Pillared interlayered clays as catalyst for wastewater treatment: Cost-effective and sustainable materials

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Abstract. Metal oxide pillared interlayered clays (PILC) represent a novel class of materials that have attracted interests in catalytic oxidative removal of organic pollutants in wastewater. In this work, South African bentonite clay were modified by polymeric Al/Fe, Al/Zr and Al/Cr species, and the obtained pillared solids were characterized and as potential catalysts in catalytic wet air oxidation (CWAO) of phenol in aqueous solution. The placement of metal oxide pillars between bentonite clay sheets modifies their physicochemical properties (surface area and basal spacing) and catalytic activity. The Al/Zr pillared clay exhibited a higher activity compared to Al/Fe and Al/Cr for phenol oxidation. All the pillared clay catalysts allowed the total oxidation of phenol and significant removal for the total organic carbon. The metal leaching was very low in all catalysts studied.

1. Introduction

Environmental problems related to water pollution has been described as one of the major issues and recently attracted much attention [1–5]. One of the major pollution sources comes from wastewater containing phenolic compounds commonly discharged from dyestuffs, pesticide, petroleum, paper and pharmaceuticals industries [6]. Phenolic compounds can be present in industrial wastewaters at different concentration levels depending on the source of pollution such at low concentrations of 10–100 mg/L and high concentrations 1000 mg/L from cleaning containers or spills and wastewater generated in oil refinery, respectively [7]. Phenols are highly toxic, low biodegradability and good water solubility and, so, phenols are in the “Priority Pollutants List” by the US Environmental Protection Agency [8]. The discharge of phenols into water streams may destroy the ecological system and cause disease [6]. Therefore, more and more attention is paid to its treatment before being discharged to water bodies.

Significant efforts have been done by many researchers to find appropriate treatment methods in order to remove phenols pollutants from wastewaters [1,3,9]. Numerous conventional chemical and physical methods of phenols removal including chemical precipitation [10], electro-coagulation [11] membranes [12] and adsorption techniques [13] are currently used for this purpose. However, one of the drawbacks of these methods is the formation of secondary pollutants like sludge, moreover, phenols cannot be completely be removed in the wastewater. Recently, advanced oxidation processes (AOPs) like catalytic wet air oxidation (CWAO) has been used for removal of phenol from wastewaters by many researches [1,6,14,15]. In a typical CWAO method, phenol is oxidized by a solid catalyst under an activated O2 species, normally at pressures of 10–50 bar and temperatures of 125–250 °C. With regards to economic point of view, it is still essential to develop operating conditions at reaction temperature and partial pressures as milder as promising in order to reduce capital cost of the process. Therefore, the
development of efficient and durable catalysts with robust catalyst activity and high stability is very important. To the best of our knowledge, very few studies have been reported to evaluate CWAO of phenol using pillared clay catalyst including the use of cutting edge method to reduce the synthesis costs. Due to its outstanding properties such as low cost, environmental friendly and high chemical stability pillared clay catalysts has been utilized in AOPs related to wastewater treatment. The Al/Cr-PILC, Al/Fe-PILC and Al/Zr-PILC pillared clay solid materials were prepared by ultrasonic method with direct addition of clay into the pillaring agents solution containing Fe, Cr and Al metals, thereafter, intercalated through ion exchange. Structural and textural properties of the catalysts were characterized by XRD, SEM-EDX, Zetasizer and BET surface area measurements and catalytic activity of the solids materials were assessed by CWAO of phenol in aqueous solutions. Clay based catalysts used in this study have a great advantage in the CWAO of removal of phenol in wastewater due to their low cost and they have demonstrated high chemical stability because the concentrations of metal oxides leached in the CWAO reaction do not exceed 1 mg/L. Moreover, the CWAO process takes place at milder operating conditions and shorter residence time, making the operating cost of CWAO process to be very low.

2. Experimental procedures

2.1. Materials and chemicals

The raw clay purchased from Cape Bentonite Mine, Republic of South Africa was used as received. Table 1 shows that the South African bentonite clay was mainly composed of montmorillonite; it had the chemical composition as follows, SiO$_2$ (62.2%), Al$_2$O$_3$ (18.6%), Fe$_2$O$_3$ (3.5%), TiO$_2$ (0.2%), CaO (0.8%), MgO (3.7%), K$_2$O (0.7%), Na$_2$O (2.4%). Its cation exchange capacity (CEC), was 0.786 meq/g, its basal spacing 1.24 nm and its BET specific surface area 61 m$^2$/g. All solutions and dispersions were synthesized using an ultrapure water from Milli-Q water purification unit. Al(NO$_3$)$_3$·9H$_2$O, Zr(NO$_3$)$_4$·5H$_2$O, Cr(NO$_3$)$_3$·9H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O, HCl and NaOH were purchased from Sigma-Aldrich.

Table 1: South African bentonite clay physicochemical properties

| Sample  | BET (m$^2$/g) | Mg (%) | Na (%) | Si (%) | Al (%) | Ca (%) | Fe (%) | K (%) | Ti (%) | Si/Al | CEC (meq/g) | $d_{001}$ (nm) |
|---------|---------------|--------|--------|--------|--------|--------|--------|-------|--------|-------|------------|----------------|
| Bentonite | 61            | 3.7    | 2.4    | 62.2   | 18.6   | 0.8    | 3.7    | 0.7   | 0.2    | 4.25  | 0.786      | 1.24           |

2.2. The pillaring solution synthesis

The Al-pillaring solutions were prepared by adding 0.4 M sodium hydroxide solution slowly into definite amount of 0.4 M Al(NO$_3$)$_3$·9H$_2$O solution at room temperature under vigorous stirring using a separating funnel at approximately 5 mL/min constant dropping rate in order to obtain a molar ratio [OH$^-$]/[Al$^{3+}$] = 2:1. It was the same procedure with Cr, Fe and Zr-pillaring solution. The obtained Al, Cr, Fe and Zr-pillaring solutions were set aside for use during intercalation of bentonite clay and their SEM images are shown in Figure 1.
2.3. Synthesis of pillared clays
The pillared bentonite clay was prepared using ultrasonic treatment starting with dry clay material. In typical procedure, 0.01 M ratio of (Al + Cr, Fe or Zr)/g clay (25 mL /1 g) was produced by the direct addition of the dry bentonite clay into pillaring solutions and stirred vigorously for 30 minutes at 25 °C. Ion exchange was done by ultra-sonication of the suspensions for 10 minutes at 25 °C. Then, the solid was separated by centrifugation for 8 minutes and dried overnight at 120 °C and finally calcined for 2 h at 500 °C, at a 1 °C/min heating rate. These solids were designated as Al/Zr-PILC, Al/Cr-PILC and Al/Fe-PILC.

2.4. Characterization studies
All solids materials were characterized by X-ray diffraction (XRD), N$_2$ adsorption/desorption, Fourier transform infrared (FTIR), Thermogravimetric analysis (TGA) and zeta potential. X-ray diffraction patterns were obtained using a Brucker D8 Advance instrument employing Co-K$_\alpha$ emission of 40 kV using a LinxEye detector. The specific surface area, average pore diameters and pore volume of the raw bentonite and prepared solids were determined using N$_2$ adsorption/desorption at -196.15 °C, by the use of a Micromeritics (ASAP TriStar 3000) instrument. FTIR spectra were obtained by means of an Attenuated Total Reflectance (ATR) technique using a Varian 640-IR FTIR spectrometer (PIKE Technologies) at room temperature on the built-in diamond ATR crystal. Steady-state FTIR spectra were recorded over the range 400 to 4000 cm$^{-1}$ over 200 scans. Thermogravimetry of the materials was performed using a Perkin–Elmer 6000 TG analyser. Zeta potential measurement was measured using Zetasizer Nano ZS (Malvern Instruments).

2.5. Phenol removal by catalytic wet air oxidation
The phenol oxidation experiments were performed in a autoclave semi-batch reactor (model 4531M) of 0.35 L capacity, stainless steel, equipped with an adjustable speed agitator, and a blanket which allows control of the reaction temperature and the gas phase addition was measured using needle valve that records the pressure input. The phenol removal experimental runs were stirred at 800 rpm, ensuring desirable mass transfer, which allow gas addition to the liquid phase and sampling of liquid. The reactor was charged with nitrogen gas at 10 bar for 5 minutes to create inert atmosphere inside the reactor and the vessel was evacuated again to take out any remaining nitrogen from the reactor system. After reaching preset reaction conditions the time was defined as zero time and volume of 5 mL solution was sampled at different time intervals during the reaction. An autoclave reactor was charged with a volume of 200 mL of 100 mg/L initial phenol concentration solutions and catalyst of 2 g/L to the reactor, partial oxygen of 5 bar and then 5 bar of pure nitrogen. All experimental runs were done under the following experimental conditions: phenol initial concentration = 1000 mg/L, partial pressure of oxygen = 10 bar, reaction temperature = 100 °C, reaction time = 120 min. All experimental runs were performed three times in order to check the reproducibility and evaluate the experimental error of the results. It was found that the standard deviation was less than 5%.
2.6. Analytical methods
Phenol concentration was measured by using the high performance liquid chromatography (HPLC) model LC-10AD (Shimadzu, Kyoto, Japan). The mobile phase was a mixture of methanol and water (v/v, 60:40) with 0.1% acetic acid aqueous solution added and with a flow rate of 1.0 mL min\(^{-1}\). Total organic carbon (TOC) measurements were performed using TOC analyser by TOC-VCPN, Shimadzu, Japan.

3. Results and discussion
3.1. Phenol removal by catalytic wet air oxidation
In this series experiments, blank tests were conducted without a catalyst (WAO) and under raw bentonite clay (adsorption), and pillared clay catalysts modified with different metal oxides were investigated. Figure 2 shows the removals of phenol and TOC after 180 min of CWAO using different catalytic materials. No significant catalytic activity was observed during the blank tests experiments, showing the stability of phenol under our operating conditions in this study. These findings can be attributed high bentonite clay negative charge (as indicated in Figure 3) which repel the negatively charged phenol and also the absence of catalytic. In contrary, a maximum conversion of 100% phenol and very high removal of TOC was attained in 120 min of reaction. The catalytic activities of different catalytic materials were found to be in this; Al/Cr-PILC (1:1) < Al/Fe-PILC (3:1) < Al/Zr-PILC (3:1). The obtained results can be ascribed to the enhancement of surface electrical properties and new functional groups in the clay after pillaring [6]. Therefore, to study the relationship between pillared clay catalysts activity and catalysts structure and surface properties, solids materials were characterized.

![Figure 2: Phenol conversion (a) and TOC concentration removal (b) as a function of time for bentonite clay catalysts CWAO of phenol.](image)

3.2. Characterization of catalysts
3.2.1. XRD
The XRD patterns of the samples were presented in Figure 3. It is observed that after intercalation with metal oxides pillars the basal spacing (d\(_{001}\)) peaks of bentonite clay shifted a little near small 2 theta values thus enhancing the basal spacing. The (d\(_{001}\)) was 1.24 nm for natural bentonite clay but increase to 1.61 nm, 1.50 nm and 1.92 nm for Al/Fe-PILC, Al/Cr-PILC and Al/Zr-PILC, respectively. Al/Cr-PILC and Al/Zr-PILC gives an intense and well defined (d001) diffraction peak whereas Al/Fe-PILC produce less intense diffraction peak, but noticeable peak. Therefore, the XRD data indicate that the pillared clay catalyst modified with Cr and Zr metal oxides have more ordered structure compared to Al/Fe-PILC. Main compounds composed of montmorillonite with impurities like muscovite, calcite and quartz. The obtained XRD patterns in this study were in concordance with similar studies reported in the literature [1,3,6]. The XRD patterns of the materials before and after pillaring were very similar, which suggests that the starting clay structure was not destroyed during the pillaring method.
3.2.2. The specific surface area

The specific surface area of pillared bentonite clay improved significantly after pillaring process, indicating that metal oxides were efficiently intercalated into the interlayer space of natural clay layers. Table 2 shows the specific surface area of pillared clay materials ranged from 150 to 230 m$^2$/g. The BET surface area of bentonite catalysts Zr and Cr metal oxides were higher than that of Fe metal oxide catalyst. Usually, the BET surface area and pore structure are significant factors of catalysts in a solid phase, since catalytic activity reported in this study is directly proportional to their specific surface area. Owing to more porous structures of pillared bentonite clay materials being formed, Al/Zr-PILC (230 m$^2$/g) and Al/Cr-PILC (200 m$^2$/g) display much higher BET surface area than Al/Fe-PILC (150 m$^2$/g).

Table 2: Textural characterization of prepared catalysts (specific surface area, pore volumes and pore diameter)

| Sample         | Metal ratio | $S_{\text{BET}}$ (m$^2$/g) | $V_{\text{pore}}$ (cm$^3$/g) | $V_{\text{mic}}$ (cm$^3$/g) | $d_{\text{pore}}$ (nm) |
|----------------|-------------|----------------------------|-----------------------------|-----------------------------|------------------------|
| Bentonite      | -           | 61                         | 0.11                        | 0.089                       | 10.1                   |
| Al/Fe-PILC     | 3:1         | 150                        | 0.29                        | 0.1                         | 8.1                    |
| Al/Cr-PILC     | 1:1         | 200                        | 0.37                        | 0.113                       | 7.5                    |
| Al/Zr-PILC     | 3:1         | 230                        | 0.38                        | 0.115                       | 7.1                    |

1 Specific surface area ($S_{\text{BET}}$); 2 Total pore volume at p/p$^0$ ~ 0, 99; 3 Micropore volume; 4 Pore diameter
3.2.3. SEM-EDX

SEM investigations of all samples revealed the presence of untied and randomly distributed closely packed porous materials (images not shown here). Thus, natural bentonite clay mechanical structure can be appreciated and was not destroyed by pillaring process supporting our reported XRD results. The elemental composition of the bentonite clay materials were determined by EDX analysis (Table 3). The EDX profiles confirm the presence of Fe, Al, Si, Mg, Na, Cr, Ca and K elements for all samples. EDX results, shows that Al, Fe and/or Cr metal oxides contents enhanced with replacement of small interlayer polycations, such as Na and Ca due to pillaring by metal oxides pillars. The presence of impurities such as quartz and muscovite can be confirmed by the higher ratio of Si/Al [5].

Table 3: Physicochemical properties of the catalysts using EDX.

| Materials          | Al/Cr ratio | Mg (%) | Na (%) | Si (%) | Al (%) | Ca (%) | K (%) | Cr (%) | Fe (%) | Si/Al |
|--------------------|-------------|--------|--------|--------|--------|--------|-------|--------|--------|-------|
| Bentonite          |             | 2.29   | 3.73   | 65.09  | 15.31  | 2.09   | 2.39  | 0.00   | 9.10   | 4.25  |
| Al/Fe-PILC (1:3)   | 1.3         | 1.25   | 0.91   | 57.70  | 20.55  | 0.14   | 1.48  | 17.97  | 17.01  | 2.81  |
| Al/Cr-PILC (1:1)   | 1.1         | 1.22   | 0.97   | 59.01  | 19.02  | 0.21   | 1.61  | 13.58  | 4.38   | 3.10  |
| Al/Zr-PILC (3:1)   | 3.1         | 1.29   | 0.26   | 54.47  | 23.65  | 0.04   | 1.41  | 17.31  | 1.61   | 2.30  |

3.2.4. Zeta potential

The obtained results for zeta potential measurements are presented in Figure 4. The values of zeta potential for pure natural bentonite clay appear to be in agreement with those reported in the literature for a pH between 3 - 10 [16]. According to Baloyi et al., [6], the permanent negative charge of natural bentonite clay comes from isomorphous substitution of Si$^{4+}$ by Al$^{3+}$ and, also pH dependent charge from the hydroxyl groups at the edges of the clay sheets. As shown in Figure 4, at pH lower than the pH_{PZC}, all pillared clay catalysts are positively charged and at pH higher than the pH_{PZC}, it is negatively charged. These values may be associated with the formation of oxide pillars between starting bentonite clay sheets because of the hydration of Zr, Cr or Fe metal oxides intercalated into the intermellar space, during calcination.

Figure 4: Natural and pillared bentonite clays materials zeta potential (mV) values as a function of pH.
3.3. Leaching test
Since the stability of a catalyst is significant in the evaluation of catalyst performance, six consecutive runs were performed with all pillared bentonite clay catalysts. After each run, the CWAO effluent was filtered using 0.45 μm size Whatmann filter paper and the residue was washed with distilled water followed by drying at 120 °C for 16 h in an oven. The amount of Fe$^{3+}$, Zr$^{4+}$ and Cr$^{3+}$ metal leached were detected, in order to measure the stability of pillared bentonite catalysts, and results are shown in Table 4. The leaching amount of all metal oxides were lower than 0.5 mg/L after six times catalysts reuse, which can be neglected and this showing a stronger interaction of the metal oxides with the pillared bentonite clay catalyst surfaces and the higher stability of the catalysts and its suitability for continuous operation.

| No. of runs  | Leaching of Fe$^{3+}$ (Mg.L$^{-1}$) | Leaching of Zr$^{4+}$ (Mg.L$^{-1}$) | Leaching of Cr$^{3+}$ (Mg.L$^{-1}$) |
|--------------|-----------------------------------|-----------------------------------|-----------------------------------|
| First use    | 0.175                             | 0.001                             | 0.065                             |
| Re-use 1     | 0.198                             | 0.003                             | 0.096                             |
| Re-use 2     | 0.214                             | 0.005                             | 0.110                             |
| Re-use 3     | 0.221                             | 0.009                             | 0.118                             |
| Re-use 4     | 0.263                             | 0.010                             | 0.124                             |
| Re-use 5     | 0.275                             | 0.162                             | 0.160                             |
| Re-use 6     | 0.295                             | 0.283                             | 0.297                             |

4. Conclusions
In conclusion, the pillared clay catalysts used showed an increase in CWAO catalytic activity and efficiency of the materials. Intercalation of polyoxocation in interlamellar region of bentonite clay enhanced phenol oxidation. The major drawback for application of these materials which is the cost of pillaring agents that modify the bentonite clay, was overcome by applying the ultrasound treatment method during the synthesis of pillared bentonite clay catalysts. Moreover, starting raw bentonite clay was added directly as received to the pillaring solution. Therefore reducing the periods of synthesis and volume of water utilized during the preparation method, which decreases the capital cost of process. Findings in the current study provides the advantages for pillared clay synthesis method to be escalated to industrial production scale.

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