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Research article

Biosorptive uptake of ibuprofen by steam activated biochar derived from mung bean husk: Equilibrium, kinetics, thermodynamics, modeling and eco-toxicological studies

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ABSTRACT

The present study explores the use of steam activated mung bean husk biochar (SA-MBHB) as a potential sorbent for the removal of non-steroidal and anti-inflammatory drug ibuprofen from aqueous solution. SA-MBHB was characterized by SEM, FTIR, BET, TGA, point of zero charge (pH_{PZC}) and UV–Vis spectrophotometer. The relation between removal percentages of ibuprofen and parameters such as adsorbent dose (0.05 g–250 g), contact time (5 min–210 min), pH (2–10), speed of agitation (40–280 rpm), temperature (293–308 K) and initial ibuprofen concentration (5–100 ppm) was investigated and optimized by a series of batch sorption experiments. The optimized conditions achieved were: adsorbent dose 0.1 g/L, agitation speed 200 rpm, pH 2, initial ibuprofen concentration 20 mg L^{-1}, equilibrium time 120 min and temperature 20 °C for more than 99% adsorptive removal of ibuprofen. The equilibrium adsorption data were well fitted into the Langmuir isotherm model while kinetic data suggested the removal process to follow pseudo second order reaction. The adsorption phenomena were optimized and simulated by using response surface methodology (RSM) and artificial neural network (ANN). Effect of process variables viz. dose, agitation speed and pH on the sorbed amount of IBP was studied through a 2^3 full factorial central composite design (CCD). The comparative analysis was done for ibuprofen removal by constructing ANN model training using same experimental matrix of CCD. The growth of *Scenedesmus abundans* was also observed to be affected by the IBP solution whereas the biochar treated with IBP solution did not significantly affect the growth of the *Scenedesmus abundans*. The results revealed that SA-MBHB could be a cost-effective, efficient and non-hazardous adsorbent for the removal of ibuprofen from aqueous solution.

1. Introduction

Ibuprofen (IBP) is one of the most widely used drugs for the treatment of inflammatory disorders such as rheumatoid arthritis and relief of pain. Ibuprofen [2-(4-isobutylphenyl) propanoic acid] is chemically a non-steroidal, anti-inflammatory (NSAID), antipyretic and analgesic drug (Sabri et al., 2012). 4-isobutylacetophenone (4-IBAP) is the toxic degradation product of IBP and produces adverse effects on the central nervous system. IBP, along with human body, degrades metabolites such as hydroxy-IBP, carboxy-IBP and carboxy-hydratropic acid (Fent et al., 2006). The concentrations of IBP in different European countries along with Canadian wastewater system are found to be ranged from 60 to 3400 ng/L (Andreozzi et al., 2003; Öllers et al., 2001; Ternes, 1998).

Several techniques have been reported by researchers towards removal of ibuprofen viz. ultrasonic irradiation (Méndez-Arriaga et al., 2008), ultrafiltration membrane (Sheng et al., 2016), combined advanced oxidation processes (Madhavan et al., 2010), nanofiltration (Vergili, 2013), electrochemical degradation (Ciríaco et al., 2009), microcosm constructed wetlands (Dordio et al., 2010), adsorption on commercial carbon from coal (Mestre et al., 2009), adsorption on SBA-15 (Bui and Choi, 2010), zeolites (Martucci et al., 2012), magnetic nano-composite (Singh et al., 2012) or activated carbons (Kyzas et al., 2015; Baccar et al., 2012). Among them, adsorption process has been proved to be an efficient contaminant

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removal technique where the material activated carbon is used to purify low concentrated water contaminants (Mestre et al., 2009). However, commercial carbon has some limitations viz. economically non-feasible; short lifetime, expensive and less regeneration capacity. So the low cost or zero cost precursors such as MBH has dual advantages like cost-effective precursor for preparation of carbonaceous adsorbent along with solution for waste disposal problem and recycling (Cabrita et al., 2010; Mestre et al., 2011).

Easy availability and very negligible purchasing cost of several agricultural waste materials make them suitable candidates for their use in pollutant remediation either as a raw material or modified form like activated biochar. Till date, several researchers have reported on removal of different pollutants by using sorbent materials in powdered form derived through various agricultural wastes such as sugarcane biomass, peanut husk etc or modified into useful product such as cork powder waste modified carbon (Mestre et al., 2007), potato peels modified carbon (Kyzas and Deliyanni, 2015), pine chips bark modified carbon (Jung et al., 2013) etc. In this context, application of modified activated biochar indigenously developed from mung bean husk as an adsorbent is the first attempt reported yet for removal of IBP from aqueous media.

Mung bean (*Vigna radiate*) is a leguminous species grown in different parts of the world, especially in Asia (90%) including India, China, Burma, and Thailand. India is the leading producer of this crop (Lambrides and Godwin, 2007). During milling of mung bean, huge quantity of husk is generated. This agro by-product has been effectively used as a precursor of the adsorbent for IBP removal in the present study.

The unicellular microalgae *Scendesmus* sp. is ubiquitously present in aquatic system and frequently used as a eukaryotic model organism in eco-toxicity studies through the growth inhibition toxicity test (Lewis, 1995). Eco-toxicity analysis was performed for assessing whether the treated water was biologically safe and fit for discharge or reuse.

The main objective of the present study was to evaluate the efficacy of SA-MBHB as low cost adsorbent for the removal of IBP from contaminated water. Various operational parameters viz. dosage of adsorbent, pH, agitation speed, adsorbate concentration, contact time and temperature were optimized in the batch process. Out of six process parameters three process parameters were chosen to study IBP removal process by thoroughly characterized activated carbon prepared from the mung bean husk. Adsorption kinetics, equilibrium isotherm and thermodynamic parameters related to this process were also performed and analyzed. Percentage removal of IBP was optimized by developing models using RSM and ANN; both models were compared by analysing their root mean squared error (RMSE) and coefficient of determination (R^2) with experimental data. Cost analysis of the adsorbent preparation is another novel task which was also performed and compared with the commercial activated carbon. The investigation reportedly first time so far was extended to assess the toxicological effect of the mixture of biochar and IBP on the *Scenedesmus abundans* in order to account for ecological risk in aquatic environment during disposal and accidental spill.

2. Materials and methods

2.1. Chemicals and reagents

Ibuprofen and methanol used were purchased from Sigma Aldrich (St. Louis, MO) where de-ionized water was obtained from the Merck Millipore water system (Merck, Germany). Sodium nitrate ($NaNO_3$), Potassium hydrogen phosphate (K_2HPO_4), Magnesium sulphate ($MgSO_4 \cdot 2H_2O$), Calcium chloride ($CaCl_2 \cdot 2H_2O$), Sodium carbonate (Na_2CO_3), EDTA, Ferric ammonium citrate and citric acid were purchased from Merck (Germany). The purity of these chemicals was reported to be 99% or higher.

A 1 L stock solution comprising 100 mg L^{-1} IBP concentration was prepared according to standard procedure by dissolving 100 mg of ibuprofen in 10% of methanol (Chromasolv for HPLC, 99.9%, Sigma–Aldrich) and 90% of distilled water. A desired concentration of working solutions was obtained by using successive dilutions.

2.2. Superheated steam activated biochar preparation

The mung bean husk (MBH) was purchased from a milling shop in Durgapur, West Bengal, India. MBH was thoroughly washed with double-distilled water followed by drying under the sun for five days. The dried unprocessed material was placed inside a spherical shelled furnace chamber and heated up to 550 °C for 1 h (heating rate 55 °C/15 min). The produced char was taken out and percentage yield was calculated. Then the char was again placed into the chamber and heated up to 650 °C at the rate of 55 °C per 15 min. In that hot atmosphere superheated steam was passed through the furnace chamber to physically activate biochar for 1 h. After cooling, the steam activated biochar was grinded and sieved to a particle size of $\leq$100 μm and used for the experiment.

2.3. Characterization of biochar

FTIR (PerkinElmer RXI, USA) was employed to predict the different functional groups present on the surface of activated biochar by analyzing infrared spectra of the adsorbent. In this study, activated carbonized biochar along with KBr at a specific ratio (1:20) was used to prepare translucent sample discs. The ionic state of the functional groups on the activated biochar surface was measured by using point of zero charge (pHpzc). SEM was used to analyze the topographical morphology of the adsorbent using Hitachi S–3000N (Japan). In order to know about the elemental composition of the precursor of adsorbent and steam activated biochar, ultimate analysis was done using a PerkinElmer 2400 Series II Elemental Analyzer (PerkinElmer, Waltham, MA, USA). The content of oxygen was obtained by subtracting the sum of the percentages of ash, carbon, hydrogen, nitrogen and sulfur from total percentage (100 wt %) of elemental composition. Elemental analysis of *Vigna radiata* and steam activated biochar for the estimation of carbon, hydrogen, sulfur and nitrogen is presented in Table 1.

The thermal properties of Ibuprofen, MBH and MBH-Ibuprofen were checked by Diamond TG/DTA (Perkin Elmer) and the data was analyzed using Pyris Manager Software. The studies were conducted at a temperature range of 50–900 °C, using silica crucibles with about 2–5 mg of samples, at a heating rate and Nitrogen gas flow rate of 10 °C/min and 20 mL/min respectively.

2.4. Batch mode adsorption studies

All batch mode sorption experiments were performed in a desired quantity of IBP concentration along with a known quantity of SA-MBHB in 100 mL working liquid sample. The reactor incubator shaker (Model Innova 42, New Brunswick Scientific, Canada) was operated at different adsorbent dose (50 mg – 3 g), pH (2–10), agitation speed (80–240 rpm), initial ibuprofen concentration (1–100 mg/L) and contact time (15 min-240 min) to find out the optimum conditions of the experiment. At a specified time interval, sample was taken out from the flask and centrifuged for 20 min at 4000 rpm. Then the supernatant was collected and used for analysis of IBP in the remaining solution at a maximum adsorption value of 220 nm by using UV–visible spectroscopy (Model Rayleigh