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Efficient oxidative degradation of methylene blue catalyzed by Moroccan clay using hydrogen peroxide

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ABSTRACT

Natural clays have been widely used in several applications, particularly in catalysis. This study reports the successful use of natural mixed Moroccan clay minerals as heterogeneous catalyst to degrade methylene blue (denoted MB) from aqueous solutions. The X-ray fluorescence, X-ray diffraction, Fourier transform infrared spectroscopy, and scanning electron microscopy techniques were used to study the chemical composition and the structural features of natural mixed Moroccan clay. The characterization results showed that the sample is a mixed illite-chlorite-kaolinite (denoted I-C-K). Various experimental parameters were analyzed namely clay catalyst amount, initial dye concentration, and the amount of hydrogen peroxide. Degradation of methylene blue was greatly depressed in the presence of ethylenediaminetetraacetic acid, which is a powerful ligand used for the complexation of iron species. Inductive coupled plasma by atomic emission spectrometry analyses showed that no traces of iron were released into the final solution. Moreover, there was no noticeable loss of activity and damage of the clay structure after five recycles. The oxidation role of hydroxyl free radicals was evaluated using isopropanol (i-Pr-OH).

Keywords: Mixed illite-chlorite-kaolinite; Hydrogen peroxide; Methylene blue; Oxidative degradation

1. Introduction

Dyes are colorful chemical substances that, in aqueous solution, have natural binding affinity to several substrates. Nowadays, dyes are extensively used in various industries [1], and its vital use is unequivocal in today's lifestyle. However, dyes are chemically and naturally toxic substances that harm natural environment particularly aquatic biomass [2]. In fact, with low concentrations, dyes affect aquatic life such as planktons and therefore the entire food web. Moreover some dyes were proved to be carcinogenic and mutagenic [3]. Among well-known dyes, methylene blue represents a major concern to environment due to its worldwide use. It can reveal very harmful effects on the living things. For these reasons, the treatment of industrial waste containing dyes is increasingly of great interest in recent years [4–8]. There are many possible methods for removing dyes such as ozonation [9,10], Fenton's oxidation [11], electrochemical treatment [10], coagulation/flocculation [12], biological treatment [13,14], advanced oxidation processes [15,16], photocatalytic degradation [17], degradation by modified clays [18,19], and adsorption [20].

Adsorption is a commonly used treatment method to remove dyes from wastewater due to its operational simplicity, low cost and high capacity to remove various types of dyes [21–24]. Activated carbon is the most preferred for adsorption process as a commercial adsorbent due to its excellent adsorption capacity for dyes [25,26]. But, the overlying cost of activated carbon [27] and its regeneration problems [28] lead researchers to use natural clays as low-cost

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adsorbents in recent years [29,30]. However, it should be noted that adsorption methods lead only to the accumulation of dyes on the adsorbent surfaces, without any neutralization or degradation capacity.

The heterogeneous solid catalysts combined with hydrogen peroxide as a clean oxidant are environmentally friendly routes. Hydrogen peroxide is an attractive option for oxidants that can produce water as the only waste treatment product [31]. Other advantages of using heterogeneous catalysts are its easy separation, regeneration, and operation. In this aspect, the development of solid and eco-friendly catalysts with high performance and using H_2O_2 is a key for dye wastewater degradation.

The chemical properties of clay allow it to be used in a multitude of applications including catalysis. Our previous studies showed that commercial and natural clays are highly effective catalysts for liquid–solid oxidation of a wide range of ketones [32,33]. The results obtained motivated us to examine the performance of such type of catalysts for the degradation of MB as module substrate.

Therefore, the main aim of this study is to investigate the suitability of Moroccan mixed clay minerals (I-C-K) as low-cost catalyst for the removal of MB from aqueous solutions. Several process parameters were systematically investigated.

2. Materials and methods

2.1. Chemicals

Methylene blue (Fluka (United Kingdom), 95%), is a cationic basic dye as denoted by the presence of the positive charge in its structure [34], Malachite green (cationic dye) and Methyl orange (MO; anionic dye), were provided by the Sigma-Aldrich Chimie s.a.r.l. (Lyon, France) (85%). Hydrogen peroxide (Sigma-Aldrich, 30%), $FeCl_3$ (General purpose reagent, 98%), NaCl (Sigma-Aldrich, 99%), isopropanol (Acros Organics (New Jersey, USA), 99%), and ethylenediaminetetraacetic acid (EDTA) (Normapur (Belgium), 99%) were used with no further modification. Natural clay samples were collected in Beni Hassan rural district, near Tétouan (north of Morocco). Once at the lab, they were crushed and sieved to obtain fractions <80 μm and underwent no treatment. The clay used is composed of a mixture of illite, chlorite and kaolinite, clay minerals.

The transition-metal free montmorillonite, an Mg-containing synthetic clay, denoted S-MMT, was prepared in our previous work [35].

2.2. Technical characterization

X-ray fluorescence analyses were carried out using a PANalytical MiniPal 4 spectrometer wavelength dispersion–Type Axios. X-ray diffraction patterns were obtained with a PANalytical X'Pert Pro diffractometer equipped with an X'Celerator detector using Fe-filtered Cu-Ka radiation. The data were collected at room temperature with a 0.0670° step size in 2q (scan step time = 121 s) from 2q = 3° to 90°. The crystalline phase was identified by comparison with ICSD reference files. Fourier transform infrared spectrometry analysis was carried out using a Varian 640-IR spectrometer in the region of 4,000–400 cm^{-1}. Samples were thoroughly mixed and grinded with KBr powder to make a pellet for the Fourier transform infrared spectroscopy (FTIR) measurements. The surface morphology was examined by scanning electron microscopy Quanta 200. Prior to analysis, the samples were coated with a 5-nm carbon layer using a Cressington 208 carbon high vacuum carbon coater. Inductive Coupled Plasma by Atomic Emission Spectrometry type (Ultima 2 Jobin Yvon) was used for the determination of trace elements leached from the clay after catalytic reaction.

A decrease in the MB absorption was evaluated by measuring the absorbance at the wavelength 664 nm and 614 nm using a V-630 UV–Vis spectrophotometer, JASCO V 630. The concentration of MB was calculated from the calibration plot. In all measurements bi-distilled water was used as a reference.

The determination of clay's cation exchange capacity was performed using the dosage method of the copper complex triethylenetetramine [36]. The organic matter was determined by the method of Mingorance et al. [37]. It is based on the partial oxidation of clay with $K_2Cr_2O_7$ in the presence of sulfuric acid.

2.3. Degradation tests

All catalytic tests were carried out using batch reactor techniques. In a typical experiment, the reactor was charged with 10 mg of catalyst and 40 mL of MB solution with concentration of 25 mg L^{-1}. The reaction was started by the addition of 18 mmol of H_2O_2(30%) and the mixture was stirred magnetically for 12 h at room temperature. At different time intervals, the concentration of MB in the supernatant solution was followed with the UV–Vis spectrophotometer. The degradation efficiency was determined according to the following equation:

$$\text{Degradation efficiency} = [(C_0 - C_t)/C_0]\cdot 100 \tag{1}$$

where C_0 is the initial concentration of the dye and C_t is the concentration at time t.

After catalytic test, the catalyst was recovered by filtration, washed three times with distilled water and dried at 333 K for 24 h.

BOD and COD of the MB solution were determined to follow its mineralization level. The BOD value was determined by measuring the dissolved oxygen levels in the sample before and after reaction, according to Winkler's iodometric method [38]. BOD is calculated using Eq. (2):

$$\text{BOD}\left(\text{mgL}^{-1}\right) = \frac{D_0 - D_f}{P} \tag{2}$$

where D_0 is defined as the initial dissolved oxygen concentration in the sample, D_f is a dissolved oxygen concentration after 12 h, and P is a decimal volumetric fraction of used sample.

The COD concentration was measured by a closed reflux titrimetric method according to the standard methods [39]. And COD removal efficiency was calculated as follows:

$$\text{R}_{\text{COD}}\left(\%\right) = \frac{\text{COD}_0 - \text{COD}}{\text{COD}_0} \times 100 \tag{3}$$

COD represents the COD value in the solution after reaction, and COD_0 is the COD in the initial solution.

3. Results and discussion

3.1. Characterization of natural clay

Initially, the clay chemical and physical properties were studied. The results obtained are listed in Tables 1 and 2. The clay analysis using X-ray fluorescence (XRF) shows that the sample is primarily composed of silica (47.7%) and alumina (18.4%). The calcium oxide (CaO) and magnesium oxide (MgO) are slightly present with 6.8% and 6%, respectively, suggesting the presence of dolomite ($CaMg(CO_3)_2$) and calcite ($CaCO_3$) minerals. Furthermore, iron oxide (Fe_2O_3) content shows relatively high value (3.88%) (Table 1). K_2O, Na_2O, TiO_2, and P_2O_5 are present only in small quantities. The loss of ignition was 12.77%.

The sample cation exchange capacity (CEC) was proved to be 7.40 meq/100 g (Table 2). The low value of CEC indicates that the material should be an alternative method for dye removal as a catalyst, but not as an adsorbent. This result is a signal of the presence of non-swelling clay minerals in the natural sample. Besides, the presence of K^+ in the interlayer space with a relatively high percentage (2.05%) suggests the presence of illite. It should be noted that sample contain low amount of organic matter (OM = 0.24%).

The mineralogical composition of natural clay was subjected to analysis and identification by X-ray diffraction. The X-ray pattern of the collected clay powder is given in Fig. 1(a). Based on previous studies on clays and ICSD reference files, the X-ray pattern of the sample can be explained [40–44]. There is a presence of quartz, as identified by the sharp peak (3.34 Å), calcite, and dolomite as associated minerals. The d-value of (060) reflection is 1.5 Å, suggesting that the 2:1 layers of clays in the sample are dioctahedral.

Table 1
Chemical composition of clay

Component	Weight (%)
SiO_2	47.7
Al_2O_3	18.4
CaO	6.8
MgO	6
Fe_2O_3	3.88
K_2O	2.05
Na_2O	1.44
TiO_2	0.5
P_2O_5	0.14
Trace[a]	0.32
LOI	12.77

LOI: Loss of ignition.
[a] Trace: $\%ZrO_2 + \%SO_3 + \%SrO + \%MnO_2$.

Table 2
Physicochemical properties of clay

Parameters	Value
Color	Yellow
CEC (meq/100 g)	7.40
O.M. (%)	0.24

To identify the clay minerals composition, X-ray diffraction (XRD) was performed over oriented aggregates, which were previously glycolated or heat-treated at 550°C for 2 h. As shown in Fig. 2, the ethylene glycol solvation and the heat treatment did not affect the d(001) basal spacing at 10.01 Å, but the peak at 14.23 Å was disappeared after heating. Hence, illite mineral was identified with the presence of a few quantity of chlorite. The small reflection at 7.08 Å was not affected by solvation (Fig. 2(b)), but vanished after heating (Fig. 2(c)). It was identified as a kaolinite.

The mineralogical composition of the sampled clay indicates the presence of non-swelling minerals illite, chlorite, and kaolinite, (I-C-K) which is in agreement with the low value of CEC.

The infrared analysis of the I-C-K sample is shown in Fig. 3. The FTIR spectrum of the present powder displayed a band at 3,624 cm^{-1} attributed to the hydroxyl groups in Fe-rich illite [45]. An intense absorption band observed at

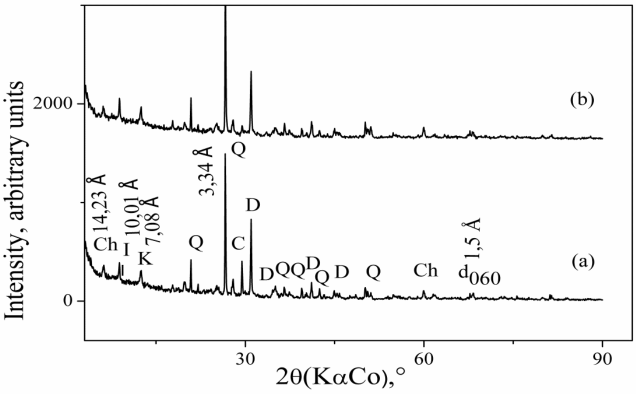


Fig. 1. X-ray diffraction patterns for: (a) raw clay and (b) clay after reaction with H_2O_2(30%) (Ch: chlorite, I: illite, K: kaolinite, C: calcite, D: dolomite, Q: quartz).

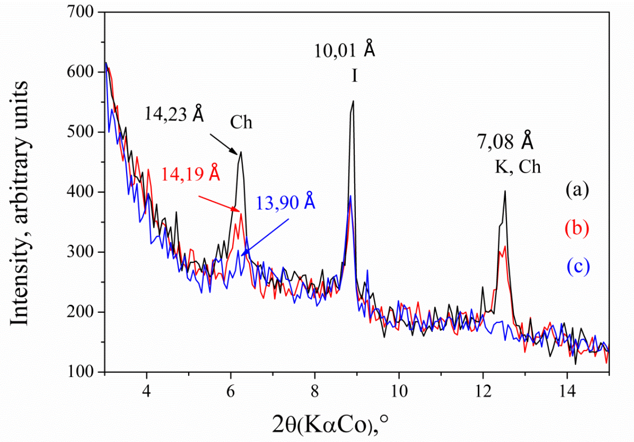


Fig. 2. X-ray diffraction patterns of clay: (a) air-dried, (b) ethylene glycol solvated, (c) heated to 550°C.

1,025 cm^{-1}, corresponding to the Si-O-Si stretching vibration of the tetrahedral layer. The two bending bands, at 522 cm^{-1} (Si-O-Si) and 470 cm^{-1} (Si-O-Al), revealed the substitution of Si by Al in the tetrahedral layer [33]. The bands at 3,749 and 691 cm^{-1} are typical of kaolinite mineral [45]. A broad band at 3,430 cm^{-1} is indicative of water adsorbed on the clay surface, and its presence was confirmed by the deformation band at 1,652 cm^{-1}. A band at 1,436 cm^{-1} appears in the clay, which is assigned to the CO_3^{2-} asymmetric stretching of calcite. Quartz was detected in the sample according to its characteristic band at 794 cm^{-1}. The band at 881 cm^{-1} in the powder is assigned to the vibrational mode of Al-Fe-OH. This indicates that I-C-K sample is Fe-rich [46], which is in good agreement with the chemical composition.

To obtain information about the morphology of the mineral particles, we carried out an observation by scanning electron microscopy. Fig. 4 shows the micrograph of the natural powder particles. The scanning electron microscopy (SEM) image indicates that the I-C-K sample contains several aggregates of clay particles with micrometric different sizes.

Overall, results of I-C-K characterization indicate the existence of mixed clay minerals with dioctahedral layers.

After characterization, the catalytic activity of I-C-K was evaluated toward the degradation of a basic dye methylene blue.

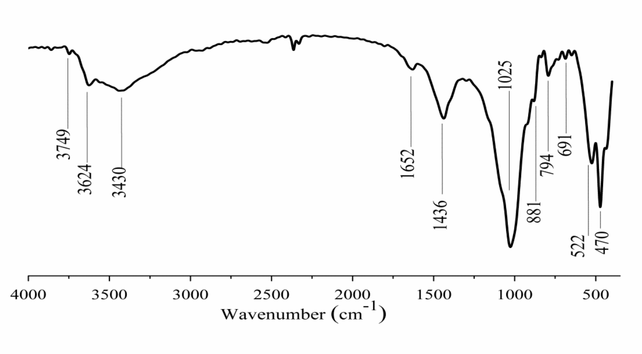


Fig. 3. FTIR spectrum of clay.

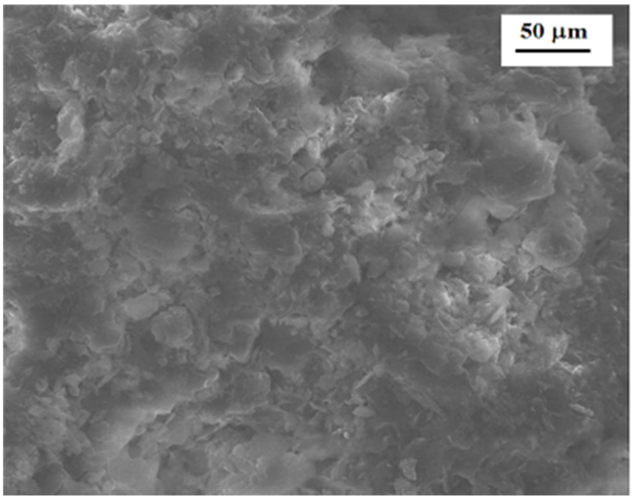


Fig. 4. SEM image of clay.

3.2. *Catalytic activity of I-C-K*

To investigate the catalytic activity of the I-C-K clay, degradation reaction of MB was carried out in the presence of H_2O_2(30%) for 12 h at room temperature and atmospheric pressure. Fig. 5 shows the effect of the amount of I-C-K catalyst on the degradation efficiency of MB in the presence of 40 mL of MB solution (25 mg L^{-1}), and 18 mmol of H_2O_2(30%). The amount of I-C-K catalyst was increased from 0 to 20 mg. On careful examination of this figure, one can notice a remarkable elimination of MB with the increase in the amount of our catalyst, reaching a maximum of 98% for 10 mg of I-C-K clay. When the mass of the catalyst increases above the optimum value, the degradation does not change significantly. The blue color of solution in interaction with natural clay was vanished, and all peaks characteristic of MB (664 and 614 nm) have disappeared after 12 h of reaction (Fig. 6). Contrary, in absence of I-C-K the solution was always blue; with any modification of methylene blue UV–Vis spectra (inset Fig. 6).

Thus, it appears that the role of I-C-K clay in the present degradation process was indeed indispensable.

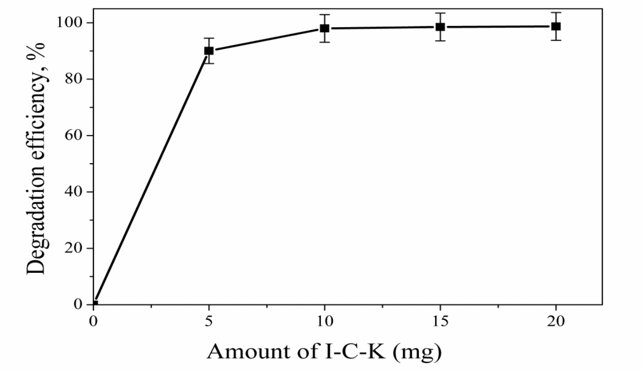


Fig. 5. Effect of catalyst mass on degradation efficiency of MB. Conditions: MB (40 mL, [MB] = 25 mg L^{-1}), H_2O_2(30%) (18 mmol), t = 12 h, pH = 6.7, room temperature. Error bars indicate the standard deviations of three individual experiments.

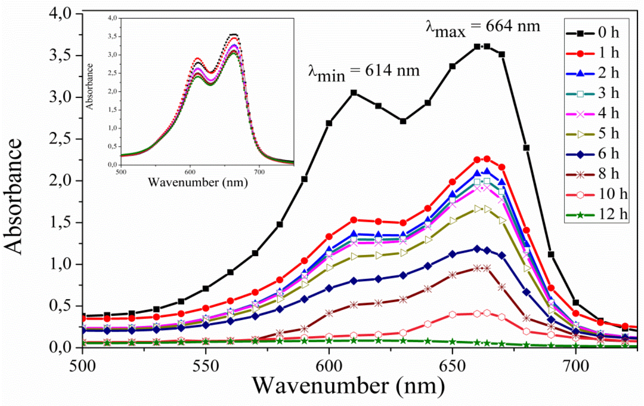


Fig. 6. Absorbance of MB solution vs. time during the degradation reaction in the presence of I-C-K and in the absence of I-C-K (inset). Conditions: I-C-K (10 mg), MB (40 mL, [MB] = 25 mg L^{-1}), H_2O_2(30%) (18 mmol), t = 12 h, pH = 6.7, room temperature.

The catalytic degradation of MB was performed at different pH values from 4 to 10 in the I-C-K/H_2O_2 system with constant process parameters. The degradation efficiency of MB is listed in Fig. 7. Clearly, the reaction occurred at a wide pH range from acidic to alkaline. However, the degradation efficiency was decreased with the decrease in initial pH.

The interpretation of pH effects on the efficiency of dye catalytic degradation process, by clay catalyst in the presence of H_2O_2, is a very difficult task because of its multiple roles. First, is related to the ionization state of the surface [47]. At low pH, the silanol groups attract the protons from the solution. A solid surface will usually become more positive, with consequent increase in the adsorption of anionic dyes and decrease in the adsorption of cationics. At acidic media, electrostatic repulsion occurred between the dye ions and the edge groups with positive charge (Si-OH_2^+) on the surface as follows [46,48]:

$$-\text{SiOH} + \text{H}^+ \rightarrow -\text{SiOH}_2^+ + \text{OH}^- \qquad (4)$$

At high pH, the hydroxyl anion (OH^-) attracts the silanol groups. The surface of clay becomes more negative and the electrostatic repulsion decreases thus resulting in an increase dye adsorption. This mechanism can be shown as follows [48,49]:

$$-\text{SiOH} + \text{OH}^- \leftrightarrow -\text{SiO}^- + \text{H}_2\text{O} \qquad (5)$$

$$-\text{SiO}^- + \text{Dye}^+ \rightarrow -\text{Si–O–Dye}^+ \qquad (6)$$

Second, it must also be noted that low pH such as 4.0 would result the partial dissolution of the raw material, giving rise to a mixture of protonated clay and amorphous hydrous silica phase [50]. Thus, the surface area available for dye adsorption would be reduced.

The results indicate that the catalytic activity of I-C-K increases with the increase of initial pH (Fig. 7). Similar conclusions have been reported in degradation of organic contaminant, by other catalytic processes [31,51]. In this study, the degradation efficiency of MB after 12 h was 98% and 99% at pH values of 6.7 and 10, respectively. The optimal pH range for the degradation was 6.7–10. A pH = 6.7 is preferable because operation under near-neutral conditions can easily apply to most wastewater.

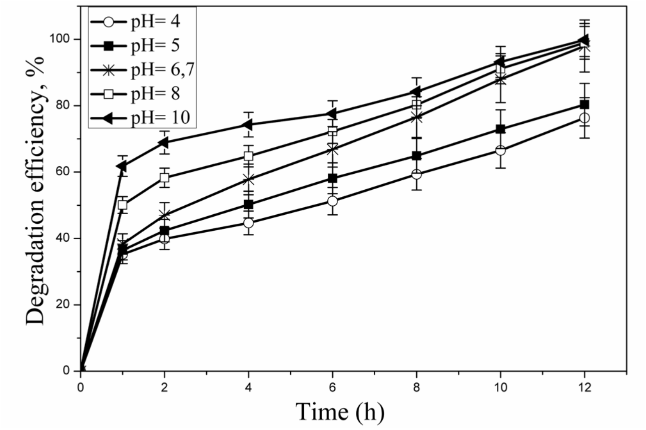


Fig. 7. Effect of pH medium on degradation efficiency of MB. Conditions: MB (40 mL, [MB] = 25 mg L^{-1}), I-C-K (10 mg), H_2O_2(30%) (18 mmol), *t* = 12 h, room temperature. Error bars indicate the standard deviations of three individual experiments.

The effect of temperature on the degradation of MB was studied at different levels of room temperature, 30°C, 40°C, and 50°C. The results show (Fig. 8) that raising temperature has a positive impact on the degradation of MB. The degradation efficiency after 12 h of reaction increased from 98% to 99.6% as temperature increased from room temperature to 50°C. Additionally, the period of time required for the degradation of MB was also much shorter at higher temperature. We chose to work at room temperature to minimize the cost of the experiment and avoid adjustments in case of application.

Dye dose is known to have an inverse influence on vanishing efficiency [52]. Fig. 9 shows the experimental results of MB degradation by I-C-K clay for various initial dye concentrations. The complete vanishing (98%) of MB was observed for 10 and 25 mg L^{-1} values within 12 h. The increase in dye concentration beyond 25 mg L^{-1} affects catalytic performance.

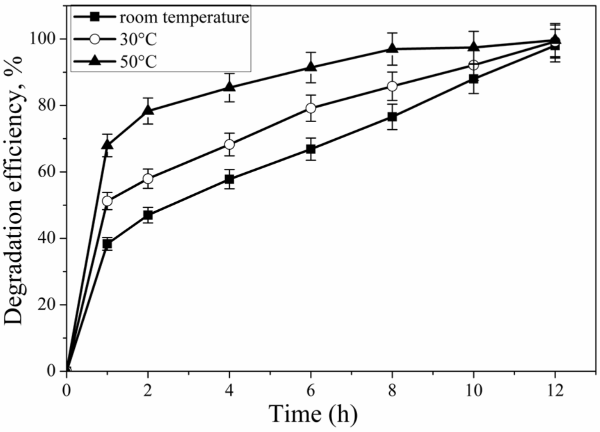


Fig. 8. Effect of temperature on degradation efficiency of MB. Conditions: MB (40 mL, [MB] = 25 mg L^{-1}), I-C-K (10 mg), H_2O_2(30%) (18 mmol), t = 12 h, pH = 6.7. Error bars indicate the standard deviations of three individual experiments.

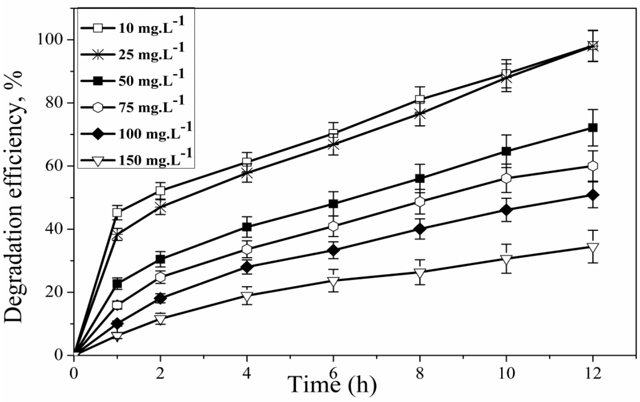


Fig. 9. Effect of dye concentration on degradation efficiency. Conditions: I-C-K (10 mg), H_2O_2(30%) (18 mmol), pH = 6.7, *t* = 12 h, room temperature. Error bars indicate the standard deviations of three individual experiments.

Indeed, 78%, 50%, and 36% removal efficiency were observed at 50, 100, and 150 mg L^{-1}, respectively. Hence, in this study, further degradation experiments were carried out using 25 mg L^{-1} of MB.

In the catalytic degradation of dyes by hydrogen peroxide, one of the main uncertainties is whether oxidation proceeds via a non-radical reaction mechanism or via a radical-mediated pathway. In the last one, several species are believed to be responsible for the degradation of organic dyes, which include free radical species, such as HO$^\bullet$, a very strong oxidizing agent, or HOO$^\bullet$, who is less reactive than HO$^\bullet$ species [53].

Isopropyl alcohol has a high affinity to HO$^\bullet$ radical due to its continued high-rate reactivity with similar radicals [54]. To verify the role of HO$^\bullet$ radical in the reaction, the degradation of MB carried out in the presence of i-Pr-OH inhibited and only 40% of MB was degraded within 12 h (Fig. 10). It should be noted that in the presence of secondary alcohol, this low disappearance of methylene blue is due only to the adsorption and not to the degradation. The overall result suggests the important contribution of free hydroxyl radicals in the reaction route.

Hydrogen peroxide quantity is an important parameter for the degradation of the dye in homogeneous as well as in heterogeneous catalysis. Fig. 11 displays the effect of H_2O_2 amount on the degradation of methylene blue. It would be observed that with the increase of H_2O_2 quantity from 4 to 27 mmol, at 10 mg of I-C-K clay, the degradation of MB increased greatly and reached the maximum value (98%). This can be attributed to the increased production of more HO$^\bullet$ radicals in the system [55]. It is noteworthy that the quantity of hydrogen peroxide had barely diminished after 12 h of reaction in the absence of MB. The value of 18 mmol of hydrogen peroxide was considered as the optimum.

For the comparison purpose, the adsorption of MB on I-C-K clay was investigated under the same conditions as applied in the degradation reaction but in the absence of hydrogen peroxide. Comparative studies of catalytic degradation and adsorption for MB are given in Fig. 12. After 12 h of reaction, the total amount of removed dye using adsorption was significantly smaller than catalytic degradation.

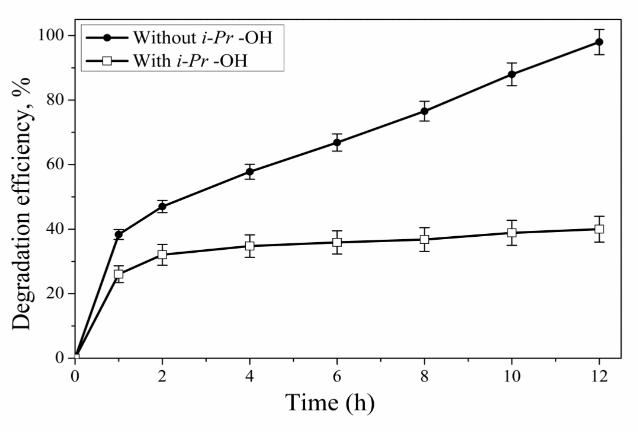


Fig. 10. Effect of i-Pr-OH on degradation of MB. Conditions: I-C-K (10 mg), MB (40 mL, [MB] = 25 mg L^{-1}), H_2O_2(30%) (18 mmol), pH = 6.7, i-Pr-OH (4 mL, 0.5 mmol), t = 12 h, room temperature. Error bars indicate the standard deviations of three individual experiments.

After reaction in the absence of H_2O_2(30%), FTIR spectrum of catalyst showed the characteristic peaks of both I-C-K clay and MB (Fig. 13). In addition, the clay became blue after interaction with MB (Fig. 14(b)). In this case, a small amount of MB was attached onto the external surface of the clay by adsorption. This result is in good agreement with the low value of cation exchange capacity of the clay (Table 2).

It was noticed that, in the presence of H_2O_2(30%) under optimum conditions, most characteristic peaks of the MB (1,337 and 1,353 cm^{-1} [CH_3 vibrations], 1,396 and 1,492 [C–N stretching vibrations], and 1,601 cm^{-1} [aromatic ring]) were disappeared (Fig. 13(c)). The catalyst almost stays in its original yellow color at the end of the reaction, indicating that dye pollutant adsorbed onto the catalyst surface had been degraded completely (Fig. 14(c)). These results corroborated very well with those obtained from UV–Vis studies. As a result, the degradation of MB at neutral conditions can be undoubtedly attributed to the oxidation reaction following the adsorption of MB on the catalyst.

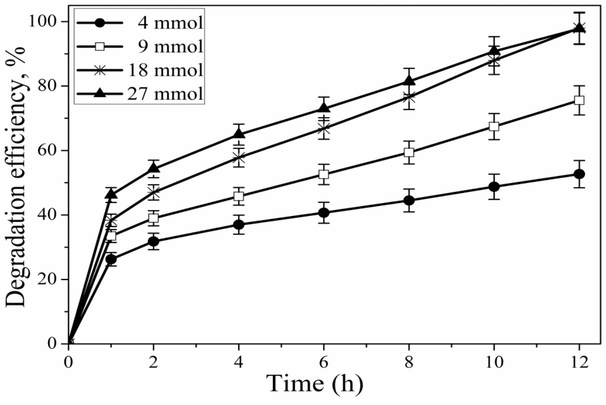


Fig. 11. Effect of H_2O_2(30%) quantity on degradation efficiency of MB. Conditions: I-C-K (10 mg), MB (40 mL, [MB] = 25 mg L^{-1}), pH = 6.7, t = 12 h, room temperature. Error bars indicate the standard deviations of three individual experiments.

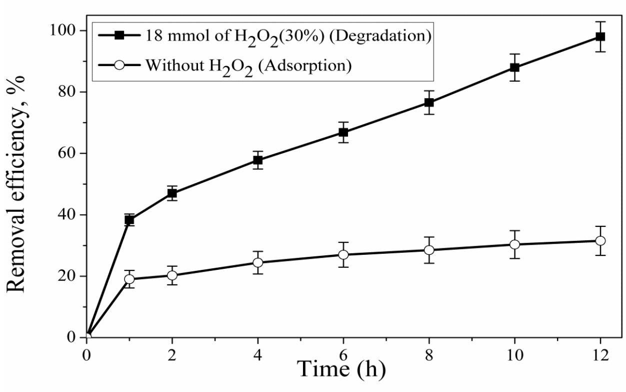


Fig. 12. Comparison with adsorption and degradation of MB. Conditions: I-C-K (10 mg), MB (40 mL, [MB] = 25 mg L^{-1}), pH = 6.7, t = 12 h, room temperature. Error bars indicate the standard deviations of three individual experiments.

The iron often exists in different chemical environments simultaneously in layered clay, including structural iron atoms that substitute for the aluminum atoms at the octahedral sites, interlayer iron cations that balance the negative charges of the clay layers, and are exchangeable with other cations, and surface iron complexed by surface hydroxyl groups [56,57].

The layered clays containing iron species have been shown to be active toward the degradation of organic dyes [57]. X-ray fluorescence analyses have shown the presence of iron in I-C-K clay (Table 1). It is known that EDTA is a powerful ligand being widely used for the complexation of Fe^{3+} [58,59]. Thus, EDTA was added into the reaction mixture to explore its effect on the degradation of MB (Fig. 15). Interestingly, the presence of EDTA inhibits the degradation reaction of MB. Chen et al. [58] have found that this is mainly attributed to complexation of this aliphatic compound with the Fe^{3+}, which makes the reaction between Fe^{3+} and H_2O_2(30%) less probable. These observations prove the fundamental role of Fe^{3+} in the reaction pathway.

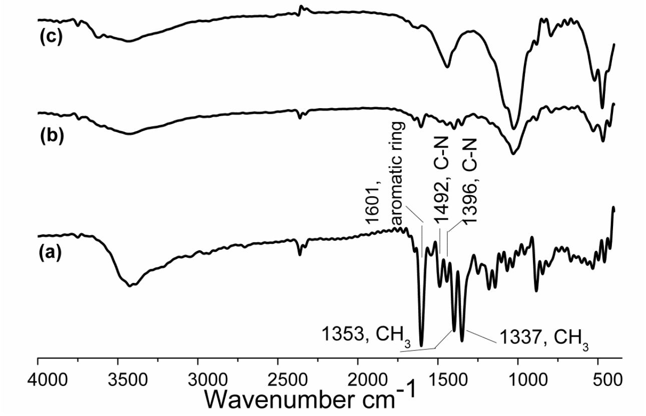


Fig. 13. Comparison between adsorption and degradation of MB by FTIR analysis: (a) MB, (b) I-C-K after reaction without H_2O_2(30%) (adsorption) (c) I-C-K after reaction with H_2O_2(30%) (adsorption–degradation). Conditions: I-C-K (10 mg), MB (40 mL, [MB] = 25 mg L^{-1}), H_2O_2(30%) (18 mmol), pH = 6.7, *t* = 12 h, room temperature.

In order to confirm the role of Fe^{3+}, we performed the following experiment: we added methylene blue, H_2O_2 and some amounts (e.g., 0.06 mmol) of $FeCl_3$. After 1 h of the reaction, we obtained a total degradation of the MB (99%).

Also, a transition metal-free synthetic clay (SMMT) was tested. The SMMT solid showed no catalytic activity at all, even after 12 h of reaction indicating that the transition metal species are needed.

It is well known that structural Fe^{3+} in the octahedral lattice is sandwiched by two silica tetrahedral sheets and the exchangeable Fe^{3+} ions mainly located on the silica surface, which makes it difficult for structural Fe^{3+} to complex with ligands such as EDTA, while exchangeable Fe^{3+} should be more accessible. But, knowing that the cation exchange capacity of I-C-K clay is weak (Table 2), the interaction between the EDTA and exchangeable Fe^{3+} ions in I-C-K, coordinated with water molecules, should be considerably comparable with that of the structural (Fe^{3+}) .Thus, the active species should correspond to Fe^{3+} species complexed by surface hydroxyl groups on the edge of a clay sheet.

This material is stable toward leaching under oxidizing conditions of MB in the liquid phase. This was proved by

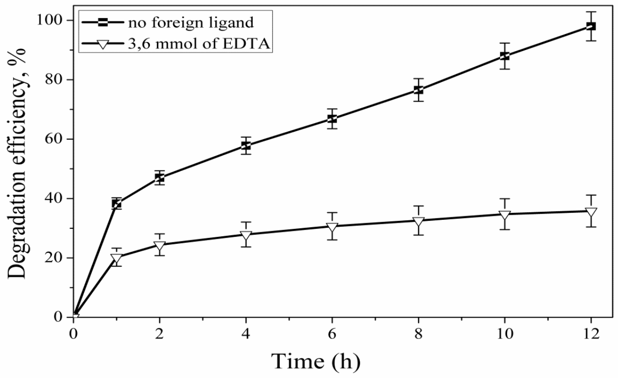


Fig. 15. Effect of foreign ligand on the degradation of MB. Conditions: I-C-K (10 mg), MB (40 mL, [MB] = 25 mg L^{-1}), H_2O_2(30%) (18 mmol), pH = 6.7, *t* = 12 h, room temperature. Error bars indicate the standard deviations of three individual experiments.

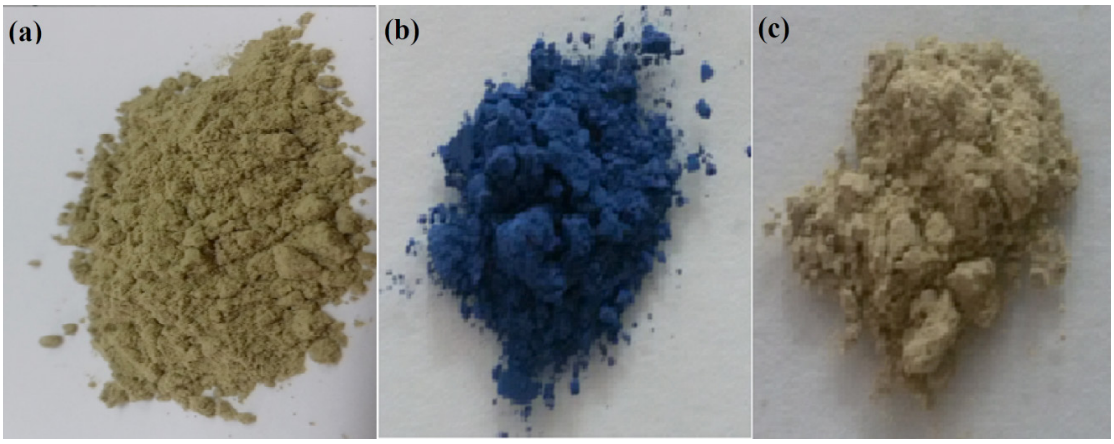


Fig. 14. Camera pictures of I-C-K before and after interaction with a MB solution: (a) I-C-K, (b) I-C-K after reaction without H_2O_2(30%) (adsorption), and (c) I-C-K after reaction with 18 mmol of H_2O_2(30%).

evaluating the Fe^{3+} concentration at the end of the reaction by ICP-AES. The results showed that no Fe^{3+} was detected in the solution. To confirm this outcome, at the end of the first run we separated the I-C-K clay from the mixture by filtration. Then, both of MB and H_2O_2(30%) were added to the filtrate in the same conditions. As expected, no degradation of MB was noticed. At first glance, such an observation should favor a heterogeneous catalyzed process.

3.3. *Effect of ionic strength*

The adsorption of dyes depends greatly on electrostatic parameters such as ionic strength [60]. In this work, the effect of the additional amounts of NaCl on the degradation efficiency of the sample was studied by keeping constant all the other parameters. It can be seen from Fig. 16 that the degradation efficiency of the catalyst decreased with increasing concentration of the inorganic salt. The result is consistent with that of Baybars et al. [48]. They studied the variation in adsorption of MB on bentonite as a function of ionic strength. The reason is that the hydrated cations in the aqueous phase compete effectively for the adsorption sites on the clay. On the other hand, ionic atmosphere may be progressively formed around MB molecules with increased NaCl concentration and results in the reduction of MB adsorption onto I-C-K. Another team pointed out that the ionic strength may also lead to the dimerisation process of MB molecules, thereby reducing electrostatic force in the presence of high concentration of Na^+ and Cl^- ions [60].

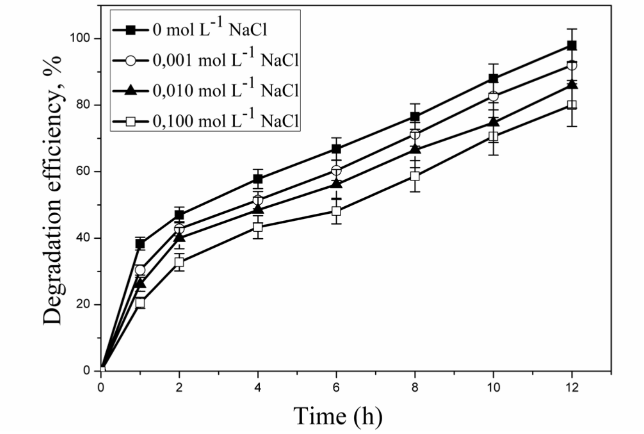


Fig. 16. Effect of ionic strength on degradation efficiency of MB. Conditions: MB (40 mL, [MB] = 25 mg L^{-1}), I-C-K (10 mg), H_2O_2(30%) (18 mmol), t = 12 h, pH = 6.7, room temperature. Error bars indicate the standard deviations of three individual experiments.

3.4. *Removal of BOD and COD*

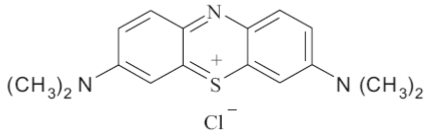
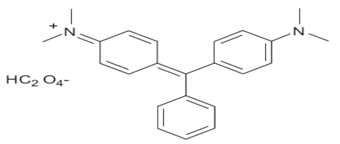
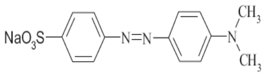
BOD and COD are widely used methods to determine organic matter in wastewater, their removal efficiencies at the end of MB degradation were 69% and 75%, respectively. The MB degradation efficiency was much higher than the corresponding COD removal efficiency. The maximum COD removal efficiency was only 75% while the color completely disappeared (98%). The high MB degradation efficiency but low COD removal efficiency illustrates that only chromophores were destructed and reduced instead of completely oxidizing the organic pollutant to CO_2 and H_2O [61].

The results obtained for BOD and COD indicated that I-C-K catalyst has the ability to decolorize MB in contaminated water.

3.5. *Degradation of different dyes*

Encouraged by the remarkable obtained results with the above reaction conditions, and in order to show the scope and possible generalization of this new protocol, we proceed the use of this catalytic system, I-C-K/H_2O_2(30%) for the degradation of other dyes (Table 3). The degradation efficiency of the Malachite green was 90% after 12 h. I-C-K clay has a lamellar structure which contains permanent negative charges on the clay layers. Thus, in natural conditions, the clay has a capacity for the electrostatic attraction of cations due to their negatively charged layers, but the contrary in the

Table 3
Degradation of used dyes

Entry	dye	Molecular structure	Nature	Degradation efficiency, %
1	Methylene blue		Cationic	98
2	Malachite green		Cationic	90
3	Methyl orange		Anionic	10

case of the anions. We have already showed in this study that the MB was totally degraded in the presence of I-C-K. This was caused by strong attractive forces between the dye molecules and the clay, fast diffusion onto the external surface was followed by fast adsorption in the surface solid.

However, the degradation of the anionic dye Methyl orange by I-C-K/H_2O_2(30%) catalytic system does not exceed 10% after 12 h of reaction; this slight value can be explained by the low adsorption of MO on the surface of the catalyst.

3.6. Recycling and structural stability

Obviously, recovering catalysts from reaction mixtures for recycling is important. Repeated usage of solid catalysts substantially reduces the production costs and chemical waste. Furthermore, the simple properties of heterogeneous catalysts make separation of these materials from the reaction media very easy. After the end of the first experiment, in optimal conditions, the used catalyst was recovered by filtration of the reaction mixture. The resulting I-C-K clay was washed with distilled water three times, dried at 333 K for 24 h, grounded into a fine powder and used again to study its activity for the degradation reaction. The results obtained are illustrated in Fig. 17.

We found that the catalyst was recyclable and could stay active at least five times without any noticeable change of catalytic activity. These results are in agreement with the XRD (Fig. 1(b)) and FTIR spectra (Fig. 13(c)) indicated before and after the completion of the first run, which has no change, confirming the structural stability of I-C-K clay. This is particularly interesting from the practical point of view due to the possibility of reusing I-C-K for a long operation time.

3.7. Proposed mechanism

Based on the obtained experimental results, the degradation of methylene blue could be considered to be a consecutive process including two steps, that is, adsorption and degradation (Fig. 12). From the facts obtained from the radical scavenger experiment (see section 3.2), it is confirmed that the I-C-K/H_2O_2(30%) system involves $HO^{\bullet}$ radical species.

According to the overall experimental findings of this study and the general literature review on catalytic processes, a proposed mechanism of I-C-K catalysis may be described as follows: first, the MB^+ cations and H_2O_2(30%) are adsorbed on the surface of I-C-K, at natural pH. Second, the mechanism of the H_2O_2 activation by I-C-K may involve the initial formation of a complex between I-C-K(Fe^{3+}) and H_2O_2(30%), being assigned as I-C-K(Fe^{3+})H_2O_2(30%) (Eq. (8)). H_2O_2 (30%) is decomposed into hydroxyl radicals induced by the highly active catalyst (Eqs. (9) and (10)). The nascent radical specie has high oxidizing ability and causes degradation of the MB. Finally, the reaction products are desorbed off the clay surface and the catalyst is, thus, recovered (Eq. (11)).

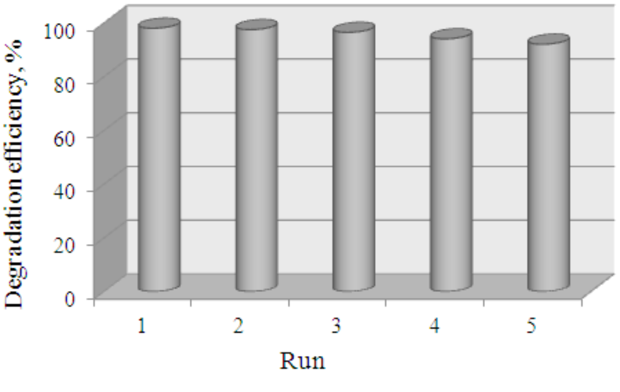


Fig. 17. Recycling of I-C-K in the degradation of MB by hydrogen peroxide (reaction conditions: see Fig. 6).

The following mechanism may thus be proposed [62].

$$\text{I-C-K} + \text{MB} \rightarrow \text{I-C-K} - \text{MB}_{(\text{ads})} \tag{7}$$

$$\text{I-C-K}(\text{Fe}^{3+}) + \text{H}_2\text{O}_2 \rightarrow \text{I-C-K}(\text{Fe}^{3+})\text{H}_2\text{O}_2 \tag{8}$$

$$\text{I-C-K}(\text{Fe}^{3+})\text{H}_2\text{O}_2 \rightleftarrows \text{I-C-K}(\text{Fe}^{3+})\,(\text{HO}_2^-) + \text{H}^+ \tag{9}$$

$$\text{I-C-K}(\text{Fe}^{3+})\,(\text{HO}_2^-) \rightarrow \text{I-C-K}(\text{Fe}^{2+}) + \text{HO}^{\bullet} + 1/2\text{O}_2 \tag{10}$$

$$\text{I-C-K–MB}_{(\text{ads})} + \text{HO}^{\bullet} \rightarrow \text{I-C-K} + \text{reaction products} \tag{11}$$

However, further investigations on the mechanism of the catalytic reaction are necessary to determine the dye degradation products at the end of the reaction.

4. Conclusion

The mixed illite-chlorite-kaolinite clay was characterized by XRF, XRD, FTIR, and SEM techniques, and was evaluated in the heterogeneous catalytic degradation of methylene blue in the presence of hydrogen peroxide. It was demonstrated that the quantities of catalyst and H_2O_2 and the concentration of methylene blue highly affect the overall process of efficiency. The methylene blue was completely degraded under nearly neutral conditions. We have demonstrated that the degradation efficiency was due to the presence of iron in the I-C-K clay. The ICP-AES analysis revealed both that Fe^{3+} species are not leached and that the degradation is a heterogeneous process. However, the addition of isopropanol inhibits the degradation of MB proved the existence of hydroxyl radicals. Probably, the latter are responsible for the oxidation process of methylene blue in the presence of hydrogen peroxide. Furthermore, the catalyst can be recovered and reused at least five times without any loss of catalytic activity. Because of it many advantages including the abundance of the layered clays, its low price and its non-aggressive characteristics toward the environment, its utilization in wastewater treatment is so promising. Future efforts will be directed to the degradation of other colorants. Furthermore, elucidating the mechanism of catalytic degradation will also be developing.

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