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RESEARCH ARTICLE

Wastewater treatment by catalytic wet air oxidation process over Al-Fe pillared clays synthesized using microwave irradiation

Halima Sassi[1,2], Gwendoline Lafaye (✉)[1], Hédi Ben Amor[2], Abdelaziz Gannouni[2], Mohamed Razak Jeday[2], Jacques Barbier-Jr[1]

1 Institute of Chemistry of Poitiers, University of Poitiers, 86073 Poitiers Cedex 9, France
2 Research Unit of Energy and Environment Gabes, National Engineering School of Gabes (ENIG), 6029 Zrig, Gabes, Tunisia

HIGHLIGHTS

- Tunisian clay has been successfully pillared with Al and Fe by microwave irradiation.
- Microwave method reduces considerably the synthesis time and the water consumption.
- AlFe-pillared clays are highly stable in the severe operating conditions of CWAO.
- Oxidation takes place through a heterogeneous mechanism.
- Microwave pillared-clays are good candidate for CWAO industrial water treatment.

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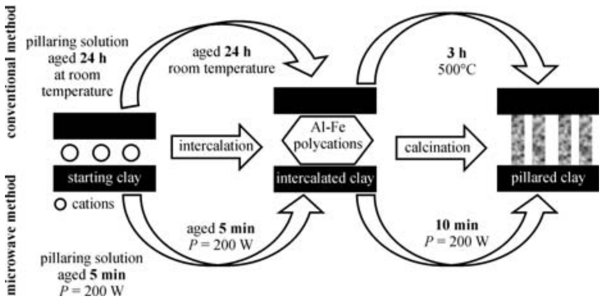
GRAPHIC ABSTRACT



ABSTRACT

Microwave irradiation has been used to prepare Al, Fe-pillared clays from a natural Tunisian smectite from the El Hicha deposit (province of Gabes). Chemical analysis, XRD spectra and surface properties evidenced the success of pillaring process. The obtained solids present higher surface area and pore volume than conventionally prepared Al-Fe pillared clays. The main advantages of the microwave methodology are the considerable reduction of the synthesis time and the consumption of water. The microwave-derived Al-Fe pillared clays have been tested for catalytic wet air oxidation (CWAO) of phenol in a stirred tank at 160°C and 20 bar of pure oxygen pressure. These materials are efficient for CWAO of phenol and are highly stable despite the severe operating conditions (acidic media, high pressure, high temperature). The catalyst deactivation was also significantly hindered when compared to conventionally prepared clays. Al-Fe pillared clays prepared by microwave methodology are promising as catalysts for CWAO industrial water treatment.

1 Introduction

Around the world, industrial processes generate a wide variety of wastewaters containing organic pollutants with negative impact for ecosystems. The development of advanced and economic viable oxidation processes is a need for the destruction of organic pollutants. Catalytic Wet Air Oxidation (CWAO) is an efficient and promising oxidative pollution removal process for the treatment of effluents which are too diluted to be incinerated and too concentrated to consider any biological treatment [1]. CWAO is known as a green process whose powerfulness is based on the combination of high temperature (130°C–300°C) and oxygen or air pressure (5–60 bar) together with a high active catalyst. The key factor for this process to achieve wider industrial applications is the catalyst. Indeed, for a perennial process, this latter must be ecologically and economically acceptable, that is a catalyst

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✉ Corresponding author
E-mail: gwendoline.lafaye@univ-poitiers.fr

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without the presence of noble metals, stable in the CWAO operating conditions, inexpensive and abundant in nature. This is a very challenging task. Clays could be the right solution. Indeed, in the literature the use of modified clays is highlighted in many catalytic reactions concerning for instance the environmental protection, the selective oxidation or the refinery/biorefinery [2]. The clays are modified by pillaring process, which means the intercalation of large polyoxocations, which generate stable oxide pillars by calcination. The resulting interlamellar galleries are accessible to molecules. The presence of transition metals ions as intercalant species gives rise to very efficient pillared clays for oxidation of organic substrates in water with the use of hydrogen peroxide as oxidant (Fenton-like and photo-Fenton-like processes) [3–7]. Only few papers deal with CWAO, i.e. oxygen as oxidant, over natural or modified clays [8–12]. In a previous study, we have reported the high potentiality of Al-Fe pillared clays for CWAO of phenolic effluents [13]. However, pillaring process must be less time-consuming so that these materials can be produced at large scale and thus increase the industrial interest for them. In fact, the conventional synthesis of pillared clays consists of three main steps: 1) preparation of the pillaring solution, 2) intercalation of the clay and 3) formation of the pillars. Steps 1) and 2) need long aging periods from several hours to days. Different authors have demonstrated that the use of microwave irradiation can shorter the aging time to only few minutes [14–20]. In addition, these authors revealed that the resulting solids present more homogeneous pillar distribution and higher surface area than conventionally prepared clays. Simultaneously, the microwave technique allows one to significantly decrease the water consumption in the pillaring process, which means a greener and less costly process. Concerning step 3), microwave irradiation has also been proposed for the pillars formation as an alternative procedure for slow heating calcination [21,22]. In that case, the obtained solids present similar characteristics to conventionally calcined pillared clays.

In the present work, we propose the combination of microwave irradiation in the three preparation steps described above for Al-Fe pillared clays. Therefore, a high scale production of pillared clays could be economical. The resulting materials were tested as heterogeneous catalysts for the CWAO of phenol and compared to their conventionally prepared counterparts.

2 Experimental

2.1 Preparation of the catalysts

The starting clay is a natural Tunisian smectite from the El Hicha deposit (province of Gabes, Tunisia). The characterization and purification protocol of this clay are described elsewhere [13]. The clay has been intercalated with Al and Fe hydroxy-polycations using a conventional method and a microwave assisted method. With the aim of comparing the two techniques, the % molar ratio Fe/(Al + Fe) was fixed to 1% and 20%. It is noteworthy that the preparation by the two methods is well reproducible. Table 1 summarizes the conditions of synthesis.

2.1.1 Conventional method

The conventional procedure used in this study has been described in a previous work [13]. In brief, each pillaring solution was prepared by dissolving 0.1 $mol \cdot L^{-1}$ $AlCl_3 \cdot 6H_2O$ and 0.01 $mol \cdot L^{-1}$ $Fe(NO_3)_3 \cdot 9H_2O$ in an aqueous 0.2 $mol \cdot L^{-1}$ NaOH solution. The hydrolysis molar ratio OH/(Al + Fe) was 2 and the % molar ratio Fe/(Al + Fe) was fixed to 1% and 20%. The resulting solution was aged for 24 h at room temperature. The intercalation process was carried out at 70°C by mixing the pillaring solution to a 2% suspension of the clay using an Al + Fe/clay ratio of 0.01 $mol \cdot g^{-1}$ clay. The resulting suspension was aged for 24 h. Once separated from the liquid phase, the solid was washed with distilled water and dried at 90°C for 24 h. The pillared solids were then obtained by calcination of the intercalated ones at 500°C ($2°C \cdot min^{-1}$) for 3 h. In this manuscript, these catalysts are referred as PIL-AlFex, where x corresponds to Fe/(Al + Fe) molar ratio %.

2.1.2 Microwave method

The procedure described by Olaya et al. has been followed [23]. Each pillaring solution was prepared by dropwise addition of a 0.4 $mol \cdot L^{-1}$ NaOH into a solution of 0.4 mol $\cdot L^{-1}$ $AlCl_3 \cdot 6H_2O$ and 0.4 $mol \cdot L^{-1}$ $Fe(NO_3)_3 \cdot 9H_2O$. The hydrolysis molar ratio OH/(Al + Fe) was 2.4 and the % molar ratio Fe/(Al + Fe) was fixed to 1% and 20%. The obtained pillaring solution was aged by irradiation for 5

Table 1 Conditions for preparation of Al-Fe pillared clays

preparation method	catalyst nomenclature	aging of pillaring solution	intercalation process	calcination (pillars formation)
conventional	PIL-AlFe1 PIL-AlFe20	24 h at room temperature	24 h at room temperature	500°C ($2°C \cdot min^{-1}$) for 3 h
microwave	PIL-AlFe1M PIL-AlFe20M	microwave 5 min, $P = 200$ W	microwave 5 min, $P = 200$ W	microwave 10 min, $P = 300$ W

min at 200 W in a commercial microwave oven (Samsung model ME-711K, Tunisia) operating at 2.45 GHz. The intercalation process was performed at room temperature by mixing the pillaring solution to the clay using an Al + Fe/clay ratio of 20 mmol·g^{-1} clay. After 30 min of stirring, the resulting suspension was aged by microwave radiation for 5 min at 200 W. The solid was recovered by centrifugation and repeatedly washed until the filtrate reached the conductivity and the pH of distilled water. Afterwards, the solid was dried at 70°C overnight. Finally, the pillared solids were then obtained by microwave radiation for 10 min at 300 W. The materials obtained by microwave radiation are referred as PIL-AlFexM, where M stands for Microwave and x corresponds to Fe/(Al + Fe) molar ratio %.

2.2 Catalyst characterization

Elemental analysis of the different catalysts were determined, after digestion in an acid solution, by inductively coupled plasma-optical emission spectroscopy (ICP-OES, model optima 2000 DV, France).

Powder X-ray diffraction (XRD) patterns of the catalysts were recorded using CuKα radiation on a Panalytical EMPYREAN diffractometer operating at 40 kV and 40 mA. The diffraction patterns were recorded in the 2θ range 2°–80° with a step size of 0.033°. Identification phases were identified by comparison with the information of the JCPDS database (Joint committee on powder diffraction standards) integrated in the PANalytical X’Pert HighScore Plus software. These recordings allowed calculating the d (001)-spacing which was shown to be characteristic of the interlamellar spacing for a pillared clay. The basal spacings d_{001} are derived from Bragg’s law ($n\lambda = 2d\sin\theta$).

The BET specific surface areas were measured by nitrogen adsorption-desorption at −196°C using a Micromeritics Tristar apparatus. The BJH method was used to determine the mean pore size. Prior to these physisorption measurements, the samples were degassed at 250°C overnight.

2.3 Catalytic test

Catalytic wet air oxidation reactions were carried out in a 0.44 L Hastelloy C22 autoclave equipped with a magnetically driven stirrer, as described elsewhere [24]. In a typical experiment, 160 mL of an aqueous solution containing phenol (2.098 g·L^{-1}) and the catalyst (4 g·L^{-1}) were poured into the autoclave that was flushed with helium. The reactor was heated up to 160°C and the stirring speed was set at 1000 r·min^{-1}. At the initial time of the reaction, 25 bar of pure O_2 were introduced into the reactor. The pressure was maintained constant throughout the experiment by regularly refilling with O_2. Liquid phase samples were periodically collected for analysis. They were previously filtered by the use of a Durapore membrane (0.2 μm; Ø = 4.7 cm) to eliminate all catalyst residues and then analyzed by HPLC using a 250 mm × 4.6 mm C18 reverse phase column (Microsorb- MV 100-5, Varian). The mobile phase was a mixture of 45% methanol and 55% water (flow rate: 1 mL·min^{-1}). The HPLC system is equipped with a UV-visible detector set at 270 nm. The total organic carbon (TOC) values were measured in a Total Organic Analyzer Shimadzu LCPH/CPN (France). HPLC and TOC analyzer are calibrated with standard solutions of phenol in water.

After 180 min of reaction, the reactor was cooled down to room temperature. Inductively Coupled Plasma (ICP, Perkin–Elmer Optima 2000 DV, France) of the remaining solutions were performed to determine the Fe leaching from the materials. It is worth noted that the reproducibility of the experimental protocol was verified for several reference catalysts and the experimental error was found to be lower than 5%.

3 Results and discussion

3.1 Catalyst characterizations

The elemental analysis of all the samples are summarized in Table 2. Whatever the preparation method (conventional or microwave), the starting clay is effectively modified in its chemical composition. The variations in the Al and Fe contents are in accordance with their concentration in the pillaring solutions. As a global trend, for the PIL catalysts, the content of Fe increases with x and that of Al decreases. These results are consistent with those reported in the literature regarding Al-Fe pillared clays prepared by conventional method [25–27] and by microwave proce-

Table 2 Aluminum and iron contents, basal spacing and specific surface area of the modified clay and of the calcined natural clay for comparison

sample	content/(wt.%)		d_{001}/Å	S_{BET}/(m^2·g^{-1})	$V_{p\ total}$/(cm^3·g^{-1})
	Al	Fe			
natural clay	6.1	3.2	9.93	74	0.100
PIL-AlFe1M	21.5	3.6	18.95	224	0.180
PIL-AlFe20M	17.2	6.6	18.13	176	0.133
PIL-AlFe1	12.8	4.3	17.08	143	0.140
PIL-AlFe20	11.2	8.0	16.65	128	0.171

dure [15,23]. Moreover, in accordance with the results reported by Olaya et al. [15,23], Table 2 indicates that for a given $x = \mathrm{Fe}/(\mathrm{Al} + \mathrm{Fe})$ molar ratio %, the microwave method leads to a greater introduction of Al. By opposite, the incorporation of Fe is better with the conventional method. Olaya et al. have observed the same phenomena with Al-Fe system [23]. They have explained this trend by the fact that only the Fe associated to the Keggin structure is intercalated in the case of microwave procedure, while by the conventional method the species independently hydrolysed are also intercalated.

The effective incorporation of Al and Fe in the modified solids is established for the two methods. Nevertheless, two important additional conditions must be fulfilled to evidence the formation of pillared clay: an increase of 1) the basal spacing, which could be used to estimate the interlayer distance between the clay sheets, and of 2) the specific surface area of the clay [28].

Powder XRD patterns of the calcined natural clay and the modified clay (Fig. 1) are similar to those reported in the literature for Al-Fe pillared clays [29–31]. Upon pillaring with Al and Fe by the conventional method and by microwave, the ordered layered structure of clays survives the pillaring process since the main characteristic signals associated to smectites are observed [25,26]. On the other hand, the XRD patterns of the PIL synthesized by microwave present a clear second diffraction order (002) (Fig. 1), which indicates that the resulting materials are relatively well-ordered 2D solids [22]. Moreover, the d_{001} pillaring signals of the PIL synthesized by microwave are more homogeneous and intense than those of the PIL synthesized by the conventional method [15,23]. The use of microwave seems to improve the pillaring process leading to a greater degree of organization in the structure [15,23].

Table 1 shows that whatever the PIL preparation method, by comparison to the calcined natural clay, the basal spacing has been enhanced considerably due to the intercalation of alumina and iron species. The values obtained are typical for pillaring clays with Al Keggin polycations [27,32,33]. Likewise, a significant increase in the specific surface area and total pore volume is observed for all PIL samples (Table 2). These results confirm the successful pillaring of the material by the two methods [28]. Besides, PIL-AlFe1M and PIL-AlFe20M have surface areas of 224 and 176 $\mathrm{m^2 \cdot g^{-1}}$, respectively, while PIL-AlFe1 and PIL-AlFe20 have surface areas of 143 and 128 $\mathrm{m^2 \cdot g^{-1}}$. Therefore, in agreement with the literature, the microwave method allows one to obtain porous solids with higher surface areas than the conventional method [14–23]. Finally, the microwave method improves the pillaring process.

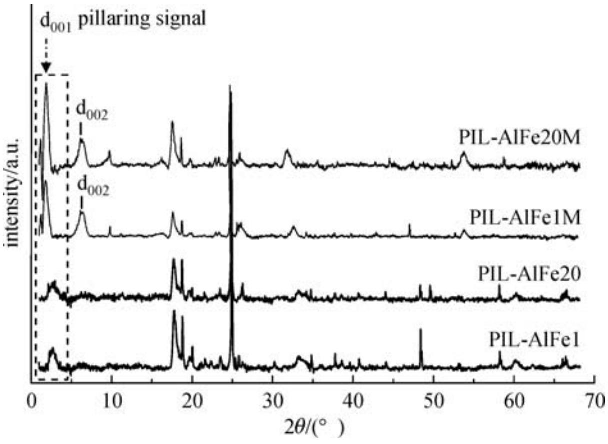

Fig. 1 X-ray diffraction patterns of the modified clay by microwave and conventional methods

3.2 Catalytic results

CWAO of phenol was carried out at 160°C under 25 bar of pure oxygen on the calcined natural clay and the PIL catalysts.

Figure 2 shows that the increase of catalytic properties of the PIL catalysts compared to the natural clay is remarkable. They all present a good catalytic activity, 80%–95% phenol conversion and 70%–80% ΔTOC are achieved after 180 min of reaction. For a given method (conventional or microwave), the phenol conversion and ΔTOC increase with the Fe nominal % [13].

If we compare the two different methods of preparation, for a same Fe nominal %, that is PIL-AlFe1 versus PIL-AlFe1M and PIL-AlFe20 versus PIL-AlFe20M, the catalytic results are similar after 3 h of reaction. But the shape of the curves is significantly different. Indeed, PIL catalysts prepared by a conventional procedure present higher performance from the beginning of the reaction (Fig. 2). Figure 2 (a) indicates that they present a rapid oxidation of phenol during the first hour, then their activity decrease after this first period. Concerning the TOC abatement (Fig. 2 (b)), comparing PIL-AlFe1 and PIL-AlFe20, we can observe that this activity drop is all the more significant as the iron content of the catalyst is high. By opposite, the microwave catalysts do not exhibit a deactivation phenomenon (Fig. 2 (a)). Usually, for the PIL solids, a deactivation phenomenon is explained by generation of carbon (adsorbed compounds) on the catalysts that leads to the blocking of the channels and, thus to a decrease in the number of actives sites [10,13]. It suggests that the difference of behavior between our two sets of catalysts can be correlated to the higher surface area and higher pore volume size obtained by microwave (Table 2), which allows one to inhibit the deactivation phenomenon.

The lower TOC abatement reached by PIL-AlFe1M, by comparison with PIL-AlFe1, after 3 h of reaction, can be related to its lower incorporation of Fe (Table 2). On the other hand, PIL-AlFe20M and for PIL-AlFe20 give similar CWAO results after 3 h of reaction (Fig. 2), although the

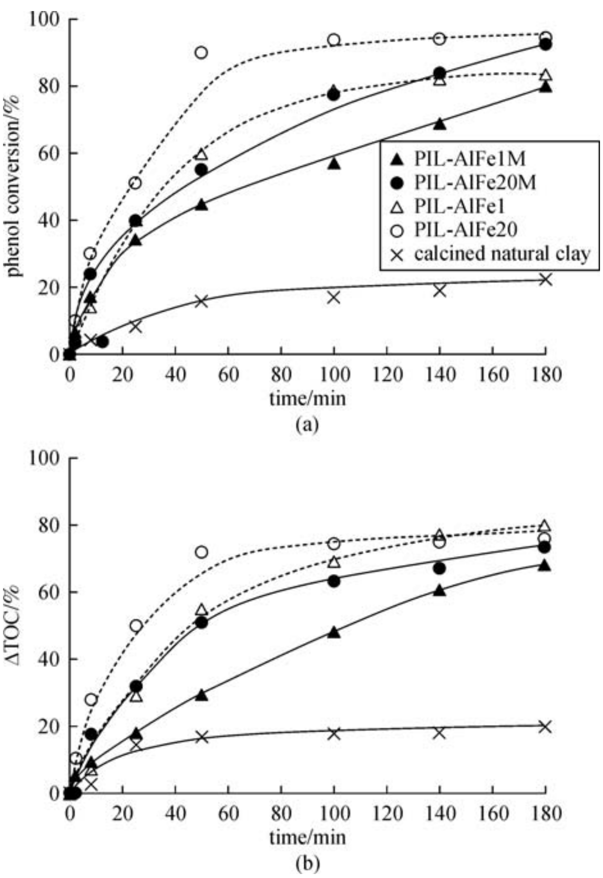

Fig. 2 (a) Phenol conversion and (b) abatement of total organic carbon (ΔTOC) over the calcined natural clay (X, continuous line) and over PIL catalysts prepared by a conventional method (empty marks, dotted lines) and by a microwave method (black marks, continuous lines)

incorporation of Fe by microwave (PIL-AlFe20M) is much smaller than by conventional method (PIL-AlFe20) (Table 2). This result suggests that the microwave method improves the accessibly of the actives sites, that is Fe for the considered reaction. That is in perfect agreement with the higher surface area observed for microwave catalysts (Table 2).

Concerning the leaching of iron species, despite the severe conditions of reaction, which are acidic medium, high pressure and temperature, PIL catalysts prepared by conventional method appear to be quite stable since the Fe leaching is reasonably small (ICP on the CWAO remaining solutions), around 2–3 ppm in the remaining solutions (Table 3) [19]. It is important to point out the very low levels of iron leaching obtained in the case of microwave catalysts (0.6–0.7 ppm) (Table 3). Therefore, the two preparation methods lead to Fe species highly stabilized by the clay matrix and not simply dispersed over the clay surface. All the more for the catalysts prepared by microwave, where the active phase is particularly strongly linked to the support [23].

Even if the iron leaching is quite small, in a previous work dealing with CWAO over conventionally prepared Al-Fe pillared clays [13], in order to discriminate between homogeneous and heterogeneous oxidation, several experiments were done in similar experimental conditions: 1) with the solution obtained after the catalyst filtration. We have shown that the fraction of iron leached from the catalyst is not capable of oxidizing the phenol. 2) With soluble iron species (2 ppm). The rate of homogeneous phenol oxidation was much lower than the rate of the heterogeneous reaction, in agreement with Xu et al. [8]. These results confirmed the prevalent contribution of the heterogeneous reaction path. Accordingly, given that the iron leaching is even smaller with the catalysts prepared by microwave, it makes sense that in that case the oxidation also takes place essentially through a heterogeneous mechanism.

Since the stability of a catalyst is one important aspect in the general evaluation of its performance, PIL-AlFe20M and PIL-AlFe20 were reused in consecutive CWAO reactions. The catalysts were recovered, washed with distilled water and dried overnight at 90°C. Table 4 shows that the two solids still present a good efficiency under two consecutive runs. Moreover, no significant structural change was observed in the catalysts after reaction. Therefore, microwave irradiation is a very quick method leading to catalysts as stable as those prepared by the time-consuming conventional method. These results are very encouraging.

4 Conclusions

A natural Tunisian clay was successfully pillared with Al-Fe using microwave irradiation during the aging and the

Table 3 Stability toward iron leaching under CWAO process of the modified clay and of the calcined natural clay for comparison

sample	Fe leaching/ppm[a)]	Fe leaching/%[b)]
natural clay	0.0	0.0
PIL-AlFe1M	0.6	0.4
PIL-AlFe20M	0.7	0.3
PIL-AlFe1	3.2	1.9
PIL-AlFe20	2.0	0.6

Notes: a) Fe concentration in the CWAO remaining solution after 180 min of reaction; b) % of Fe initially present in the sample

Table 4 Phenol conversion and TOC abatement (ΔTOC) after 180 min of CWAO of phenol over fresh and reused PIL-AlFe20M and PIL-AlFe20 and the structural and textural properties of these catalysts

catalyst	phenol conversion/%	ΔTOC/%	d_{001}/Å	surface area/ $(m^2 \cdot g^{-1})$	$V_{p\ total}$/ $(cm^3 \cdot g^{-1})$
PIL-AlFe20M					
fresh	92.6	73.6	18.13	176	0.133
after run 1	93.2	74.0	18.02	173	0.127
PIL-AlFe20					
fresh	94.4	76.0	16.65	128	0.171
after run 1	95.3	77.5	16.59	123	0.164

intercalation steps of the pillaring solution but also by replacing the conventional calcination to consolidate the pillars. This methodology generates a considerable decrease in the synthesis time as well as the volume of water compared to the conventional synthesis method. For both preparation methods, Al-Fe pillared clays showed high organics removal efficiencies, which demonstrates the potentiality of these catalysts for CWAO process. Those prepared by microwave irradiation present similar catalytic performance than their conventional counterparts whereas they contain less Fe content, thereby reducing the costs of the process. Moreover, the microwave-derived catalysts are remarkably stable despite the severe conditions of CWAO reaction. Only 0.3%–0.4% of the initial Fe was leached into the solution. The catalyst deactivation was also significantly hindered since the microwave catalysts present a higher specific surface area and higher pore volume than their conventional counterparts. Therefore, Al-Fe pillared clays prepared by means of microwave methodology are good candidate for CWAO industrial water treatment.

In summary, the microwave irradiation method, by comparison to the conventional one, presents the advantage of reducing considerably the time of synthesis and the consumption of water. Hence, the resulting materials are ecologically and economically viable. These materials could be then produced at large scale, increasing so the added value of clay, which is an abundant natural resource. Therefore, CWAO, which is a green process to degrade organics into carbon dioxide, could achieve wider industrial applications.

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