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Mechanistic modeling of glyphosate interaction with rice husk derived engineered biochar

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ABSTRACT

Biochar (BC), a carbon-rich solid product of biomass, and its surface activation via steam have been recognized as alternative economically viable strategy to decontaminate wastewaters. Existence of glyphosate, the most extensively used non-selective herbicide, in waters at elevated concentrations has received worldwide attention due to its ill consequences. The main objective of the present study was to investigate the potential of steam activated BC produced from rice husk (RHBC) via slow pyrolysis at 700 °C to remove glyphosate from aqueous solution. Batch adsorption experiments were carried out to evaluate the effects of pH, reaction time and glyphosate loading on the RHBC adsorption process. Results showed that a maximum removal of glyphosate (82.0%) occurred at pH 4, and the adsorption capacity decreased significantly with increasing pH. Both the Freundlich and Langmuir models fitted best to the equilibrium isotherm data suggesting physisorption as well as chemisorption mechanisms governing the glyphosate adsorption. The Langmuir maximum adsorption capacity was 123.03 mg/g. The kinetics of the adsorption process was well described by the pseudo-first order indicating that the glyphosate adsorption onto RHBC would be more inclined towards physisorption depending on the initial glyphosate concentration. Pore diffusion, $\pi-\pi$ electron donor–acceptor interaction and H-bonding were postulated to be involved in physisorption, whereas electrophilic interactions led to chemisorption type of adsorption. Overall, steam activated RHBC could be a promising remedy of glyphosate removal from aqueous solution.

1. Introduction

Contamination of water by pesticides at elevated concentrations has manifested the whole world due to its adverse effects on human health as well as the surrounding environment. Glyphosate ($C_3H_8NO_5P$) is a type of organophosphorous herbicide that is widely used in controlling unnecessary growth of some grasses, sedges, weeds and plants [1]. Glyphosate was introduced into the market in 1974, and it now accounts approximately 60% of the global herbicide sales with the total worldwide consumption of over 70,0000 tons per year [2]. Several surveys conducted in some countries documented that glyphosate is the most predominant herbicide used in UK arable crop production. In Denmark, the consumption of glyphosate accounts for 35% of all pesticides used in agricultural production and also Germany applies glyphosate on 4.3 million hectares (39%) of agricultural land per year [3].

Glyphosate can contaminate water systems via agricultural runoff by rain or water irrigation, and leakage to the groundwater from infected crop residues [4]. The fate of glyphosate is mainly associated with the soil, since it can easily drain off into surrounding water reservoirs. Consequently, humans have been subjected to numerous health consequences of glyphosate exposure, such as eye and skin irritation, contact dermatitis, eczema, cardiac and respiratory problems and allergic reactions [4]. The negative impacts of glyphosate in the environment mainly depend on its chemical formulation and speciation rather than on the concentration [5]. The use of glyphosate as a herbicide has been recently banned in Sri Lanka and El-Salvador due to the hypothesized

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involvement in chronic kidney disease of uncertain etiology (CKDu). However, its high demand and excessive usage have posed widespread contamination of water bodies due to remaining glyphosate residues [6].

Adsorption is an efficient and widely used phenomenon of decontaminating water. Because of various types of pesticides and their residues can exist in contaminated water systems, choosing a non-selective adsorbent is of particular concern. Carbon-rich solid materials such as activated carbon and biochar (BC) have been recently used as an alternative and economically viable adsorbent to remove or immobilize inorganic as well as organic pollutants, such as heavy metals, nutrients and veterinary drugs found in soil and water systems [1,7–10]. The high adsorption of pollutants onto BC is supposed to be due to the high surface area, micro-, meso- and macro-pores of BC and pH of the medium [8]. Many studies have focused on the production of BCs, their characterization and application in the remediation of antibiotics and heavy metals contaminated in water and soil systems [9,11,12]. However, only few studies have recently been found to be focusing on the use of engineered BC for the removal of some contaminants including heavy metals, pharmaceuticals, and nutrients (phosphates and nitrates) present in the environment [10,13–16].

It is presumed that steam activation of BC is capable of escalating its adsorption capacity. Steam can act as an effective oxidizing agent that may increase the surface area and pore volume of the BC. The functional groups attached on the BC surface are also capable of enhancing the adsorption process, which is directly influenced by the production conditions such as pyrolysis temperature, gas purging and steam activation. In a recent study, steam activated BC produced from tea waste was proposed as an assured treatment for the removal of sulfamethazine from water with a sorption capacity of 33.81 mg/g [8]. Activated carbon derived from waste newspapers has been successfully used as an adsorbent to remove glyphosate from aqueous solution [17], and this study estimated that the maximum adsorption capacity of activated carbon for glyphosate adsorption is 48.4 mg/g. More recently, it has been reported that birch wood BC is capable of controlling the fate of glyphosate in the soil by decreasing its leaching capability [18]. However, to our knowledge, the adsorption behavior of glyphosate on engineered BCs has not previously been evaluated, although it has been reported as one of the most widely used pesticide in the world. Hence, this is the first time reporting of engineered BC on the removal or immobilization of herbicide glyphosate along with postulated mechanisms.

In the present study, the adsorbent was produced by pyrolyzing rice husk biomass at 700 °C and produced rice husk biochar (RHBC) was further activated by purging steam in order to improve its capacity for glyphosate adsorption. The adaptability of different adsorption isotherm models to describe the experimental equilibrium data and different kinetic models to study the dynamic behavior of glyphosate adsorption process are investigated. Potential mechanism(s) of glyphosate adsorption onto the steam activated RHBC also are discussed at the end the paper.

2. Experimental

2.1. Biochar production and characterization

The RHBC samples were produced from rice husk collected from Sri Lankan rice mills. Rice husk was then washed several times with distilled water and air dried. The dried biomass was crushed and ground to <1.0 mm in particle size. Rice husk was pyrolyzed at 700 °C with a heating rate of 7 °C min^{-1} for 2 h under limited O_2 in a modified N11/H Nabertherm (Germany) furnace. Char samples were then treated with 5 mL/min of steam for an additional 45 min under the peak temperature after the 2 h pyrolysis period had elapsed. The pH of the steam activated RHBC was measured in a suspension of 1:5 (w/v) BC/de-ionized water, using a digital pH meter (Orion, Thermo Electron Corp., Waltham, MA, USA). Moisture was determined by calculating the weight loss after heating the BC at 105 °C for 24 h to a constant weight. Mobile matter (analogous to volatile matter), which reflects the non-carbonized portion in BC, was determined as the weight loss after heating in a covered crucible at 450 °C for 30 min [12]. Ash content was also measured as the residue remaining after heating at 700 °C in an open-top crucible. The portion of the BC not ashed, referred to as resident matter (analogous to fixed matter), was calculated by the difference in moisture, ash, and mobile matter. Each sample was analyzed in triplicate.

Exchangeable Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} present in steam activated RHBC were extracted via the ammonium acetate procedure [19] and concentrations of metals were determined using an atomic absorption spectrophotometer (AAS, GBC933, Australia). The organic matter content was determined following the Walkley–-Black method [20]. The surface functional groups of steam activated RHBC were characterized by Fourier-transform infrared spectroscopy (FTIR) (Bio-Rad Excalibur 3000MX spectrophotometer, Hercules, CA, USA). The specific surface area, total pore volume, and pore diameter were determined using a gas sorption analyzer (NOVA-1200; Quantachrome Corp., Boynton Beach, FL, USA). Surface functional groups present on the steam activated RHBC were determined by the method Boehm titration. Surface titration was carried out to determine the point of zero charge of the steam activated RHBC.

2.2. Materials and measurements of glyphosate

Analytical grade herbicide glyphosate (N-(phosphonomethyl) glycine) was used for this study. All the reagents used were obtained from Sigma Aldrich and were of analytical reagent grade.

Residual aqueous glyphosate concentration was measured following the method described by Tzaskos et al. [21]. This is a colorimetric method, in which a purple colored complex is developed due to the reaction of glyphosate with ninhydrin and sodium molybdate. Standard glyphosate solutions including 4, 6, 8, 10 and 14 mg/L were prepared from a stock solution of 1000 mg/L, followed by the addition of 0.5 mL of 5% ninhydrin and sodium molybdate solutions. The tubes were then sealed and the mixtures were heated in a water bath at a temperature of 85–95 °C for 12 min. The samples were cooled to room temperature and transferred to 5 mL volumetric flasks and the volume was made up to the mark with distilled water for the quantification. The color intensity of samples was measured at 570 nm (λ_{max}) using a UV–visible spectrophotometer (UV-160A, Shimadzu, Japan). Finally, the concentration of glyphosate in each sample was determined by using the calibration curve in the range from 4 to 14 mg/L ($R^2 = 0.9963$). The blank solution was prepared with 0.5 mL of ninhydrin and sodium molybdate solutions to a total volume of 5 mL for the base line correction of the instrument.

2.3. Effect of initial pH

The effect of pH on glyphosate adsorption onto steam activated RHBC was studied by adjusting the pH of glyphosate solutions with 1 M HNO_3 or NaOH solution in the range of 3.0–9.0 and glyphosate concentration of 20 mg/L and BC dosage of 0.5 g/L.