Cost effective and practically viable oil spillage mitigation: Comprehensive study with biochar

Ramesh Kandanelli, Lavanya Meesala, Jatin Kumar, Chinthalapati Siva Kesava Raju, V.C. Rao Peddy, Sriganesh Gandham, Pramod Kumar*

Hindustan Petroleum Green R&D Centre (HPGRDC), KIADB Industrial Area, Devanagonthi, Bengaluru 560067, India

ABSTRACT

Biochar is carbonaceous mass that is produced from pyrolysis or gasification of biomass. It is so far majorly explored for soil remediation application, but recently it has attracted a lot of interest because of its unexplored applications in the area of adsorption. In this work, detailed study on biochars produced from two different feeds (rice husk and saw dust), at two different temperatures (450 and 550 °C) and two different rates (fast and slow) of pyrolysis are discussed for oil spill mitigation. Biochar is characterized in detail by various techniques such as FTIR, ^{13}C CPMAS, FESEM, RAMAN, TGA to determine the structural composition and observe the extent of pyrolysis. Tests to assess the performance of produced biochars as sorbents for oil spill mitigation have been demonstrated. The as produced biochars selectively absorbed crude oil from oil/water biphasic mixtures in various capacities.

1. Introduction

Biomass pyrolysis and gasification are the emerging technologies for the production of renewable fuels and various platform chemicals (Oladeji et al., 2015; Molino et al., 2016). Pyrolysis is a process where organic material decomposed in an oxygen free environment where-as gasification is the thermal decomposition under limited supply of oxygen (Chhiti and Kemiha, 2013). During both these processes a lot of biochar is generated as a byproduct and it is only going to pile up further. It is a less valued material and would be abundantly available once the pyrolysis/gasification processes get commercialized at industrial scale (Gonzáleza et al., 2017).

Because of its physicochemical properties, efforts have been made to utilize biochar for various applications. It has been used in the area of catalysis, (Hale et al., 2012) for instance a sulphonated biochar was used to catalyze transesterification of vegetable oils for biodiesel production (Dehkhoda et al., 2010). In another report from Li's group, biochar prepared from lignocellulosic biomass acts as catalyst to convert corncob into furfural by hydrolysis (Liu et al., 2017). Biochar has been significantly used also as a soil amendment to improve fertility and mitigate climate change as soil amendment (Brennan et al., 2014; Cheng et al., 2008; Liang et al., 2006; Chan et al., 2007; Chan et al., 2008; Smebye et al., 2016; Beesley et al., 2010). It's micro/macro porous structure works as a habitat for microorganisms and is helpful to accommodate beneficial micronutrients for higher crops' yield (Asai

et al., 2009; Galinatio et al., 2011). Biochar improves the structure and properties of soil, such as water holding capacity, aeration, pH, organic matter content and reduces nutrient losses. Moreover its porous structure, functional groups and charged surface may reduce bioavailability of heavy metals and toxic chemicals as well (Tang et al., 2013; Ulyett et al., 2014; Chowdhury et al., 2014) Biochar has also been used as an effective adsorbent for removal of acid gases such as H_2S and CO_2 from a mixture (Hanieh et al., n.d.). Though biochar has been explored for a variety of applications a study for implementation of biochar for oil adsorption needs to be fully developed (Silvani et al., 2017; Nguyen and Pignatello, 2013).

Oceans, beaches and sea-bed sands are adversely hampered by oil spills that cause significant environmental damage, as well as chronic effects on ecosystems (Crone and Tolstoy, 2010; Peterson et al., 2003; Bragg et al., 1994). Due to the rapidly growing industrial development and oil exploration and production, spillage has increased in the last few decades (Jernelöv, 2010). Therefore, it is necessary to develop an effective, fast and cheap methods to minimize or mitigate the negative consequences of spilled oil (Camilli et al., 2010; Reddy et al., 2012). Nowadays several physical, chemical and biological methods which are in use to collect spilled oil (Tewari and Sirvaiya, 2015; Wahi et al., 2013; Adebajo et al., 2003a; Broje and Keller, 2006; Srinivasan and Viraraghavan, 2010). By using physical methods such as floating blooms and manual labor, merely 10–15% content of spilled oil can be recovered (Alade et al., 2011; Zhu et al., 2001; Zahed et al., 2005).

Other practices such as using sorbent materials, dispersants, skimmers and emulsifiers, are also adopted (Kujawinski et al., 2011; Broje and Keller, 2007; Wei et al., 2003; Rico-Martínez et al., 2013). Application of emulsifiers and dispersants is associated with dilution effects (Lessard and DeMarco, 2000). In other situations, chemical methods are not extensively used due to concerns on their effectiveness, possible toxicity and long-term environmental effects (U.S. EPA, 1999). Among the different methods, adsorption is probably the most widely used one. Dispersants and emulsifiers break spilled oil into small droplets which get dissolved in sea water. Therefore, recommendation for using these substances is avoided due to pollution of the water beds. In recent years, hundreds of various natural and synthetic materials have been tested as possible oil sorbents (Adebajo et al., 2003b; Hu et al., 2013; Gupta et al., 2017).

In the present study effectiveness of biochars from rice husk and saw dust pyrolysis were tested as possible sorbent materials for oil spill. Biochars obtained from these biomasses were tested for adsorption capacity with five different crudes. Different conditions were tested in lab to resemble sea water conditions. The sorption test conditions were: i) saline water in still condition; ii) saline water in stirring condition, to resemble sea water situation, and iii) deionized water in still condition, iv) deionized water in stirring condition as controls.

2. Materials and methods

2.1. Results and discussion

2.1.1. Biochar samples

Biochars used in this study were prepared by pyrolyzing two different biomass feeds: rice husk and saw dust. Both of them were obtained from local mills nearby in Bangalore. Feedstocks were oven dried at 105 °C for 2 h prior to cooling in desiccator and were subsequently subjected to pyrolysis. Particle size of feed stocks were about 300 to 500 μ. Compositional analysis of the feed samples is summarized in the Table 1. Pyrolytic process was carried out into two different reactors at different heating rates and temperatures to produce four different biochar samples, as summarized in Table 2.

2.1.2. Fast pyrolysis reactor

Biochars used, are produced by pyrolyzing rice husk and saw dust as feedstocks. Fast pyrolysis of biomass was carried out in fluidized bed pyrolyzer at two different temperatures viz., 450 and 550 °C. The yields of biochars in this process was in the range of 22–25%. The residence time of biomass was 4–5 s. Nitrogen flow rate was kept at 25 SL/min. The process flow scheme of the fast pyrolyzer equipment is provided in supporting information (Fig. S1). Pyrolyzer operating pressure is 1 bar.

2.1.3. Slow pyrolysis reactor

For generating biochar in slow pyrolysis mode, Parr batch autoclave was used (USA). Slow pyrolysis of rice husk was carried out at 400 °C. The Parr apparatus has the max operating temperature limitation of 400 °C. The yield of biochar in this process was 70%. Nitrogen flow rate in this case was about 15 SL/min. The process flow scheme of the slow pyrolysis equipment is provided in supporting information (Fig. S2).

2.1.3.1. Thermogravimetric analysis (TGA). Thermal Analysis of biochars were carried out on SDT750 model (TA instruments, USA).

Table 1
Compositional analysis of feed stocks.

Component	Rice husk	Saw dust
Cellulose	43.8%	39%
Hemicellulose	11.9%	17.7%
Lignin	23.1%	17.6%

Table 2
Type of biochars prepared and studied.

Names	Feed	Rate of pyrolysis/equipment	Temperature (°C)
RHBC-450	Rice husk powder	Fast/fluidized pyrolyzer	450
RHBC-550	Rice husk powder	Fast/fluidized pyrolyzer	550
SDBC-450	Saw dust powder	Fast/fluidized pyrolyzer	450
RHBC-SP	Rice husk powder	Slow/batch autoclave	400

Analysis was carried under N_2 atmosphere with a flow rate of 100 mL per min with two alumina crucibles with one of them acting as a reference pan. The extent of decomposition was monitored for various biochars in the temperature range 30 to 1000 °C. Heating rate was maintained at 10° per minute.

2.1.3.2. Fourier transform infraRed (FTIR). FTIR spectra of biochars were recorded in the range 450–4000 cm^{-1} on Frontier FT-IR spectrometer (Perkin Elmer, USA) in ATR (Attenuated Total internal Reflection) mode having MCT detector.

2.1.3.3. CPMAS NMR (cross polarization magic angle spinning nuclear magnetic resonance) spectroscopy. CPMAS NMR were acquired from biochar samples at ^{13}C resonating frequency of 125 MHz on JEOL (Japan) 500 NMR spectrometer. Rotation speed was kept 12 kHZ and temperature during the experiment was constant at 25 °C.

2.1.3.4. Raman spectroscopy. Raman measurements of biochar samples were investigated on R4 Raman Micro spectrometer from Renishaw (UK) using laser of 532 nm.

2.1.3.5. Powder-X-ray diffraction. Biochar samples were also characterized by P-XRD measurements on a X'pert³ X-ray diffractometer from Panalytical, Netherlands. Source being Cu K-alpha, 0.15418 nm (Bragg-Brentano geometry).

2.1.3.6. FE-SEM (field emission scanning electron microscope). Field Emission Scanning Electron Microscopy measurements were carried out on biochars. FESEM images of biochar samples were obtained on JSM-7610F (JEOL, Japan). Samples were sputter coated with Pd-Pt prior to imaging. Varying magnifications were used to compare structural and surface characteristics.

2.1.3.7. Crude oil properties. Crude oil is a complex mixture of various hydrocarbons that comes with varying properties especially if they are coming from different geographical locations. Main properties include API (density), TAN (Total Acid Number) and Sulphur content though many other parameters of crude are studied for refining process (Speight, 2007). The properties of the crude oils studied for adsorption are summarized in Table 3.

2.1.4. Oil adsorption studies

An oil adsorption study was performed with each biochar against crude oils. The properties of studied crude oils are presented in Table 3. The crude oils used in this study all fall in the API range 18–33 which majority of the crude oil densities belongs (Speight, 2007). Four different conditions were created for testing. First case includes adsorption

Table 3
Various crude oils and their properties.

Crude oil	C1	C2	C3	C4	C5
API	30.26	27.12	28.12	33	18.82
TAN (mg KOH/g)	0.13	N.A.	0.33	0.30	0.16
Sulphur (wt%)	2.87	3.52	2.795	0.076	1.438

N.A.-not available.