



Lignocellulosic-derived modified agricultural waste: Development, characterisation and implementation in sequestering pyridine from aqueous solutions



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ABSTRACT

The development and characterisation of modified agricultural waste (MAW) by H_3PO_4 activation is addressed in this study for sequestering pyridine from aqueous solutions. The adsorbent is characterised by carbon, hydrogen and nitrogen content of 55.53%, 3.28% and 0.98% respectively. The adsorbent also shows acidic (carboxylic, lactonic, phenolic groups) and basic carbon surface functionalities, functional groups viz. hydroxyl, carboxylic acid and bounded water molecules, BET surface area of $1254.67 \text{ m}^2 \text{ g}^{-1}$, heterogeneous surface morphology and graphite like XRD patterns. Adsorption of pyridine is executed to evaluate the adsorptive uptake in batch ($q_e = 107.18 \text{ mg g}^{-1}$) as well as in column system ($q_e = 140.94 \text{ mg g}^{-1}$). The adsorption process followed the pseudo-second-order kinetics with the Langmuir isotherm best representing the equilibrium adsorption data. The thermodynamic parameters ($\Delta H^\circ = 9.39 \text{ kJ mol}^{-1}$, $\Delta G^\circ = -5.99 \text{ kJ mol}^{-1}$, $\Delta S^\circ = 50.76 \text{ J K}^{-1} \text{ mol}^{-1}$) confirm the endothermic and spontaneous nature of the adsorption process with increase in randomness at solid/solution interface. The adsorption mechanism is governed by electrostatic and π - π dispersive interactions as well as by a two stage diffusion phenomena. Thermally regenerated spent MAW exhibited better adsorption efficiency for five adsorption–desorption cycles than chemically regenerated. The low-cost of MAW (USD 10.714 per kg) and favourable adsorption parameters justifies its use in the adsorptive removal of pyridine.

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1. Introduction

Pyridine is a colourless, volatile, highly inflammable, foul-smelling, toxic organic liquid which when decomposed (in bare atmosphere) gives extremely toxic vapours of NO_x [1]. Pyridine vapours cause eye irritation and its exposure can lead to dermatitis, headache, dizziness, nausea, insomnia and anorexia. It is potentially carcinogenic [2] and can cause immune system failure, gastrointestinal disorder, reproductive malfunctioning, liver and kidney damage. It is an amphiphilic molecule with pretty high solubility in polar solvents (water) and apolar solvents (alcohol, benzene, ether, etc.). It is extensively used for chemical applications viz. production of piperidine, denaturation of alcohol and in anti-freezing mixture [3]. Pyridine acts as an industrial solvent [4] in the preparation of paints, adhesives, textile water-repellents, polycarbonate resins and corrosion inhibitors. Pharmaceutical industries also use pyridine for drug synthesis and extraction of plant hormones. Pyridine derivatives act as analgesic, local anaesthetics and respiratory stimulants [5]. It also acts as an intermediate in the

manufacturing of herbicides, insecticides and fungicides for agricultural applications [6]. The carbonisation of coal gives rise to pyridine and several of its derivatives which constitute the effluents of coking industries. Among the organic components of coal tar, 5% are heterocyclic compounds, out of which 0.2% accounts for pyridine [4]. Pyridine concentration in the industrial effluents of India is in the range of $20\text{--}300 \text{ mg L}^{-1}$ [1]. However, emergency spills can amount to considerable values. The hazardous and enduring nature of pyridine and its derivatives can be a potential threat to diverse ecosystem [7]. Therefore, the exclusion of pyridine from contaminated water stream is of utmost concern to prevent diseases and environmental pollution.

Pyridine bearing water/wastewaters are treated by diverse techniques which include adsorption [8,9], adsorption and electrosorption [10], biodegradation via free and immobilized cells [11–14], ozonation [15], photocatalytic degradation [16], electrochemical oxidation [17], and ion exchange [18]. Amidst these techniques, adsorption is the best choice as it works on ambient temperature and pressure, without the generation of hazardous by-products. Moreover there are means of adsorbent regeneration and reuse. The popular and efficient adsorbent widely used is activated carbon but its use in wastewater treatment is highly

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expensive. This justifies the use of low cost alternatives to activated carbon. The viability of inexpensive adsorbents such as ion exchange resins [18], zeolites [19], different clay minerals [20–21], rundle-spent shell [22], combusted oil shell [23], bagasse fly ash [1], activated carbon derived from coconut shells and fibres [24], rice husk ash [25], and expensive adsorbents like granular activated carbon (commercial) [25], activated carbon cloth [26], apatite [27], and carbon nanotubes [28] was explored by researchers for the removal of pyridine from aqueous phase.

The present study utilizes modified agricultural waste, a low-cost adsorbent prepared by chemical impregnation of coconut coir by H_3PO_4 for the removal of pyridine. Although coconut coir was used for the removal of pyridine by other researchers [24], the adsorbent prepared by the reported method shows highest adsorption capacity so far reported in the literature. The adsorption process was carried out in batch/column system with emphasis on kinetics, isotherm modelling, error analysis and thermodynamic feasibility as well as regeneration/reusability studies. Cost estimation of the developed adsorbent, comparative assessment of its adsorption capacity with other conventional/non-conventional adsorbent was also done.

2. Materials and methods

2.1. Chemicals and materials

All the chemicals/reagents used in the present study were of analytical reagent grade and procured from Merck (India) Ltd. Ultra-pure water (18.0 M Ω cm) for the experiments is obtained from a Merck Millipore Milli-Q system. Pyridine (acronym: Py, chemical formula: C_5H_5N , formula weight: 79.10 g mol $^{-1}$, purity: 99%) is the adsorbate under investigation in the present study.

2.2. Simulated Pyridine (Py) solution

A stock solution of Py (1000 mg L $^{-1}$) was prepared in the laboratory and was further diluted to attain the requisite test concentration (50–600 mg L $^{-1}$).

2.3. Adsorbent/material – collection and development

The investigated precursor material – coconut coir, a hard endocarp lignocellulosic agricultural waste was collected from nearby areas of NIT Silchar, India. The collected biomass is cut into small pieces, thoroughly washed with water to remove dirt and impurities adhered to its surface and oven-dried at 378 K for 5 h. The dried biomass is then chemically impregnated (impregnation ratio = 2.0) by ortho-phosphoric acid (98%) at 373 K for 1 h till the formation of paste. The paste was then transferred to an alumina crucible and carbonized in a PID controlled muffle furnace (heating rate: 293 K min $^{-1}$) under N_2 flow (100 cm 3 .min $^{-1}$) to a temperature of 723 K maintained for 1 h. The activated product was then exhaustively washed with ultra-pure water to remove free acids until the washings reached pH~7 and dried in an oven at 383 K for 6 h. The adsorbent thus developed is referred to as modified agricultural waste and henceforth abbreviated as MAW.

2.4. Characterisation of the developed adsorbent

2.4.1. Yield of modified agricultural waste (Y_{MAW}) and chemical recovery (CR)

The yield of modified agricultural waste (Y_{MAW}) and chemical recovery (CR) [29] were computed according to the following equations:

$$Y_{MAW}(\%) = \frac{W_{MAW}}{W_{AW}} \times 100 \quad (1)$$

$$CR(\%) = \frac{W_{SB} - W_{MAW}}{W_{IC}} \times 100 \quad (2)$$

where W_{MAW} is the weight of the obtained modified agricultural waste, W_{AW} is the weight of agricultural waste used, W_{SB} is the weight of the sample before washing, and W_{IC} is the weight of impregnated chemical.

2.4.2. Physico-chemical characterisation

The proximate and ultimate analysis of MAW was performed as per ASTM standard (American Standard for Testing and Materials). The proximate/macro analysis (ASTM D-3172) of the adsorbent encompass the determination of moisture content, volatile matter, ash and fixed carbon content as wt%. (as received), using a Hot Air Oven and a Muffle Furnace. The ultimate/micro analysis (ASTM D-3176) includes determination of carbon, hydrogen and nitrogen content as wt%. (dry ash free basis) which was done on a Thermo Finnigan FLASH EA 1112 series CHN Analyzer.

The identification of oxygen surface functional groups of the adsorbent such as carboxyl (R–COOH), lactone (R–OCO) and phenol (R–OH) was done by adopting Boehm titration [30]. The titration procedure was performed according to the standardized method described in detail elsewhere [31]. The number of moles of acidic and basic carbon surface functionalities on MAW was computed from Eqs. (S1 and S2) respectively given in the supporting information.

The point of zero charge (pH $_{ZPC}$) is the pH at which the charge on the surface of the adsorbent (MAW) is zero. In this experimental study, the pH drift method [32] is adopted to compute pH $_{ZPC}$ of the adsorbent, and the detail procedure is given in the supporting information.

2.4.3. Textural and functional group characterisation

A Micromeritics, ASAP 2010 Surface Area Analyser was used to determine the textural features of the adsorbent. N_2 adsorption isotherm at 77.71 K in the relative pressure (P/P_0) range was used to determine the Brunauer–Emmett–Teller (BET) surface area by using the Brunauer et al. Equation [33]. BJH (Barret–Joyner–Halenda) desorption method was used to calculate the average pore diameter and cumulative volume of the pores.

The particle size analysis of the adsorbent was done on a Malvern Mastersizer 2000 Particle Size Analyser. Wet type dispersion (Dispersant:Water) is adopted in determining the particle size of the adsorbent in the size range of 0.020–2000 μ m.

Fourier Transform Infrared (FT-IR) Spectroscopic analysis of the adsorbent sample was performed on a Nicolet MAGNA-550 FTIR Spectrophotometer in the range 4000–400 cm $^{-1}$ to characterize the functional groups on the surface of the adsorbent.

2.4.4. Electron microscopy and X-ray diffraction

The texture and morphology of the adsorbent was examined by a Scanning Electron Microscope (SEM, Model: Leo 1430vp). The sample was first gold coated using Sputter Coater, Edwards S150, which provides conductivity to the sample, and then the SEM images were taken.

The Powder X-ray diffraction (XRD) patterns were obtained on a X-ray Diffractometer (XRD, Make: Philips, Model: PW 1710) with X'pert software using 40 kV, 30 mA, Cu K α radiation ($\lambda = 1.546 \text{ \AA}$) with a scan speed of 1 $^\circ$ min $^{-1}$ in the scanning range of 15–80 $^\circ$ in 2θ at 298 K. Qualitative analysis was computed by comparing with JCPDS database and indexed with POWD software.

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