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Synthesis of the magnetic biochar composites for use as an adsorbent for the removal of pentachlorophenol from the effluent

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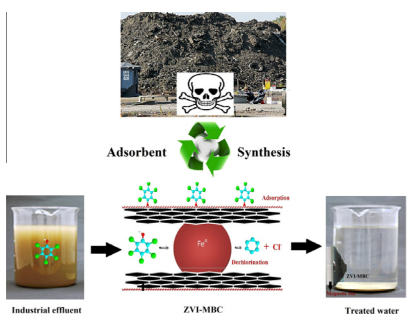
HIGHLIGHTS

- ZVI-magnetic biochar composites were synthesized from paper mill sludge biochar.
- ZVI-MBC were used for the treatment of effluent containing PCP.
- ZVI-MBC synthesis conditions were optimized to obtain high PCP removal efficiency.
- PCP removal by ZVI-MBC involves simultaneous adsorption and dechlorination mechanism.
- Leaching and ageing studies were performed to confirm the stability of ZVI-MBC.

GRAPHICAL ABSTRACT



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ABSTRACT

The zero-valent iron magnetic biochar composites (ZVI-MBC) were synthesized from the paper mill sludge biochar and used for the treatment of the synthetic and real effluent containing pentachlorophenol (PCP). During the synthesis of ZVI-MBC, $NaBH_4$ was used as the reducing agent to reduce Fe(II) to Fe(0) and cetyltrimethylammonium bromide was added as surfactant. The effect of the molar ratio of $FeSO_4$ to $NaBH_4$, dose of the surfactant and the ZVI to biochar ratio on the PCP removal efficiency was investigated. It was found that the ZVI-MBC combines the advantages of biochar and ZVI particles for the simultaneous adsorption and dechlorination of PCP in the effluent and the complete removal of PCP was obtained. The ageing tests showed that biochar prevents the formation of oxide film on the ZVI particles and leaching tests confirmed the stability of ZVI on biochar matrix as very low iron leaching was noticed.

1. Introduction

Huge quantity of sludge is generated during the paper manufacturing process in the paper mill. The disposal and management of the generated sludge is a big challenge for the paper industry as it contains significant amount of the heavy metals. The bioavailability of the heavy metals is the limiting factor for the disposal and utilization of the sludge. Pyrolysis is a promising sludge treatment method for the heavy metals immobilization leading to a significant reduction in the bioavailability and the leaching potential of the heavy metals in the biochar. The reduction in the eco-toxicity of the heavy metals in the biochar makes it suitable for use in the agricultural and other purposes like brick formation, use as an adsorbent, etc. (Devi and Saroha, 2014). The use of biochar as an adsorbent has attracted attention recently because biochar have high adsorption capacities due to their aromatic and porous structures (Liu and Zhang, 2011). The adsorption of hydrophobic organic chemicals on biochar and other carbonaceous materials has been reported in the literature (Liu and Zhang, 2011; Zhang et al.,

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2011; Lou et al., 2012). However, the tedious separation process of the exhausted powdered biochar from the effluent and the regeneration/disposal problem of the exhausted biochar limit its commercial applications.

Incorporation of some reducing agent like iron in the biochar matrix to modify the biochar to magnetic biochar composite matrix will facilitate the separation of the exhausted biochar from the effluent. Zero-valent iron (ZVI) has powerful magnetic and reducing properties, which makes it the suitable magnetic reducing media for mixing with the biochar to obtain the modified magnetic biochar composites. ZVI has been used for the reductive removal of nitroaromatics, perchlorates, hydrocarbons, and toxic metal ions in the aqueous media (Meng et al., 2006; Li et al., 2008; Hoch et al., 2008; Zhao et al., 2008; Xu et al., 2010; Chang et al., 2011). But the practical application of ZVI is limited due to the two major problems associated with the ZVI particles: (i) ZVI gets oxidized very easily in contact with air and (ii) agglomeration of the ZVI particles due to the van der Waals and magnetic attraction forces. Thus, two main approaches have been reported to improve the reducing capacity of ZVI and to prevent the agglomeration of ZVI particles. The first approach involves addition of a surfactant to increase the repulsive forces between the ZVI particles and to keep the particles dispersed in the solution (Choi et al., 2009). The second approach involves utilizing a support material for the immobilization of ZVI particles to overcome ZVI agglomeration (Wu et al., 2013).

Keeping the above facts in mind, it was decided to synthesize the novel ZVI magnetic biochar composites, where the biochar and the ZVI complement each other in overcoming the two limitations. The ZVI particles impart magnetic and reductive characteristics to the biochar, while the biochar acts as a supporting media to prevent the agglomeration of the ZVI particles. The use of ZVI magnetic biochar composites as an adsorbent for the treatment of effluent will facilitate its easy separation from the effluent and thus increasing its use in the environmental applications (Meng et al., 2006; Zhang et al., 2012).

Pentachlorophenol (PCP) is a carcinogenic, persistent and low-biodegradable organochlorine compound. It is listed in the category of priority toxic pollutants by the U.S. Environmental Protection Agency (Shih et al., 2011). It is widely used in the formulation of pesticides, herbicides, disinfectants, biocides and wood preservatives (Li et al., 2011). PCP is also produced during other industrial processes, such as the bleaching of pulp using chlorine/chlorine dioxide and the production of other chlorophenols (Patel and Suresh, 2008). Due to the raising public concern about health and the environmental effects, various technologies are used for the PCP removal from the effluent, such as membrane filtration (Du et al., 2013), biological treatment (Reis et al., 2013), adsorption (Li et al., 2011) and advanced oxidation processes (Hong and Zeng, 2002). Among these processes, adsorption is extensively used due to its relative simplicity of design, operation, scale-up and low cost. In the adsorption process, the contaminant gets concentrated at a solid surface from its liquid or gaseous surroundings. If the adsorbate is toxic, the exhausted biochar itself becomes a hazardous waste that must be treated or disposed properly. The ZVI-magnetic biochar composites (ZVI-MBC) facilitate the simultaneous adsorption and dechlorination of PCP, thus preventing the concentration of adsorbate (PCP) in the ZVI-MBC matrix.

The paper mill effluent treatment plant (ETP) sludge derived biochar was used for the synthesis of the ZVI-MBC. During the synthesis of ZVI-MBC, sodium borohydride ($NaBH_4$) was used as the reducing agent to reduce Fe(II) to Fe(0) and cetyltrimethylammonium bromide (CTMB) was added as the surfactant. The use of ZVI-MBC as an adsorbent for the removal of PCP from the synthetic and the real paper mill effluent was explored in the present study. The effect of the molar ratio of $NaBH_4$ to $FeSO_4$, the ratio of ZVI to biochar and the CTMB dosage on the PCP removal from the synthetic and real industrial effluent was investigated. Moreover, the Fe leaching and the effect of ageing on the ZVI-MBC performance was also studied.

2. Methods

2.1. Chemicals

All the reagents used in the present study were of analytical grade.

2.2. Preparation of ZVI-MBC

Paper mill sludge was pyrolyzed at 700 °C and the resultant biochar was used for the preparation of the ZVI-MBC (Devi and Saroha, 2014). Initially, the biochar–CTMB complex was prepared by adding 5 g of biochar in the CTMB solution of known concentration (0.1–0.8%; 0.1% implies 0.1 g CTMB dissolved in 100 mL of water). The mixture was agitated at 250 rpm for 2 h and was filtered through Whatman's filter paper No. 41 (pore size 20–25 μm). The resultant residue was washed with distilled water to remove the unreacted CTMB and was oven dried at 95 °C for 12 h. The dried biochar–CTMB complex was stored in air-tight container for further use.

The biochar–CTMB complex was magnetized by the impregnation of the ZVI on the biochar surface. For magnetization, the $FeSO_4{\cdot}7H_2O$ (0.2 mol) was dissolved in 100 mL of distilled water in a 3-neck flask. The contents of the flask were agitated at 250 rpm by a magnetic stirrer to maintain a uniform concentration in the flask. One neck of the 3-neck flask was used for supplying inert N_2 gas to prevent intrusion of the air into the flask. The $NaBH_4$ solution was used as a reducing agent for the reduction of $FeSO_4$ to Fe(0) and was added drop-wise from another neck into the $FeSO_4$ solution. The mixture was left for 20 min after completion of the addition of $NaBH_4$ for the reaction (Eqs. (1) and (2)) to take place. The biochar–CTMB complex (5 g) was added slowly into the above reaction mixture as the addition of the biochar–CTMB complex leads to very fast reactions (effervescence) resulting in the formation of large amount of foam. To prevent the foam from coming out of the flask, the contents were stirred vigorously at 1000 rpm for 30 min. After completion of the reaction, the solid residue was separated by filtration and washed with the distilled water. The solid residue (ZVI-MBC) was dried in the oven at 95 °C and stored in an air-tight container for further use.

$$FeSO_4 + H_2O \rightarrow FeOHSO_4 + H^+ \quad (1)$$

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe(0) + 3H_2BO_4^- + 12H^+ + 6H_2 \quad (2)$$

2.3. Characterization of ZVI-MBC

The BET surface area, the pore volume and the pore diameter of the ZVI-MBC were determined using the N_2 adsorption–desorption isotherm at 196 °C using a Micromeritics ASAP 2010 apparatus. The surface morphology of the ZVI-MBC was determined by scanning electron micrograph (SEM).

Crystal structure of the ZVI-MBC was analyzed by X-ray diffraction (XRD) using Cu-Kα radiation (λ = 1.54 Å) at 40 kV/40 mA. All the samples were scanned from 5° to 60° 2θ at a scanning rate of 3° 2θ per min. Fourier transform infrared (FT-IR) spectroscopy analysis was performed on a FTIR spectrometer where the dried ZVI-MBC samples were mixed with the dried KBr in a ratio of 1:30 and FTIR spectra was recorded at a resolution of 4 cm^{-1}.