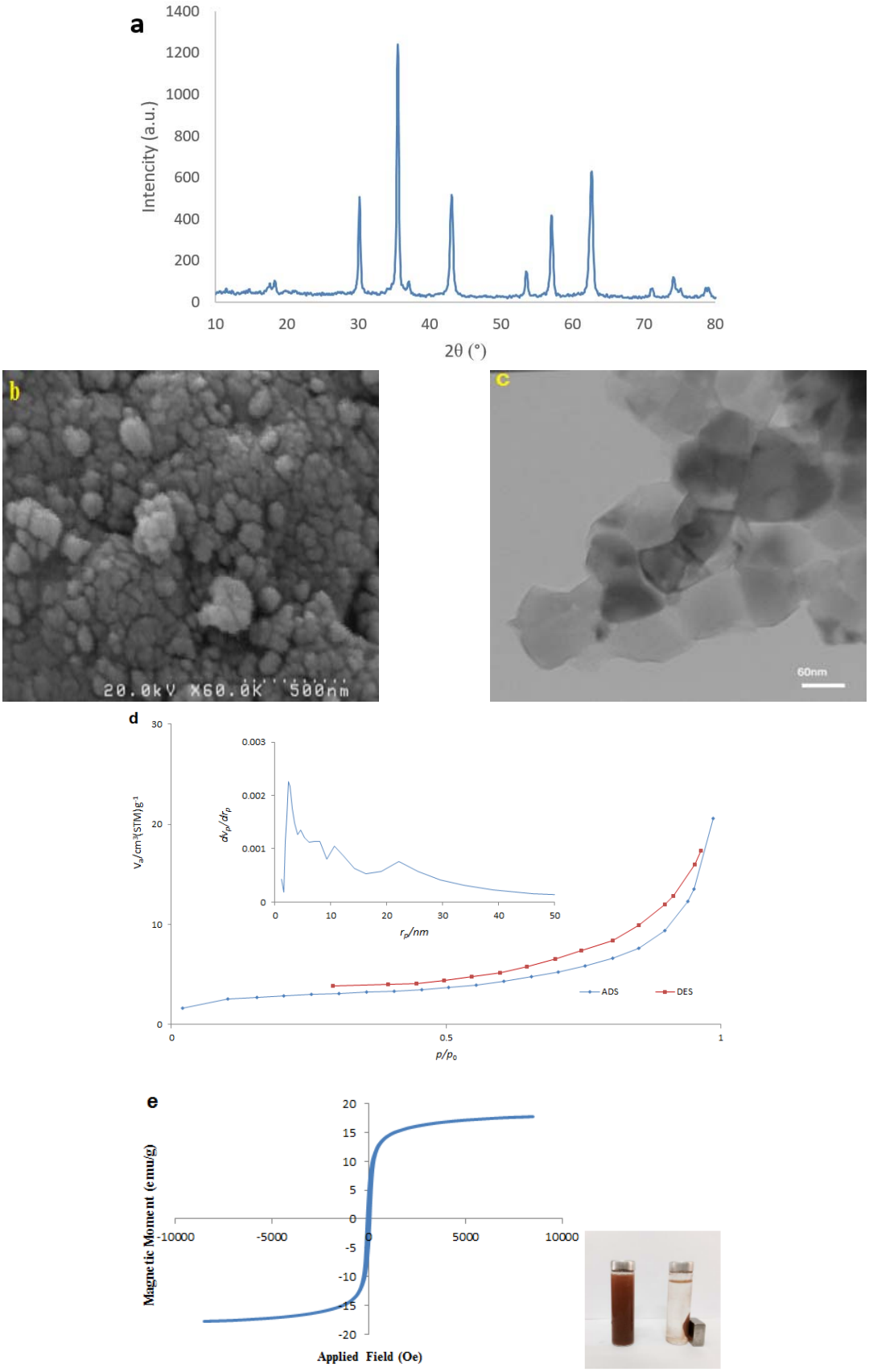

Fig. 2. Characterization of $MgFe_2O_4$: (a) XRD pattern; (b) FESEM image; (c) TEM image; (d) N_2 adsorption/desorption isotherm and pore size distribution; and (e) magnetic hysteresis loops at room temperature.

The hysteresis loop explains the soft magnetic nature of the synthesized $MgFe_2O_4$ and also the large saturation magnetization (Ms) of 17.7 $emug^{-1}$. $MgFe_2O_4$ particles can simply be recovered from the reaction solution by using an external magnetic field. Highly efficient recyclability is economically suitable for practical applications.

3.2. Comparison of ozonation alone and catalytic ozonation with $MgFe_2O_4$

Catalytic activity of $MgFe_2O_4$ for the degradation of 4-CP in aqueous solution was studied at three different processes namely ozonation alone (O_3); catalytic ozonation using $MgFe_2O_4$ nanoparticles ($O_3/MgFe_2O_4$) and adsorption on $MgFe_2O_4$ nanoparticles. To evaluate the 4-CP adsorption on the surface of the catalyst, an adsorption experiment was conducted under similar conditions with the experimental conditions used in the catalytic activity experiment, but in the absence of ozone. As observed in Fig. 3, the adsorption process on $MgFe_2O_4$ nanoparticles showed an efficiency of 25% after 30 min. The good adsorption capability of $MgFe_2O_4$ is probably due to the electrostatic attraction between 4-CP and $MgFe_2O_4$ at pH 5.5. On the other hand, as shown in Fig. 4(b), the pH_{PZC} of $MgFe_2O_4$ was 9.8, which is much higher than the solution pH of 5.5. Therefore, the surface of $MgFe_2O_4$ particles would be significantly positively charged and thus attract the 4-CP anions.

As shown in Fig. 3, ozonation process enhanced the removal of 4-CP compared with adsorption of 4-CP However, the best result was obtained for the $O_3/MgFe_2O_4$ process. At the end of the reaction (30 min), the efficiency of the combinational process of $O_3/MgFe_2O_4$ is 92.6%. When $MgFe_2O_4$ was added, the degradation of 4-CP may increase due to a combination of adsorption and/or reaction with radical species (e.g.,$^{\bullet}OH$) produced as a result of ozone decomposition in the presence of $MgFe_2O_4$. The ozone decomposition mechanisms onto metal oxide surfaces are shown in Scheme (1) and (2).[23] The lower electronegativity or the higher metallicity of Mg leads to the higher electron density of O^{2-} and Mg bond, and consequently results in the catalytic decomposition of ozone into radicals due to the electrophilic property of ozone molecules [24]:

$$\equiv OM + O_3 \rightarrow \equiv OM - O - O - O^{\bullet} \quad (1)$$

$$\equiv OM - O - O - O^{\bullet} \rightarrow O_2 + \equiv OM - O^{\bullet} \quad (2)$$

In fact, $MgFe_2O_4$ catalyst might accelerate the decomposition of O_3 molecules to hydroxyl radicals ($^{\bullet}OH$), which could enhance the oxidizing activity of the process [15,19].

3.3. Effect of pH and catalyst dosage

Since the initial pH of the solution is one of the major influential factors in production of hydroxyl radical from O_3 decomposition, ozonation experiments were performed under different initial pHs (4, 5.5, 7, 8.5 and 10). In Fig. 4 (a), the effect of initial pH on the 4-CP degradation efficiency is shown in two processes including O_3 and $O_3/MgFe_2O_4$. Surprisingly neither process was not affected by changing initial pH. Based on previous studies, the catalytic ozonation process is usually dependent on pH. For example, Qi et al investigated catalytic ozonation of 4-CP using a MnO_x/γ-Al_2O_3/TiO_2 catalyst. The process was also highly dependent on pH, which increased from 2.57 to 11.13; 4-CP degradation efficiency increased from 59.59 to 99.77% [18].

Moreover, solution pH which is one of the important parameters, determines catalyst surface charge, dissolving of semiconductors in the suspension and ionic forms of pollutant present in the suspension[26].

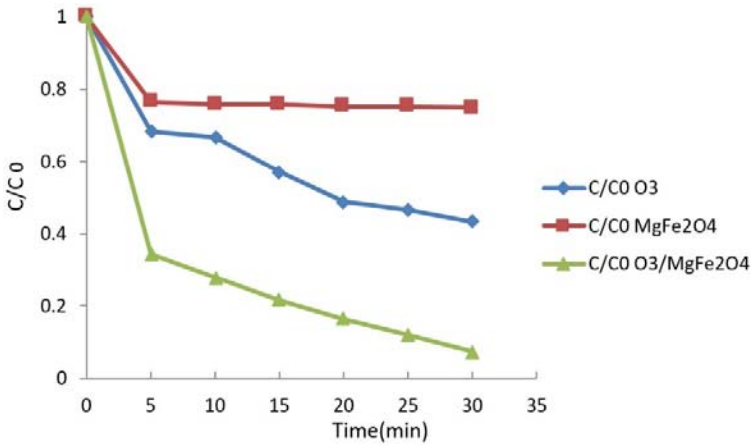

Fig. 3. Comparison of 4-CP removal in the O_3, adsorption by $MgFe_2O_4$ and $O_3/MgFe_2O_4$ processes in different reaction time. (ozone gas concentration, 1.67 mg/L; initial concentration of 4-CP, 100 mg/L; catalyst dosage = 0.2 g/L, pH= 7).

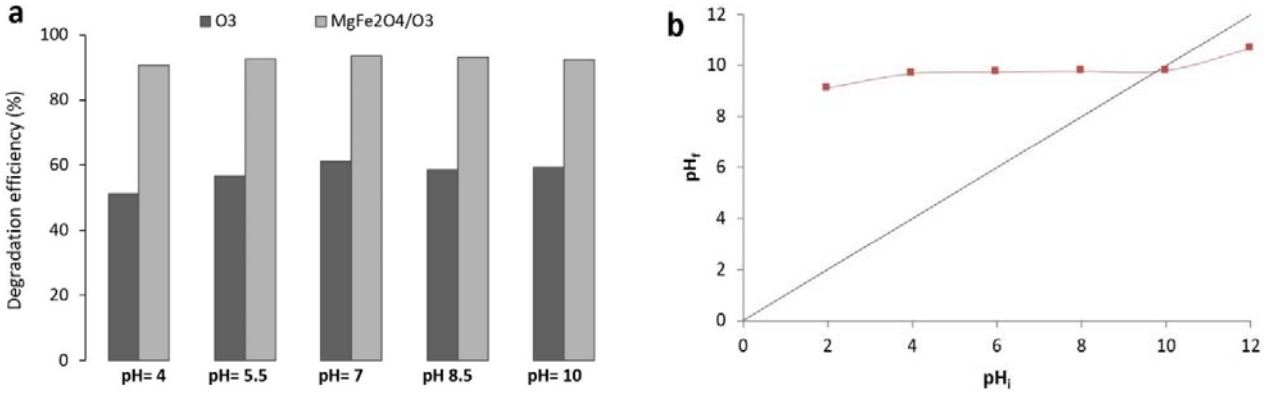

Fig. 4. Effect of pH on 4-CP degradation. (a) zero point charge of 4-CP (b) degradation efficiency of 4-CP in the O_3 and O_3/ $MgFe_2O_4$ processes (ozone gas concentration, 1.67 mg/L; initial concentration of 4-CP, 100 mg/L; catalyst dosage = 0.2 g/L)

Therefore, the reason for the suitable performance of the process was studied in this research and its independence from pH can be related to the hydroxyl functional group of 4-CP (with a pK_a=9.4), which is a type of weak acid that becomes ionized in environments with a pH below 9.4 and will have a negative charge. Good degradation rate in the alkaline medium may be attributed to more hydroxide ions (OH^-) in the solution producing more hydroxyl radicals ($OH^•$). Since hydroxyl radical is the dominant oxidizing species in the catalytic ozonation process, the degradation of 4-CP is therefore accelerated in an alkaline medium. The reason for the increase of degradation rate at low initial pH value is because of more H^+ ions in the solution; more conduction band electrons (e^-) can transfer to the surface of catalyst to react with O_2 to produce more hydroxyl radicals[27]. Besides, the catalyst surface will be charged negatively when pH> pH_{zpc}, positively when pH< pH_{zpc} and neutrally when pH ≈ pH_{zpc}. Fig. 4(b) shows the zero point charge of the prepared nanoparticle-$MgFe_2O_4$. As shown in the figure, pH of the zero point charge (pH_{zpc}) was determined to be 9.8, thus at a pH below 9.8, the surface of the absorbent will have a positive charge and can absorb negatively charged chlorophenol molecules. In addition, this increase in the rate of degradation can be due to adsorption and reaction with the obtained radical species, especially the hydroxyl radical from ozone decomposition on the surface of $MgFe_2O_4$. Finally, due to independence of the process from the initial pH, the neutral pH (pH=7) was chosen as the optimum pH and used for further experiments.

The catalyst dose which is an important parameter in the heterogeneous catalytic ozonation process, is effective in the conversion of ozone to radical species and influences adsorption of the dissolved substance [25]. Therefore, investigation of the effect of the catalyst dose on the degradation efficiency and finding the optimum dose will be essential for this process. In this study, the effect of the catalyst dose on 4-CP removal was studied within the range of 0.1-0.5 g/l. As can be seen in Fig. 5, by increasing the catalyst dose from zero to 0.2 g/l, 4-CP degradation efficiency rises from 61.2% to 93.5%, and with a further increase up to 0.5 g/l: no significant development occurs in the degradation efficiency (degradation efficiency=93.6%). Although $MgFe_2O_4$ made it possible that the chain of radical reactions could be induced and propagated by the ozone introduced in the reactor, the excess $MgFe_2O_4$ particles easily aggregated and affected the use efficiency [28]. Therefore, a dose of 0.2 g/l was chosen as the optimum dose to be used in other experiments.

3.4. Mineralization and dechlorination of 4-CP

When AOPs technologies were applied to degradation, after determining the contributors to 4-CP degradation; the formation and accumulation of chloride ions as the major inorganic product in the degradation of 4-CP by catalytic ozonation process, can be attractive. Therefore, the ‘‘dechlorination efficiency’’ is defined as the transformation process in 4-CP, that was degraded and converted to chloride ions. To this purpose, experiment of dechlorination was done for influent synthetic wastewater and optimum condition was selected for degradation of 4-CP. Under this condition, the rate of dechlorination was obtained to be 86.8%. Researchers proved that biodegradation processes have the high potential for biodegradability and free toxicity of organic compounds [29]. Also, rate of TOC removal was measured in order to investigate the mineralization degree. TOC removal efficiency was obtained to be 28.55 and 71% for O_3 and the O_3/$MgFe_2O_4$ process after 30 min, respectively. It was also observed that in the O_3/$MgFe_2O_4$ process, with the increase in the experimental time to 1 hour, TOC removal efficiency did not change significantly (75%).

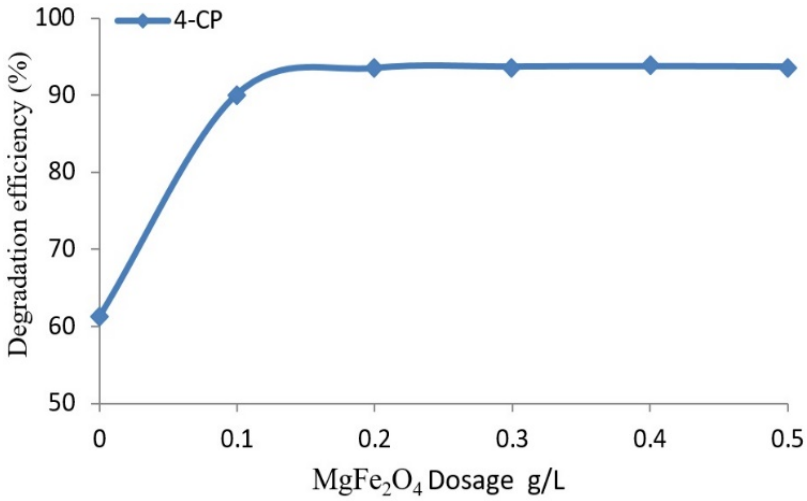

Fig. 5. Effect of $MgFe_2O_4$ dose on the removal of 4-CP. Conditions: ozone gas concentration, 1.67 mg/L; initial concentration of 4-CP, 100 mg/L; pH: 7.

The aforementioned results suggest a positive effect of the $O_3/MgFe_2O_4$ process on the mineralization of 4-CP compared with ozonation alone (the removal efficiency of $O_3/MgFe_2O_4$ was 2.5 times of ozonation alone). The reason for this increase in the efficiency of TOC removal can be attributed to catalytic decomposition of O_3 to $^{\bullet}OH$ which improved 4-CP mineralization rate [30]. According to results, it is essential to mention that $^{\bullet}OH$ produced from the catalytic ozonation process has sufficient capability to mineralize and cleave of C-Cl bound; this can reduce toxicity of 4-CP and increase biodegradability, both of which can be benefit for biodegradation processes [29].

4. Conclusions

Magnetically separable mesoporous $MgFe_2O_4$ was successfully prepared by a sol–gel combustion method and used as a new ozonation catalyst. The catalytic activity of this nanoparticle was evaluated through ozonation of 4-CP. In the $O_3/MgFe_2O_4$ process, 4-CP removal efficiency within 30 min was 93.5%. Under same conditions, TOC removal efficiency and the rate of dechlorination were 71% and 86.6%, respectively. However, in ozonation process alone, the 4-CP and TOC removal efficiencies were 61.2% and 28.55%, respectively. The independence of the $O_3/MgFe_2O_4$ process from pH allows for usage of this process in the treatment of pH-variable wastewater. Moreover, $MgFe_2O_4$ nanocatalysts could be easily and efficiently separated from the reaction mixture with an external magnet; this made it an attractive nanomaterial with prospective application in catalytic ozonation of organic pollutants in wastewater treatment.

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