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Biodegradability enhancement of industrial organic raffinate containing pyridine and its derivatives by CWAO using ceria promoted MnO_x/Al_2O_3 catalyst at atmospheric pressure

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ABSTRACT

The catalytic wet air oxidation (CWAO) of non-biodegradable industrial organic raffinate containing pyridine and its derivatives (β-picoline, 3-cyanopyridine) was carried out using MnO_x/Al_2O_3 catalyst at atmospheric pressure. The catalyst was prepared using impregnation method and characterized using various techniques. The effect of metal loading, catalyst dosage, reaction temperature and operating pressure on degradation of industrial organic raffinate was studied and the results were interpreted in terms of COD removal. Experiments were conducted using spent catalyst to explore the reusability of catalyst. The metal leaching from the catalyst was studied by determining the metal content in the CWAO effluent. The effect of ceria as a promoter on biodegradability enhancement, catalyst recycling and metal leaching was studied. The biodegradability and toxicity tests confirmed the biodegradability enhancement and complete removal of toxicity of the CWAO effluent. The biological aerobic treatment of the CWAO effluent resulted in 98.36% COD removal.

1. Introduction

Pyridine and its derivatives are nitrogenous heterocyclic compounds used as industrial solvents and intermediates in making pesticides, pharmaceuticals, dyes, explosives etc. [1]. Pyridine compounds are recalcitrant in nature and pyridine itself is listed as a priority organic pollutant by the United States Environmental Protection Agency (USEPA) [2]. The chemical industries manufacturing pyridine compounds utilize various organic compounds and ammonia at high temperature and the effluent generated from such industries is toxic in nature and has high pH due to presence of nitrogenous compounds [3]. Therefore, it is difficult to treat effluent containing pyridine compounds by conventional biological processes.

Advanced oxidation processes (AOPs) have the potential for the treatment of effluent containing refractory organic compounds. The catalytic wet air oxidation (CWAO) is a promising technology for the degradation of refractory and nitrogenous organic compounds present in the industrial effluent. The CWAO is mainly used for achieving two objectives: (i) for complete oxidation of organic compounds into carbon dioxide, nitrogen and water (ii) for enhancing the biodegradability and decreasing the toxicity of the effluent by conversion of toxic compounds to biodegradable intermediates thereby allowing the use of biological methods for its further treatment. The conversion of complex organic compounds to biodegradable intermediates is much cheaper compared to complete mineralization as complete oxidation requires more energy.

The noble metal catalysts such as Pt, Pd, Ru and Rh have very high activity and stability towards oxidation of refractory organic compounds but are expensive. The low-cost transition metal catalysts (Cu, Fe, Mn, Ni) have been used by many researchers in CWAO for effluent treatment [4–6]. However, leaching of metal is the major drawback for the stability of these catalysts and the dissolved metal ions causes secondary pollution in the CWAO effluent. The MnO_x based catalysts have been reported as the most promising heterogeneous catalysts in terms of leaching [7]. Although MnO_x catalyst was efficient in oxidation of organics but the reaction was too slow to achieve the desired oxidation of organics [8]. One of the approaches for enhancing the oxidation rate of the organics involves the incorporation of promoters like CeO_2 into the catalysts which improve the catalytic activity by facilitating more oxygen mobility and enhancing the oxygen storage capacity in the reaction system [9]. The cerium oxide in association with manganese catalyst improves the redox property of the system by causing the surface and bulk vacancy in the reaction system [10].

Therefore, in the present study, the CWAO of industrial organic raffinate containing pyridine compounds and ammonical nitrogen was carried out using manganese oxide supported on alumina. The effect of ceria as promoter on the efficiency of CWAO was investigated. The

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catalysts were characterized by different analytical methods such as Brunauer, Emmett, and Teller (BET) surface area, Field Emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), transmission electron microscopy (TEM) and thermo-gravimetric analysis (TGA). The CWAO experiments were performed for optimization of various operating parameters such as metal loading, catalyst dosage and reaction temperature and the results were analyzed in terms of COD removal of industrial organic raffinate. The effect of the operating reactor pressure on the performance of the CWAO was investigated. The catalyst stability tests were performed by repeating the CWAO experiment thrice with same catalyst to explore reusability of the catalyst. The leaching test was performed to determine the metal (manganese) leaching from the catalyst into the CWAO effluent. The biodegradability and toxicity test of the CWAO effluent were carried out. The CWAO effluent was treated by biological aerobic and anaerobic techniques to achieve the discharge limits prescribed by statutory authorities.

2. Material and methods

The industrial organic raffinate, collected from a chemical industry manufacturing pyridine compounds, was characterized for various parameters and the results are shown in Table 1. It can be noticed that the effluent has high COD (15,000 mg/L) and is highly alkaline (pH 10.8) due to presence of toxic nitrogenous compounds and ammonical nitrogen. The BOD/COD ratio of the industrial organic raffinate is 0.078 suggesting that it is not suitable for biological treatment due to the presence of toxic compounds.

2.1. Catalyst preparation

The analytical grade reagent ($MnCl_2{\cdot}4H_2O$), purchased from CDH (Central Drug House), India was used in the catalyst preparation. The catalyst was prepared using impregnation method and different metal (manganese) loadings (1, 5, 10, and 12 wt%) was supported on alumina support. The quantity of the reagent ($MnCl_2{\cdot}4H_2O$) required for the specific catalyst with pre-determined metal content was calculated from the stoichiometry. Double distilled water was used in all these experiments. Initially, the alumina spheres were dried at 300 °C for 3 h and were used for the preparation of the catalysts. The aqueous solution of manganese of known concentration was added to 10 g dried alumina spheres and the slurry was placed in a rotary vacuum evaporator maintained at 70 °C for 3 h for metal impregnation. The excess water remaining in the slurry was evaporated under vacuum to achieve complete drying. The resultant residue was dried at 110 °C in an oven for 24 h followed by calcination at 500 °C for 5 h for complete decomposition of metal salts and deposition of the metal on the support structure. The calcined catalysts with different metal (manganese) loadings were stored in air-tight container for further use in the CWAO experiments.

Table 1
Characteristics of industrial organic raffinate.

Parameter	Value
pH	10.8
COD	15,000 mg/L
BOD/COD ratio	0.078
TDS	9800 mg/L
TSS	720 mg/L
Conductivity	12.2 mS/cm
Turbidity	10.6 NTU
Ammonical nitrogen	57,000 mg/L
Pyridine	500 mg/L
β-Picoline	2200 mg/L
3-Cyanopyridine	200 mg/L

*TSS: Total suspended solids.
TDS: Total dissolved solids.
NTU: Nephelometric turbidity unit.

The ceria promoted manganese catalyst was prepared by impregnation on alumina support using ($MnCl_2{\cdot}4H_2O$) and ($Ce(NO_3)_3{\cdot}6H_2O$) salts (purchased from CDH, India) as metal precursors for Mn and Ce respectively. The different wt.% of CeO_2 loading (1, 5, 10 and 15%) was supported on alumina support using known concentration of Ce metal solution and impregnation was carried out. The impregnation of 10 wt % of Mn metal was carried out after ceria impregnation on alumina and the prepared catalysts were named as MC1, MC5, MC10 and MC15 for different ceria loadings (1, 5, 10 and 15 wt%) respectively.

2.2. Catalyst characterization

The catalysts were characterized for BET surface area, pore volume and pore diameter by nitrogen adsorption-desorption isotherm using Micrometrics model ASAP 2010. The surface morphology of the catalysts was studied with FESEM analysis using Field Emission Scanning Electron Microscope (Nova Nano SEM 450). The elemental analysis of the catalysts was investigated using EDX equipped with the scanning electron microscope. The metal particle size distribution was carried out with TEM analysis using a Tecnai G2 F20 S-twin transmission electron microscope.

The crystal structure of the catalysts was studied by XRD using Cu-Ka radiation (k = 1.54 Å) at 40 kV/40 mA. The samples were scanned in the range of 2θ = 3–80° at a scanning rate of 3° per min and the results were matched with the JCPDS files to confirm the peaks of desired compounds. The average particle size of MnO_x/Al_2O_3 catalyst was calculated using Debye- Scherrer's equation by determining the broadening of X-ray diffraction peak, measured at one-half of the height. The TGA analysis of fresh and used catalysts was carried out in a TGA analyzer (Seiko TG/DTA 32 SSC5100) to check the deposition of carbon on the catalyst after CWAO reaction. The TGA analysis was performed in the presence of air and the furnace was heated to 900 °C at ramp rate of 10 °C/min.

2.3. CWAO experiments

The CWAO experimental setup is shown in Supplementary Fig. S1 [11]. The experiments were performed in a 4-neck round bottom glass flask of 3 L capacity. For a typical run, 1 L industrial organic raffinate was charged in the flask. The air, drawn from a compressor, was bubbled through the organic raffinate in the flask via a tube having very fine holes of 0.2 mm diameter to obtain uniform distribution of air. The air flow rate was fixed at a desired value and was measured using an air rotameter. The flask was heated using a heating mantle adjusted for a specific temperature and the temperature of the flask was kept constant using the temperature controller. Continuous stirring at a constant speed of 400 rpm was carried out in the flask using a magnetic stirrer. A condenser was placed at the top of flask to condense the vapors formed during the reaction and reflux back in the flask. A known amount of catalyst was added to the flask and the reaction started at 'zero time'. The effluent sample was withdrawn at regular time intervals to monitor the reaction progress and the sample was analyzed for chemical oxygen demand (COD). The reproducibility of the experimental results was checked by repeating the experiments thrice and the error in the experimental results was found to be less than 3%.

The high pressure experiments were carried out in an autoclave made of stainless steel. The capacity of the autoclave was 100 mL with design operating pressure and temperature up to 60 bar and 1000 °C respectively. The reactor was equipped with an electrically heated jacket, a turbine agitator and a variable speed magnetic drive. The temperature and the stirring speed were controlled by a PID controller. The air inlet, air release valve, pressure gauge and cooling water feed line were located on the top of the autoclave. Initially, 50 mL organic raffinate and 150 mg catalyst dose (3 g/L) were charged in reaction