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Process optimization for the treatment of pharmaceutical wastewater catalyzed by poly sulpha sponge



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ABSTRACT

In the present investigation, an attempt was made to treat the pharmaceutical wastewater (PWW) by Iron impregnated poly acrylamide (IPA) compound in a fluidized bed reactor as heterogeneous catalyst. The IPA was characterized by XRD, SEM, EDX, TGA, DSC, fluorescence spectroscopy and diffuse reflectance spectroscopy (DRS). The experiments were carried out under batch and continuous mode operations. The quantitative removal of COD, BOD_5 , NH_4^+ -N and TKN from the PWW was evaluated. The oxidation of organics in PWW was confirmed through UV–visible, fluorescence and FT-IR spectroscopy. In this study, the mechanism of oxidation of the persistent organic pollutants in pharmaceutical wastewater in terms of the generation of •OH radical using IPA was evaluated. The •OH radical was identified by electron paramagnetic resonance (EPR) spectroscopy and with 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) spin trapping method.

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1. Introduction

The manufacturing process of pharmaceutical chemicals generally involves several stages of refining and separation processes accompanied with generation of a huge volume of wastewater. The wastewater stream has an important ecological effect on the receiving water bodies containing flora and fauna. The hazardous nature of the residual persistent organic compounds in the treated pharmaceutical wastewater (PWW) demands a modified/efficient technology for the treatment wastewater for safe discharge. Many of the antibiotic compounds in PWW are difficult to degrade because of their complicated structures, refractory nature, and the potential endocrine modulating impacts on exposed aquatic organisms [1–4].

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The occurrence and fate of antibiotics and their transformed products in wastewater streams are recognized as the emerging issues in environmental chemistry [5–7]. The presence of these persistent organic pollutants in the aqueous ecosystem causes serious environmental and health concerns [8,9]. Antibiotics are of specific concern, as they can induce microbial aberrations, even at low concentrations [10–14]. Moreover, various pharmaceutical chemicals are not removed efficiently in conventional wastewater treatment plants or biodegraded in the environment while the mandatory is for complete elimination of them [15]. Conventional technologies generate concentrated and toxic residues during the removal of pharmaceutical chemicals in wastewater. The disposal of such residues on secured landfill becomes very much frustrating the industry as the cost of the treatment has been increased by many fold due to escalation in land price [16]. Hence, technologies accompanied with complete destruction of pollutants are preferred over the physicochemical, adsorption techniques that generate solid residues. The application of fluidized bed system for biological wastewater treatment has carried a remarkable significance in environmental engineering [17,18]. The fluidized bed catalytic reactor (FBCR) achieves the discharging standard within few hours [19] compared to conventional biological wastewater treatment systems (activated sludge process) which require longer retention time [20]. The immobilized biomass/attached biomass and onto support carrier matrix permit the limited replenishment without

Abbreviations: CCD, central composite design; VDS, volatile dissolved solids; APHA, American Public Health Association; ANOVA, analysis of variance; TSS, total suspended solids; COD, chemical oxygen demand; TOC, total organic carbon; BOD₅, biological oxygen demand; ORP, oxidation reduction potential; TKN, total Kjehldahl nitrogen; NH₄⁺-N, ammonical nitrogen; T, temperature (K); IPA, iron impregnated poly acrylamide; PWW, pharmaceutical wastewater; HRT, hydraulic retention time.

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impairment in the process efficiency. A number of natural and artificial materials that possess a significant internal porosity are used as carrier matrices as well as catalysts for the oxidation of organics in PWW [21–24]. Despite many carrier matrices being reported in the literatures, the exploration of new and efficient carrier matrices is not terminated. The objective of the present investigation was to use iron impregnated poly acrylamide matrix, as the carrier matrix and heterogeneous catalyst in the fluidized bed reactor and to evaluate its removal mechanism for the oxidation of organics in PWW.

2. Materials and methods

2.1. PWW and IPA catalyst

The PWW was collected from a commercial and export oriented pharmaceutical industry in Chennai, India. The wastewater was characterized for the physicochemical parameters such as pH, total organic carbon (TOC), Biological oxygen demand (BOD₅), chemical oxygen demand (COD), oxidation reduction potential (ORP), ammonical nitrogen (NH4⁺-N), total Kjehldahl nitrogen (TKN), sulphide, total dissolved solids (TDS) and total suspended solids (TSS) as per standard protocols (APHA, 1998). The Iron impregnated poly acrylamide (IPA) compound was supplied by Good Earth Chemicals Pvt. Ltd., Hospet, Karnataka, India (Patent number EP1392874 A1). The IPA compound was used as heterogeneous catalyst in the present investigation without any modification. The IPA compound was characterized for chemical elements, surface area, pore volume and pore size distribution using an automatic adsorption instrument (Quanta chrome Corp. Nova-1000 gas sorption analyzer).

2.2. Chemicals and instruments

All pH measurements were carried out with a microprocessor based pH meter (model number HI 98107 Mumbai, India). X-ray photoelectron spectroscopy (XPS) was carried out in a SPECS XPS system using 150 W Al-K α radiation. High resolution spectra of C 1s, O 1s, N 1s and Fe 2p core levels were obtained at a pass energy of 25 eV. The spectra were fitted with Gaussian-Lorentzian components to determine different oxidation states. Particle size distribution by light intensity measurement was analyzed using Malvern (MAL 1066495). The elemental composition (carbon, hydrogen, nitrogen and sulphur) of the samples was determined using CHNS (1108 model Carlo-Erba analyzer). X-ray diffraction (XRD) analysis was carried out on a Rich Siefert 3000 diffractometer using Cu-K α 1 radiation (λ = 0.1541 nm). The EPR spectra were obtained at room temperature using a quartz liquid flat cell (Wilmad WG-812-Q) in a TE102 cavity of a Bruker ESP 300E spectrometer. An infra-red spectrophotometer (Perkin-Elmer) was used for the investigation of the surface functional groups in IPA compound and wastewater samples. The scanning electron micrograph (SEM) was recorded to study the surface morphology of IPA compound using scanning electron microscope (Hitachi-3860). The energy gap value of the compound was determined by using diffuse reflectance spectroscopy (DRS) (Carry 100 Conc UV-vis spectroscopy). The Thermo Gravimetric Analysis (TGA) was carried out under reduced nitrogen atmosphere from 30 to 800 °C, at a heating rate of 10 °C/min and scans were recorded using TGA Q50 (V20.6 Build 31). The differential scanning calorimetric (DSC) analysis was carried out using DSC Q200 (V23.10 Build 79). The total organic carbon (TOC) was measured by using the TOC analyzer (Shimadzu TOC VCPH apparatus). The UV-vis spectra of raw and treated PWW were recorded, using UV-vis spectrophotometer (Cary100). Fluorescence measurements were recorded by Fluorescence Spectrophotometer (Varian Cary Eclipse, S.no: EL07023695) equipped with a 150 W

Table 1

Characteristics	of	IPA	compound.	
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S. No.	Parameters	Values
1	Surface area (m ² /g)	99.66
2	Average pore diameter (Å)	58.32
3	Pore volume (cc/g)	0.218
4	Moisture content (%)	5.74
5	Carbon (%)	12.23
6	Hydrogen (%)	1.63
7	Nitrogen (%)	2.93
8	Sulphur (%)	0.0554
9	Fe ₂ O ₃ (%)	58.00
10	SiO ₂ (%)	15.25
11	Al ₂ O ₃ (%)	3.74
12	Mn ₂ O ₃ (%)	0.14
13	P ₂ O ₅ (%)	0.08

xenon lamp at ambient temperature of $27 \,^{\circ}$ C and a scan rate of 600 nm/min and 1 cm quartz cuvette with four optical windows was used for the analysis. All the chemicals used were of the highest purity and analytical grade. The characteristics of IPA compound are shown in Table 1.

2.3. N₂ adsorption-desorption isotherms

The N₂ adsorption–desorption isotherms of the IPA compound were determined by using an automatic adsorption instrument (Quanta chrome Corp. Nova-1000 gas sorption analyzer) for the determination of surface area and the total pore volume. Prior to measurement, the IPA compounds were degassed at 110 °C for overnight in hot air oven. The nitrogen adsorption–desorption data were recorded at liquid nitrogen temperature of 77 K. The surface area of the samples was calculated using the BET equation. The pore size distribution was determined using BJH method. In addition, the *t*-plot method was applied to calculate pore volume and external pore surface area (mesoporous surface area). The total pore volume was estimated in terms of the liquid volume of adsorbate at a relative pressure of 0.99. All surface area measurements were calculated from the nitrogen adsorption isotherms by assuming the area of the nitrogen molecule to be 0.162 nm².

2.4. Taguchi's orthogonal array experiments

Taguchi experimental design matrix, a standard orthogonal array L_{25} (4^5) was used to examine four factors in five levels. The L and the subscript (25) represent Latin square and the number of experimental runs, respectively. The levels of factors and experimental design of the L_{25} Taguchi's orthogonal array, provided by the software Minitab (Ver. 14.0, U.S. Federal Government Commonwealth of Pennsylvania, USA) are shown in Table 2. Based on the primary results, a verification test was also performed to check the optimum condition. An analysis of variance (ANOVA) for the obtained results was investigated. The total degree of freedom available in an orthogonal array is equal to the number of trials minus one. Besides determining the optimum conditions of the factor levels, the primary objective also includes the determination

Table 2Trial levels of factors in Taguchi's orthogonal array experiment.

Factors	Level 1	Level 2	Level 3	Level 4
рН	4	6	8	10
Temperature (°C)	20	30	40	50
Catalyst (g)	10	20	50	80
PWW (%)	25	50	75	100

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