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A new approach for the degradation of high concentration of aromatic amine by heterocatalytic Fenton oxidation: Kinetic and spectroscopic studies

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ABSTRACT

In the present investigation an attempt was made to degrade aniline in the synthetic effluent by homogeneous and heterogeneous Fenton oxidation process. Experiments were carried out under the batch and continuous operating conditions. The effect of time, pH and the mass of mesoporous activated carbon on the degradation of aniline in the synthetic wastewater was critically examined through eexperimental design and optimization by central composite design (CCD) under the response surface methodology (RSM). The kinetic constants and the thermodynamic parameters for the oxidation of aniline in synthetic wastewater were determined. The degradation of aniline in synthetic wastewater was confirmed using FT-IR, NMR and UV–visible spectroscopy.

1. Introduction

Aniline and its derivatives are the important chemicals with major use as antioxidants [1,2]. It is widely used in dye, coal conversion, pesticides, rubber chemicals and pharmaceutical chemical manufacturing industries [3–5]. It is also a common by-product in the paper and textile industries [6]. The conventional treatment techniques currently employed in Common Effluent Treatment Plants (CETP)/Effluent Treatment Plants (ETP) include primary clarifiers, secondary biological aerobic/anaerobic systems, secondary clarifiers, sand filter and activated carbon filter [7–16]. The biological treatment processes used in conventional ETP/CETP are inefficient to remove aniline in wastewater due to its chemical stability, bio toxicity and poor biodegradability [177]. Aniline may be regarded as bio refractory organic compound and therefore the oxidation of aniline even in its lowest concentration, requires the use of strong oxidizing agents. Advanced Oxidation Process (AOP) is the use of hydroxyl radicals (•OH) in sufficient quantities to effect wastewater treatment and many studies have been recently concentrated on the possibility to improve an economic aspect of these AOPs [18–22]. The Fenton oxidation process is one of the AOPs which involve the catalytic oxidation of organics in waste water using hydroxyl radicals generated from the reaction between the ferrous ion (Fe^{2+}) and hydrogen peroxide (H_2O_2). The advantage of the Fenton oxidation process over other AOPs is that it is economical, convenient to use, produces non-toxic by-products and does not require any sophisticated or expensive instruments. The production of hydroxyl radicals from the ferrous ion catalyzed H_2O_2 is given as follows [23].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (1)$$

The ferric and hydroxyl ions are also formed during the Fenton's process due to the reaction between the •OH radical and the ferrous ion.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^{\bullet} \quad (2)$$

$$^{\bullet}OH + Fe^{2+} \rightarrow OH^- + Fe^{3+} \quad (3)$$

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad (4)$$

$$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \quad (5)$$

Although Fe^{2+} serves as a catalyst in the Fenton oxidation process the rate of regeneration of Fe^{2+} from Fe^{3+} (Eq. 2) is very slow compared to the consumption of Fe^{2+} in the reaction. Moreover, the hydroxide ion generated (Eq. 3) reacts with ferric ion to form ferric hydroxide sludge so that periodic addition of ferrous ion is desired. The ferric hydroxide containing wastewater is to be treated before it is discharged as it causes heavy metal pollution. Moreover, ferric

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hydroxide sludge also serves as the source to decompose hydrogen peroxide. Thus, conventional Fenton oxidation system is accompanied with the huge consumption of Fenton chemicals. There has been a constant research for enhancing the effectiveness of Fenton oxidation system with minimum consumption of chemicals. This is probable with prevention of formation of hydroxyl ion by removing one electron from it, this is possible with the help of semiconducting activated carbon, which is known as heterogeneous Fenton oxidation process. The •OH radicals that are formed during the reaction are transient and are highly reactive in nature.

Under heterogeneous mode the oxidation of organics was carried out using Fenton's reagent and mesoporous activated carbon (MAC) as a heterogeneous catalyst. The active sites of MAC are available for the adsorption of organic compounds according to the energy possessed by them. The organic compounds are oxidized using hydroxyl radicals produced during the Fenton reaction and they undergo sequential reactions into their products as explained under the mechanism. In this mechanism it is shown that two hydroxyl radicals are produced for every molecule of oxygen supplied. Hence, the concentration of OH• generated is controlled by the quantity of molecular oxygen that is supplied and the mass of activated carbon used [24]. The hydroxyl radicals and the organic ions adsorbed onto the active sites of the substrate undergo oxidation thereby resulting in mineralization into CO_2 and H_2O. The focal theme of this study is to compare and determine the effectiveness of homogenous and heterogeneous Fenton oxidation systems for the treatment of synthetic aniline containing wastewater.

2. Materials and methods

2.1. Materials and reagents

Aniline, ferrous sulfate ($FeSO_4 \cdot 7H_2O$), hydrogen peroxide (H_2O_2), sulfuric acid (H_2SO_4), and sodium hydroxide (NaOH), were of analar grade chemicals. The MAC was prepared in sequential steps such as carbonization at 400 °C and activation using phosphoric acid at 700 °C, 800 °C and 900 °C (Kennedy et al. [29]). The washed samples were then dried at 110 °C to get the final product and it was labeled as MAC_{700}, MAC_{800}, and MAC_{900}.

2.2. Characterization of MAC samples

The MAC samples have been characterized for their surface area, pore volume and pore size distribution using an automatic adsorption instrument (Quantachrome Corp. Nova-1000 gas sorption analyzer). The free electron density of MAC samples was determined using electron spin resonance spectroscopy (Bruker IFS spectrophotometer ESR). The elemental composition (Carbon, Hydrogen and Nitrogen content) of the MAC samples were determined using CHNS 1108 model Carlo-Erba analyzer (Table 1). X-ray diffraction technique (XRD) was used to determine the crystallites present in the MAC_{800} sample with a Philips X' pert diffractometer. A Perkin-Elmer infrared spectrophotometer was used for the investigation of the surface functional groups in the MAC samples. The surface morphology of MAC_{800} was determined using a Leo-Jeol scanning electron microscope. The Energy gap value was determined by using Diffuse Reflectance Spectroscopy. XPS was carried out in a VG Scientific ESCALAB-MkII XPS system using Al Kα radiation. Core level spectra for C 1s, O 1s, N 1s, and Si 2p were taken at high resolution and analyzed for chemical state information. On the surface silicon seems to be in two oxidation states one at 102.8 eV and 104.5 eV. The one at 104.5 eV is for silicon in SiO_2 and the other at 102.8 eV is at lower oxidation state.

Table 1
Characteristics of mesoporous activated carbon.

S. no.	Parameters	Values		
		MAC_{700}	MAC_{800}	MAC_{900}
1	Surface area (m^2/g)	345	379	439
2	Average pore diameter (Å)	38.82	39.36	35.28
3	Carbon (%)	42.56	41.58	37.96
4	Hydrogen (%)	3.14	2.85	2.40
5	Nitrogen (%)	0.82	0.75	0.50
6	Free electron density (spins/g)	8.51×10^{20}	16.05×10^{21}	15.98×10^{21}
7	Energy gap (eV)	1.35	1.55	1.52
8	Ash content (%)	41.24	41.60	45.68

2.3. Experimental setup

A PVC reactor of height 50 cm and diameter 6 cm was fabricated for continuous reaction study. The volume of the reactor was 1L with a working volume of 400 mL. The reactor was filled with 150 g of MAC_{800}, provision was made to distribute air in the MAC bed to facilitate oxygen for oxidation. The preliminary experiments on the effect of pH (2.5,3.0,3.5,4.0,4.5), initial concentration of aniline (1000, 1500, 2000, 3000 mg/L), concentration of hydrogen peroxide (2.5, 5.0, 7.5 and 10 mmol/L) and concentration of $FeSO_4 \cdot 7H_2O$ (0.1, 0.2, 0.3 and 0.4 mmol/L) , temperature (303, 313, 323 K) and MAC (2.5, 5, 7.5, 10 g/L) were carried out by batch mode to arrive at the optimum conditions for the oxidation of aniline in aqueous solution.

2.4. Kinetic study of Fenton oxidation of aniline

The rate and the order of the reaction for the homogeneous and heterogeneous Fenton oxidation of aniline were arrived using the linear form of first and second order reactions. The order of the reaction was determined by the quantity of fit for the coefficient of determination (R^2).

2.5. Spectroscopic analysis of aniline

UV–vis spectroscopic measurements of the samples were performed on a Varian, CARY 100C double beam spectrophotometer using 1 cm quartz cuvette and scanned from λ 200 to 800 nm. Fluorescence spectra in synchronous scan mode were recorded on a Varian, CARY eclipse fluorescence spectrophotometer. A scan speed of 400 nm min^{-1} was used with a slit width opening of 10 nm. Synchronous scan spectra were acquired in the excitation wavelength range of 300–850 nm. The FT-IR analysis was carried out for the untreated and treated aniline samples under transmission mode using a Perkin Elmer FTIR Spectrophotometer. The Nuclear Magnetic Resonance spectrum was recorded using JEOL ^{1}H NMR having frequency of 500 MHz.

2.6. Analytical methods

The synthetic initial aniline together with the homogeneously and heterogeneously oxidized aqueous aniline samples was analyzed for pH, Biochemical Oxygen Demand (BOD_5), Chemical Oxygen Demand (COD), Total Organic Carbon (TOC) and Total Dissolved Solids (TDS) according to the methods summarized in standard methods of analysis of wastewater.

3. Results and discussion

3.1. Control experiments

The scope of this experiment was to determine the oxidation of aniline by Fenton reagent as well as their loss due to their evaporation. The results obtained and the results reported demonstrate the fact that these compounds could be effectively oxidized by Fenton reagent and the loss due to other effects like volatilization was less than 5% in all cases.