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Removal of 2,4-dichlorophenoxyacetic acid from aqueous medium using modified jute

Suvendu Manna[a], Prosenjit Saha[a,1], Debasis Roy[b,*], Ramkrishna Sen[c], Basudam Adhikari[a]

[a] Materials Science Centre, IIT Kharagpur, WB 721302, India
[b] Department of Civil Engineering, IIT Kharagpur, WB 721302, India
[c] Department of Biotechnology, IIT Kharagpur, WB 721302, India

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ABSTRACT

Aromatic hydrocarbons such as 2,4-dichlorophenoxyacetic acid (2,4-D), a common herbicide, is often found in groundwater in areas with intensive agricultural activities. Even in minute concentration, they are known to affect human health. An attempt has been made to capture 2,4-D from aqueous medium using neemoil-phenolic resin treated lignocellulosic jute. Treated jute showed 84% 2, 4-D removal efficiency. The 2,4-D removal of the biosorbent was confirmed from FTIR and ^{13}C NMR analyses. The adsorption process was found to be spontaneous and effective over a pH range between 2 and 8. Maximum 2,4-D removal capacity of treated jute was found to be 38.5 mg/g. Treated jute was found to remove 2,4-D from aqueous media economically and efficiently through polar–polar and non-polar–non polar interactions. No sludge was produced during 2,4-D removal with treated jute nor did the process introduce deleterious characteristics, *e.g.*, hardness and odor to the treated water.

1. Introduction

Aromatic hydrocarbons (AH), e.g., 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid, mertibuzine, alachlor and fluchloralin are used extensively as herbicides in agricultural fields. These AHs leach from the agricultural fields and contaminate surface and groundwater [22]. AHs even in small concentration are known to be carcinogenic, neurotoxic and bioaccumulative [1,17,25].

These chlorophenolic AHs have been removed by reverse osmosis (RO) [20]. Although reverse osmosis is very efficient in removing AHs from water, the process requires continuous electrical power to maintain the requisite pressure differences. Effectiveness of the process is also compromised because of susceptibility of RO membranes to surface polarization, biological fouling and ionic interferences. Additionally the process retains as much as 40% of the influent with elevated levels of initial ionic constituents, which is difficult to handle and dispose. AHs are also removed from water through photodegradation [6]. Although photodegradation is efficient in removal of waterborne AHs, they require metallic photocatalyst which remains in the water and could pose health hazards. In addition this process requires electrical power supply. Metal oxides [7], organo-metalic complexes [19] and clays [4,30] were used to adsorb waterborne AHs. Relative technical advantages of these adsorbents are compromised because of the need for energy-intensive pre-processing and harmful leachate generation potential. Additionally, these adsorbents are efficient only over narrow pH ranges. Carbon nanotube [3] and metal oxide nanoparticle doped within activated carbon [37] were also used for 2,4-D removal from water. These adsorbents are manufactured from energy intensive processes and are expensive. Also, these adsorbents are known to be cytotoxic and genotoxic to human cells and appear to be in need of examination for their leachate generation potential before they can be adopted for large scale water treatment [36,43]. The shortcomings of the processes surveyed above could be overcome by employing a suitable biomaterial to adsorb waterborne AHs. Granular activated carbon [8,29], chitosan–sodium alginate ([27], zinc oxide loaded chitosan [9], fungal biomass [10] and brown algae [13] were used to remove chlorophenolic AHs from water. However, these adsorbents work well only over acidic pH range and their removal efficiency were compromised in the presence of competitive anions.

Although inexpensive and widely available lignocellulosic plant matters used to adsorb waterborne AHs, showed poor removal efficiency (Fig. 1) [4,7,37]. AHs removal efficacy of lignocellulosic plant matters could be enhanced by modifying them. Since, AHs have lipophilic side chains [39,40] lignocellulosic plant matter

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[*] Corresponding author.

[1] Current address: Dr MN Dastur School of Materials Science, IIEST Shibpur, Howrah 711103, WB, India.

E-mail address: debasis@civil.iitkgp.ernet.in (D. Roy).

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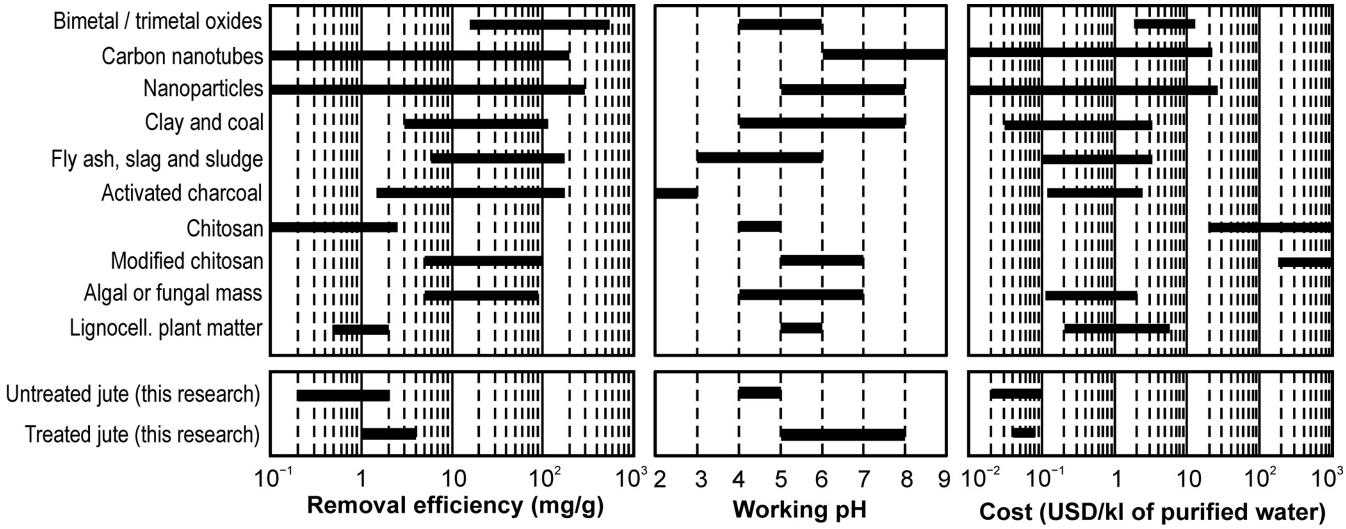

Fig. 1. Comparative assessment of available 2,4-D removal alternatives.

grafted with fatty acyl chains found in vegetable oil could be a more attractive alternative in removing these AHs. In this study lignocellulosic jute powder was grafted with vegetable oil and examined for its potential in removing 2,4-D from water. Efficacy of the grafted jute in 2,4-D removal was compared with those of available techniques. Recycle and regeneration potential of grafted jute were also investigated in this research. No report could be found in the literature on capturing AHs from aqueous medium through non polar non polar interaction as was accomplished in this study. The process was found to work over a wide pH range and compare favorably against available alternatives in terms of removal efficiency and cost.

2. Experimetals

2.1. Biomass treatment

The locally sourced jute (*Chorcorus olitorius*) fibers, was washed with distilled water, dried at 85 ± 2 °C and chopped mechanically in a mixer grinder to powder and termed UJ hereafter. Portions of UJ were kept immersed within 0.5% (w/v) NaOH (Merck) solution for 30 min at 30 ± 2 °C followed by steam treatment under 103 kPa for 30 min at 121 °C. Thereafter, the alkali-steam treated jute (AJ) fibers were washed with distilled water to bring down its pH to 7. Optimization of process parameters and conditions for alkali-steam treatment were as per the report published elsewhere [34].

An emulsion was prepared by mixing sodium hydroxide, cashew nut shell liquid, resorcinol, neem (*Azadirachta indica*) oil and formaldehyde in 0.5:1:2:5:2 proportion by weight, stirring for 1–2 h at 30 °C and diluting the mixture with distilled water to obtain 1.0% solid content. The AJ fibers were immersed in this emulsion for 15 min (1 kg jute immersed in 2 l of emulsion) for soaking. After soaking the jute was dried, cured at 105 ± 5 °C for 1 h, washed with ethanol and distilled water to remove unreacted reagents and again dried at 70 ± 2 °C for 24 h and termed NJ hereafter. The formulation and conditions of the resin treatment process stated above was achieved through rigorous optimization processes with respect to the removal efficacy of the treated biosorbent.

2.2. Characterization of biomass

2.2.1. Fourier transform infrared (FTIR) spectroscopy

Pellets were prepared from dried jute powders (1–2 mm long) and potassium bromide (KBr) in the ratio 1:100 (w/w) for FTIR spectroscopic analysis (Thermo Nicolet, Nexus 870). The IR wavenumber between 4000 cm^{-1} and 400 cm^{-1} were covered using 32 scans in the investigation. The ratio of absorption intensities representing OH vibration (at wavenumber of 3300 cm^{-1}), I_{3300}, and CH vibration (at 2980 cm^{-1}), I_{2980}, was used as an index of mean hydrogen bond strength (MHBS) [12]. The tests were run on three samples to assess repeatability.

2.2.2. ^{13}C CPMAS solid state NMR spectroscopy

^{13}C cross-polarization magic angle spinning (CP-MAS) solid state NMR spectra were obtained for 250-mg tightly-packed biomass within a 4-mm Zirconia rotor sealed with KEL-F cap with Bruker AV-300 FT spectrometer operated in 7.01-T magnetic field. A double resonance CP-MAS probe head capable of handling high radio frequency power and spinning samples at the ’magic angle’ tuned to 75.48 MHz (^{13}C) Larmor frequency matched to 50 Ω circuit impedance was used. Contact time of 13 ms was used. Data were obtained in 0–180 ppm spectral window with 10–15 Hz line broadening before Fourier transformation. The ^{13}C chemical shifts were referenced externally to tetramethylsilane (TMS). The data were processed with Bruker TOPSPIN (Version 3.0) software.

2.2.3. Scanning electron microscopy

About 1–2 mg of ethanol washed jute powder with 1–2 mm in length were oven dried at 80 ± 5 °C and coated with thin gold layer in a plasma sputtering apparatus. Tungsten filament electron gun cathode of a TESCAN VEGA$_{\text{LSV}}$, (Czech Republic, 2006) scanning electron microscope operated in high-vacuum with an electron beam generated using 5–10 kV electrical field guided to fall on the sample surface. The secondary electrons released from the sample surface were made to pass through a detector to create a digital image.

2.3. Estimation of 2,4-D in water

The amount of 2,4-D present in water was estimated by measuring the optical density of aqueous solution at 228 nm in a UV spectrophotometer (Perkin-Elmer Lambda 950) and comparing the optical density with 2,4-D standard curve ($y = 0.0074x$) [30].

2.4. Separation of 2,4-D in batch process

Influence of pH, temperature, contact time, biomass amount and concentrations of competitive ions on removal efficiency was investigated through series of batch experiments The influence of