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Catalytic oxidation of nitrobenzene by copper loaded activated carbon

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ABSTRACT

In the present study, catalytic wet peroxidation (CWPO) process has been applied for the degradation of nitrobenzene bearing wastewater using copper impregnated granular activated carbon with hydrogen peroxide as oxidant. Various catalysts were prepared by varying the Cu loading on activated carbon and these were characterized by N_2 adsorption–desorption, Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscope (FE-SEM), thermogravimetric analysis (TGA), temperature programmed reduction (TPR) and UV–visible diffuse reflectance spectra (UV-DRS). Effect of parameters such as copper loading, pH, catalyst dose, hydrogen peroxide dose and temperature were explored on nitrobenzene and total organic carbon (TOC) removal. TOC removal of 89% was achieved after 4 h treatment at optimum condition of Cu loading = 2.5 wt%, pH ≈ 3.0, catalyst dosage = 0.25 g/l, oxidant dosage = 4.5 (moles of oxidant/moles of NB) and temperature = 55 °C.

1. Introduction

Nitrobenzene (NB) is widely used as a raw material in many industrial processes which are used to make agricultural chemicals, pesticides, paper pulp production, dyes, rubbers and solvents for coating materials and explosives [1]. The large scale production, transportation and handling of NB and its derivatives inevitably releases it into the environment and poses a serious threat to the environment [2]. United States environmental protection agency (USEPA) has listed NB as a priority pollutant [3] and European Union directive identifies NB to be toxic to aquatic life [4]. NB is a carcinogenic and mutagenic environmental pollutant [5], which persists in the environment for long period and has a half-life of approximately 115 days in the aquatic atmosphere. NB and its derivatives cause serious threat to human beings. They are eye and skin irritants and affect the central nervous system also [6].

Traditional biological approaches of mineralization of organic compounds do not work with NB owing to its toxic and mutagenic activity [5]. The electron-withdrawing nitrogenous aromatic compounds also inhibit their oxidation by conventional oxidation as well as biodegradation routes. In recent years, several researchers have explored various advanced oxidation process (AOPs) for the degradation of recalcitrant organic pollutants [7,8]. In AOPs, hydroxyl radical are generated which have very high oxidation potential (2.8 V) next only to fluorine [9,10]. This hydroxyl radical reacts and oxidizes wide range of organic compounds present in water [11–13].

Catalytic wet peroxidation (CWPO) is more attractive as compared to other AOPs because of its simple process which can be carried out at near ambient temperature. CWPO is an emerging process for the degradation of recalcitrant pollutants at near ambient temperature and pressure. This catalyzed process requires lower activation energy and uses hydrogen peroxide as an oxidizing agent in the presence of a catalyst [14]. In CWPO process, different noble metal and transition metal oxides have been widely used as active phase to catalyze the oxidation of toxic organics present in the wastewater [15]. Hydrogen peroxide is a non-toxic reactant, relatively inexpensive and allows the catalytic wet peroxidation below 323 K temperature under atmospheric pressure, which reduces the operation cost [16].

Activated carbon received more attention due to its excellent catalytic support characteristics for the oxidation of organic compounds and because of its flexibility for tailoring catalysts properties to specific AOP application [17]. It is well know that activated carbon adsorbs chemical compounds from aqueous and gaseous phases, because of its has high surface area, flexible pore structure and chemical nature of the surface [17]. Activated carbon is stable under both acidic and alkaline environments and is relatively less expensive material. It can be synthesized from low cost materials (agricultural industrial wastes) [18,19]. During last decade, synthesis of metal oxide supported on activated carbon catalyst for the oxidation of organic wastewater has gained more attention. Among various metals, Cu is a common and most-effective precursor in catalytic applications [20].

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The objective of the present study was to evaluate the potential application of copper impregnated GAC (Cu/AC) catalyst for the CWPO of NB bearing wastewater. Cu/AC samples were synthesized and characterized by various techniques. The main aim of this study was to optimize the operating parameter for oxidation NB bearing wastewater using synthesized Cu/AC under atmospheric condition.

2. Methods and materials

2.1. Materials

All the chemicals used for in this study were of analytical grade. NB (S.D. Fine-Chem limited, India), activated carbon 1000 grade (Innova Corporate, India), Cu $(NO_3)_2 \cdot 3H_2O$ (Qualigens Fine Chemicals, India) and hydrogen peroxide (Merck specialties private limited, India) were purchased from various companies.

2.2. Catalyst synthesis and its characterization

Cu/AC samples were synthesized using incipient impregnation method. First GAC was washed with distilled water and dried in oven at 105 °C for 6 h. It was again washed with 4% HCl solution to remove impurities within the pores. Washed GAC was again dried in oven at 105 °C for 6 h.

To prepare 10 g of 1 wt% Cu/AC, an aqueous solution containing 0.381 g of copper nitrate $(Cu(NO_3)2 \cdot 3H_2O)$ was slowly poured into a flask containing 9.9 g of GAC. The volume of the solution was 1.78 ml/g catalyst, which represents a 10% excess with respect to the pore volume of the GAC. After impregnation of Cu, sample was dried in oven at 105 °C for 24 h to remove moisture, and then it was calcined in air atmosphere at 300 °C for about 4 h [21]. It was labeled as 1%Cu/AC. Similarly, 2.5%Cu/AC and 5%Cu/AC samples were made. Amount of Cu impregnation was checked by soaking 1 g of catalyst in 10 ml 65% nitric acid for 24 h at room temperature so as to dissolve the Cu from GAC. The concentration of the copper ion in the filtered solution was determined using atomic absorption spectrophotometer [20]. Amount of impregnation was found to be in the range of 0.9–0.96 times of that intended for different samples.

Surface area and porosity were determined by N_2 adsorption and desorption isotherms using Micromeritics ASAP 2020 instrument at −196 °C. Before analysis was performed, all samples were degassed at 150 °C to a vaccum 10^{-3} torr for 6 h. Surface area and micropore volume of samples were determined using the Brunauer–Emmett–Teller (BET) and t-plot equations, respectively, by assuming that all pores in the sample are cylindrical and parallel.

Fourier transform infrared (FTIR) spectrometer (Thermo Nicolet, USA) was employed to determine the chemical nature of activated carbon and Cu/AC over a spectral range of 4000–400 cm^{-1}. The sample powder was pressed with KBr (1:300 wt:wt ratio) to achieve a reasonable signal-to-noise ratio.

Differential thermal and thermo gravimetric analysis (DTA and TGA) experiments were carried out under air atmosphere at a flow rate of 200 ml/min in the temperature range of room temperature to 1000 °C with heating rate of 10 °C/min. Aluminum was used as a reference material and 8 mg of sample was placed in a ceramic crucible.

Temperature programmed reduction (TPR) experiments were performed out on a Micromeritics AutoChem 2920 equipment. For this, 50 mg catalyst was loaded into a U-shape quartz reactor and sample was degasified with argon (20 ml/min) at 150 °C for 2 h to remove physisorbed moisture. After cooling to room temperature, the gas was switched to 10% H_2 in argon flow (20 ml/min) and the catalyst was heated to 800 °C with a heating rate of 20 °C/min. Effluent gas was passed through a cold trap to trap moisture in effluent gas before reaching the thermal conductivity detector (TCD). The amount of H_2 consumption during reduction was monitored by a TCD.

UV–visible diffuse reflectance spectra (UV-DRS) of the Cu/AC samples was obtained in the UV region (200–600 nm) by a Shimadzu UV-2100 spectrometer with $BaSO_4$ as reference. The spectra were recorded at room temperature.

NB concentration was determined by finding out the absorbance at the characteristic wavelength using a double beam UV–vis spectrophotometer (HACH, DR 5000, USA). The wavelength corresponding to maximum absorbance (λ_{max}) was found to be 270 nm. pH adjustments was carried out by HI 2211 pH/ORP meter and purchased from Hanna Instruments.

The mineralization achieved was quantified by measuring the total organic carbon (TOC) conversion. TOC was determined by catalytic oxidation followed by quantification of the CO_2 formed through non-dispersive infrared (NDIR) detector, using a TOC-VCPH-analyzer (Shimadzu 5500A). This equipment finds out, in separate runs, the total carbon (TC) by combustion at 700 °C over a Pt catalyst bed, and the total inorganic carbon (TIC) by sample treatment with 25% phosphoric acid. TOC is obtained subtracting TIC from TC. TOC values represent the average of at least two measurements; in most cases each sample was injected three times, which is validated by the apparatus only if the standard deviation is less than 3%.

2.3. Experimentation

The experimental studies were carried out in a 250 ml three-necked round bottom glass reactor and equipped with a total reflux system. The total reflux prevented any loss of NB vapor. Magnetic stirrer was used to agitate the mixture and keep the solution homogeneous during the experimentation. The temperature of the reaction mixture was raised using the hot-plate to the desired value, and it was kept constant during the experimental run using a proportional–integral–derivative (PID) controller. In each run, the reactor was charged with 100 ml NB solution of required concentration. The oil bath was then heated up and stabilized to the desired reaction temperature called time zero (time $t = 0$ for the reaction was taken). When thermal equilibrium was reached, required amount of catalyst (Cu/AC) and oxidation agent (hydrogen peroxide) was added to reaction mixture.

3. Results and discussions

3.1. Catalyst characterization

The physical or porous structure is of vital importance in understanding the oxidation process and the catalytic activity of a catalyst. The total pore volume was estimated from the liquid volume of the adsorbate (N_2) at 0.99 relative pressure. Adsorption capacity of bare activated carbon was significantly higher than that of Cu/AC and the micropore volume of bare activated carbon was always

Table 1
Textural characteristics of the Cu/AC samples.

Sample	wt%	S_{BET} (m^2/g)[a]	V_p (cm^3/g)[b]	D_p (nm)[c]	$S_{Micropore}$ (m^2/g)[d]
AC	–	273	0.162	23	165
1%Cu/AC	1	70	0.0572	25	45.0
2.5%Cu/AC	2.5	36	0.0242	26	21.7
5%Cu/AC	5	24	0.0185	29	8.6

[a] S_{BET}: BET surface area.
[b] V_p: Total pore volumes were obtained at P/Po = 0.99.
[c] D_p: Average pore diameter calculated by BJH method.
[d] S_{BET}: t-plot Micropore area.