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Characterization and mechanism of the adsorptive removal of 2,4,6-trichlorophenol by biochar prepared from sugarcane baggase

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ABSTRACT

Biochar from sugarcane baggase was prepared by heating at high temperature for 20 min. Surface properties of the biochar were determined by Boehm titrations and FTIR. Biochar has 50.47% fixed carbon having methylene blue surface area of 361.77 m^2/g. SEM image revealed that biochar has cylindrical, well shaped porous structures that increase surface area for adsorption. Operational parameters for 2,4,6-TCP adsorption were optimized. The experimental q_{max} was found to be 253.38 mg/g. Biochar removed 2,4,6-TCP in the presence of multiple pollutants. The functional moieties present on biochar showed their affinity for 2,4,6-TCP ≠ methylene blue > phenol > mercury.

Introduction

Technology innovations have kept pace with the fast population growth through massive industrialization towards meeting the ever growing demands of food security and better living standards. A consequential dilemma has been the huge toxic chemicals burden created on the ecosystem through the discharge of industrial effluents and municipal wastewaters into natural water bodies and open landscapes. The effluents contain a complex mixture of contaminants, depending on the nature of industrial operations [1]. Phenolic compounds among these, reported as known or suspected human carcinogens, are a cause of long-term ecological damage due to their poor biodegradability and high toxicity [2–4]. Chlorine substituted phenols are called chlorophenols [5]. Five basic and 19 other chlorophenols are listed in the Agency for Toxic Substances and Disease Registry [6]. Besides their toxicity, chlorophenols give undesirable palatability to the potable water even at concentrations as low as 0.1 mg/L [5]. Mono-substituted chlorophenols are used as antiseptics, the di-substituted as pesticides, while the tri-substituted, specifically 2,4,6-trichlorphenol (2,4,6-TCP), are used as preservatives in paints, leather, wood, glue and paper products, and as pesticide, herbicide and fungicide [7,8]. The 2,4,6-TCP is extremely toxic, mutagenic, and carcinogenic due to the structural stability of the C–Cl bond position relative to the –OH group, making it recalcitrant to biodegradation [9,10]. The discharge of 2,4,6-TCP into water bodies, therefore, may lead it to become a part of the human food chain through aquatic microbes, fauna and flora [11]. Several human health problems have been linked with 2,4,6-TCP, including nervous system disorders, and respiratory ailments such as cough, chronic bronchitis and pulmonary defects [7,10].

Several procedures have been used for the remediation of 2,4,6-TCP from aquatic systems. These include, biosorption on dead, free or immobilized fungal biomass [12,13], adsorption on anaerobic granular sludge [14], and chemical removal, singly or in combination with physical methods, such as chemical degradation, chemical oxidation, incineration, wet oxidation, reverse osmosis, solvent extraction and activated carbon sorption [8,10]. Most of these nevertheless are costly, inefficient, and generate toxic by-products [4]. Although activated or granular carbon has been used to remove environmental contaminants, its usage has been limited due to high cost of the non-renewable starting material as coal [15]. Agricultural wastes, alternatively, are renewable and rich sources of carbon, primarily comprising of polymeric cellulose, hemicelluloses and lignin, and can be utilized as cheaper precursors for the production of activated carbons. Several activated carbons have been prepared from different plant

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materials, such as rice straw [16], coconut shell [8], rice bran [17], date palm seed [18], almond shell [19], which have been successfully used for the removal of chlorophenols and other pollutants. Pakistan, with the yield of 50 Million tones in 2009, is the 5th largest producer of sugarcane, which is regarded as the largest cash crop grown worldwide [20]. Huge quantity of sugarcane bagasse (SCB), which is estimated at 30% of the crop [21], are generated during the sugar manufacturing process in all the tropical and subtropical regions of the world. It is prudent to use this huge quantity of waste in the development of eco-friendly technologies. The present study, therefore, focuses on the development of a low-cost, easy to operate, and efficient system for the removal of 2,4,6-TCP using biochar produced from SCB. The study further reports the efficiency of 2,4,6-TCP biosorption by SCB-biochar in multi-contaminated systems, comprising of the binary (phenol-2,4,6-TCP), ternary (phenol-Hg^{+}-2,4,6-TCP) and quaternary (phenol-Hg^{+}-methylene blue-2,4,6-TCP) aquatic solutions. No earlier study so far has been reported on the adsorptive removal of 2,4,6-TCP by SCB-biochar, and from multi-contaminant solutions in the binary, ternary and quaternary combinations with a phenol, a toxic metal ion, and a toxic dye.

Materials and methods

Chemical analysis of sugarcane bagasse (SCB)

Sugarcane (*Saccharum officinarum*) bagasse (SCB), obtained from the local sugar manufacturing industry, was analyzed for contents of fibre and lignin [22], of cellulose [23], and of hemicelluloses [24].

Biochar preparation

The SCB was washed in tap water to remove juice remains and any particulate matter, followed by boiling for 30 min, and drying at 80 ± 2 °C for 24 h. The dried SCB was charred in a muffle furnace at different temperatures (573, 673 and 773 K) for 20 min. The SCB-biochars so produced were designated as, BC-SCB_{573}, BC-SCB_{673}, and BC-SCB_{773}. These biochars were ground, sieved, and stored in desiccators till further use. The adsorptive removal of 2,4,6-TCP as the single contaminant, and from binary, ternary and quaternary mixtures of several contaminants was done using biochars of 100–250 μm size particles. The biochars were analyzed for their physico-chemical properties using standard methods [25–27]. The acidic and basic surface groups present on the SCB-biochars, produced at different temperatures, were determined for their H^{+} and OH^{-} adsorption capacity in accordance with the Boehm titration method [28]. Based on the characterization data of SCB-biochars (Table 1), BC-SCB_{673} was selected for studies on the adsorption of 2,4,6-TCP.

Point of zero charge

The point of zero charge (pH_{PZC}) of BC-SCB_{673} was determined by transferring 45 mL of 0.1 M KNO_3 in a series of Erlenmeyer flasks, adjusted to initial pH (pH_i) between 2 and 12 with 0.1 N HNO_3 or NaOH. The final volume of each flask was made to 50 mL with 0.1 M KNO_3. This was followed by the addition of 0.1 g of BC-SCB_{673}, shaken occasionally for 48 h, centrifuged at 500 rpm for 5 min, and final pH (pH_f) of the supernatant was noted. The difference (ΔpH) between pH_i and pH_f was plotted against pH_i [29]. The intercept of the plot denotes the point of zero charge value (pH_{PZC}).

Surface characterization and functional moieties

Scanning electron microscopy (SEM; JEOL-JSM-6480, Japan) of BC-SCB_{673} was done to investigate its surface topography. The biochar was placed in a sample chamber and evacuated to high vacuum (2×10^{6} Torr). The BC-SCB_{673} sample was bombarded with a finely focused electron beam, and the image formed by the secondary electrons generated by the primary beam was recorded. For the determination of functional moieties present on BC-SCB_{673}, Fourier Transform Infrared (FTIR) spectrophotometer (Bruker, Germany), equipped with attenuated total reflectance (ATR), was done in solid phase in the range of 400–4000 cm^{-1}.

Table 1
Physico-chemical characteristics of biochar produced at varying temperatures of 573, 673 and 773 K for 20 min, respectively (BC-SCB_{573}, BC-SCB_{673} and BC-SCB_{773}).

Biochar properties	BC-SCB_{573}	BC-SCB_{673}	BC-SCB_{773}
Moisture (%)	5.82 ± 0.11	5.71 ± 0.09	6.73 ± 0.15
Ash content (%)	4.23 ± 0.17	4.17 ± 0.13	4.08 ± 0.21
Volatile matter (%)	41.79 ± 0.55	38.62 ± 0.37	37.71 ± 0.66
Fixed carbon (%)	48.16 ± 1.02	50.47 ± 0.99	49.97 ± 0.87
Water soluble matter (%)	2.50 ± 0.07	2.01 ± 0.02	1.81 ± 0.05
Acid soluble (0.25 M HCl) matter (%)	14.01 ± 0.13	14.80 ± 0.11	15.07 ± 0.19
pH of 5% slurry	4.97 ± 0.12	5.93 ± 0.17	6.12 ± 0.15
Bulk density (g/cm^3)	0.043 ± 0.01	0.045 ± 0.01	0.046 ± 0.02
Decolourizing power (mg/g)	264.38 ± 1.72	288.71 ± 2.37	280.23 ± 2.15
Surface area (m^2/g)	224.07 ± 3.77	361.77 ± 4.07	291.37 ± 3.02
Total basic group (mmol/g)	0.24 ± 0.02	0.31 ± 0.07	0.33 ± 0.05
Total acidic groups (mmol/g)	0.28 ± 0.01	0.38 ± 0.01	0.42 ± 0.03

Preparation of stock solutions

Stock solutions of 2,4,6-TCP (1000 mg/L), phenol (1000 mg/L), methylene blue (1000 mg/L), and Hg^{2+} (1000 mg/L) from Hg_2Cl_2 were prepared in double distilled water. Adsorption of 2,4,6-TCP as the single contaminant in the aquatic medium, from the binary solutions containing two organic compounds (2,4,6-TCP + phenol; 2,4,6-TCP + methylene blue) or an inorganic metal ion (2,4,6-TCP and Hg^{2+}), from the ternary combination of two organic chemicals and an inorganic metal ion (2,4,6-TCP + phenol + Hg^{2+}) or of three organic chemicals (2,4,6-TCP + phenol + methylene blue), and from the quaternary combination of three organic chemicals and an inorganic metal ion (2,4,6-TCP + phenol + methylene blue + Hg^{2+}) was investigated. The desired concentrations were freshly prepared from their respective stock solutions for each adsorption experiment.

Adsorption experiments

The adsorption capacity of BC-SCB_{673} was determined in batch experiments in 250-mL Erlenmeyer flasks by contacting 1.0 g/L biochar with 100 mL of the 2,4,6-TCP solutions of known concentrations (10–900 mg/L), and orbital shaking at 100 rpm for 60 min at room temperature (25 ± 2 °C). The supernatant was collected by filtration and analyzed for residual 2,4,6-TCP by high performance liquid chromatography (HLPC; Perkin Elmer 200, USA). The chromatographic analysis was done on samples pre-filtered through 0.2 μm Millipore filters on Brownlee C-18 HPLC column (30 mm × 4.6 mm). The mobile phase of solvent A (acetonitrile) and B (water) in the ratio of 60% and 40% was used. The sample injection volume was 20 μL at 0.7 mL/min flow rate. The UV–visible detector was set at 296 nm for 2,4,6-TCP. The data acquisition and integration was done using software Total Chrom Workstation. The rate of 2,4,6-TCP adsorption by BC-SCB_{673} was determined by contacting adsorbent–adsorbate at various intervals of time (5–180 min). The optimum adsorbent dosage was determined by varying BC-SCB_{673} quantity (0.1–10 g/L). The best pH for the removal of 2,4,6-TCP by BC-SCB_{673} was determined by varying initial pH value in the range of 2–10. The competitive removal of 2,4,6-TCP in binary, ternary and