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Simultaneous adsorption and dechlorination of pentachlorophenol from effluent by Ni–ZVI magnetic biochar composites synthesized from paper mill sludge

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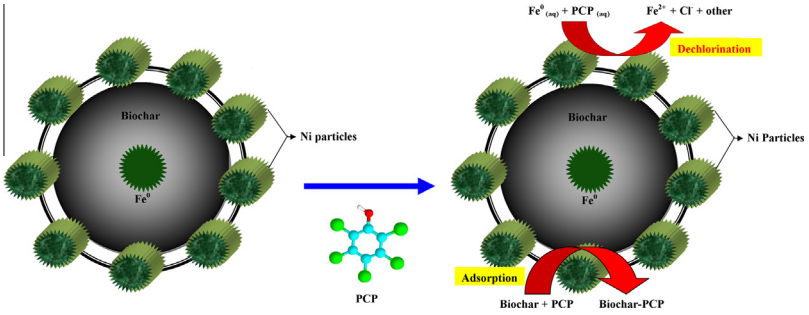
HIGHLIGHTS

- Ni–ZVI-MBC was synthesized from paper mill sludge and used for PCP removal.
- PCP removal on Ni–ZVI-MBC occur by simultaneous adsorption and dechlorination.
- Ni acts as catalyst and help in enhancement of PCP dechlorination efficiency.
- Adsorption and dechlorination kinetics was used to determine rate limiting step.
- The feasibility of brick formation from exhausted Ni–ZVI-MBC was studied.

GRAPHICAL ABSTRACT



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ABSTRACT

The Ni–zero-valent iron magnetic biochar composites (Ni–ZVI-MBC) were synthesized from paper mill sludge and used as an adsorbent for the removal of pentachlorophenol (PCP) from the synthetic and real paper mill effluent. The synthesized Ni–ZVI-MBC was characterized and analyzed for the stability of Ni and ZVI particles in the biochar matrix. The Ni–ZVI-MBC involves simultaneous adsorption and dechlorination mechanism resulting in higher PCP removal efficiency. The presence of Ni as a catalyst in Ni–ZVI-MBC enhances the dechlorination rate and the adsorption of PCP by preventing the accumulation of PCP in the biochar matrix. The effect of operating parameters (solution pH, Ni loading, initial PCP concentration in the solution and temperature) on adsorption and dechlorination efficiency was studied. The exhausted Ni–ZVI-MBCs were used for the brick formation and the bricks showed good compressive strength and negligible heavy metal and PCP leaching.

1. Introduction

Pentachlorophenol (PCP), an organochlorine compound, is listed as a priority pollutant by U.S. Environmental Protection Agency (EPA) due to its toxic, carcinogenic and persistent nature [1]. PCP can be found in air, water, and soil and the permissible limit (prescribed by US EPA) of PCP in drinking water is 0.3 μg/L. The chronic exposure of PCP can cause various health problems related to kidney, liver, blood and nervous system. It is widely used in the formulation of pesticides, herbicides, disinfectants and wood preservatives, thus finding its way in the effluent of these industries [2]. PCP is also generated during the industrial operations like pulp bleaching in pulp and paper industry [3]. Various processes such as

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membrane filtration [4], biological treatment [5], adsorption [2] and advanced oxidation processes [6] are employed for the treatment of the effluent containing PCP and among these processes, adsorption is extensively used due to its relative simplicity of design, operation, scale-up and low cost.

Biochar has attracted attention as an adsorbent for the treatment of effluent due to its extraordinary adsorption properties for organic contaminants [7,8]. It has been reported that the adsorption capacity of the biochar is 10–1000 times more than other type of carbon adsorbents due to its surface area, porosity and surface functional groups [9,10]. Various studies have been reported in the literature on the use of biochar as an adsorbent for the treatment of effluent containing various toxic pollutants like phenol [11], atrazine [12], 4-chlorophenol [13], naphthalene [14] and polycyclic aromatic hydrocarbons [15]. Since the disposal of the exhausted adsorbent limits its practical applications, it is desirable to desorb the adsorbate from the adsorbent to increase the life of the adsorbent. The doping of the adsorbent materials (organobentonite, activated carbon, biochar) with zero-valent iron (ZVI) has been found to be a promising approach to remove the pollutant from the adsorbent insitu by reduction [1,16]. The impregnation of ZVI particles in the biochar matrix made from pulp and paper mill sludge [ZVI-magnetic biochar composites (ZVI-MBC)] facilitates the simultaneous adsorption and dechlorination of PCP in the effluent [1]. The combination of ZVI and carbon exert synergistic effect for the removal of pollutant from the effluent resulting in the high removal efficiency of the adsorbent. Wu et al. [16] reported that the bromate removal reaction rate was 4.15 times higher on ZVI immobilized activated carbon compared to unsupported *n*ZVI. Similarly, organobentonite supported ZVI particles showed high PCP removal rate (4–6 times) than the unsupported ZVI due to the simultaneous adsorption and reduction of PCP on the organobentonite surface [17]. Although, ZVI-MBC was efficient in the dechlorination of PCP from the aqueous solution but the dechlorination reaction was too slow to achieve the desired PCP removal. Devi and Saroha [1] obtained 85% dechlorination efficiency of PCP in 24 h. One of the novel approaches for enhancing the dechlorination rate of the ZVI-MBC involves impregnation of ZVI-MBC with some catalyst like nickel (Ni), copper (Cu), palladium (Pd) and platinum (Pt). The doping of the metals such as Cu, Ni, Pt, and Pd has been reported in the literature [18–20]. Nickel is a preferred doping metal in the ZVI-system because it is comparatively cheap and provides better hydride generation potential [19]. Additionally, the Ni doping on ZVI primarily controls the ZVI passivation by preventing its corrosion and thereby enhancing the removal rate of the contaminants [20]. Therefore, it is proposed to synthesize the Ni–ZVI magnetic biochar composites (Ni–ZVI-MBC) by doping with Ni as a catalyst for the removal of PCP from the synthetic and real industrial effluent. The synthesized adsorbent will provide higher PCP removal efficiency by utilizing the high adsorption capacity of biochar along with the high reductive potential of Fe–Ni bimetals.

In the present study, Ni–ZVI-MBC was synthesized by the impregnation of ZVI on the biochar obtained by the pyrolysis of paper mill sludge and subsequent doping of Ni on ZVI-MBC. The synthesized Ni–ZVI-MBC was characterized for the surface area, porosity, surface morphology, surface functional groups and crystal structure. The ageing and leaching studies were performed to determine the stability of Ni–ZVI-MBC. The Ni–ZVI-MBC was used as an adsorbent for the removal of PCP from the synthetic and real industrial effluent. The adsorption and dechlorination kinetics and the thermodynamics studies were performed to characterize the adsorption and dechlorination mechanisms. Since, the disposal of the exhausted adsorbent after the adsorption process is a problem; the feasibility of using the exhausted Ni–ZVI-MBC for the brick formation was also explored.

2. Materials and methods

2.1. Chemicals

PCP (C_6HCl_5O; molecular weight – 266.34 g/mol) of 98% purity was procured from Sigma–Aldrich chemical company. All reagents used in the present study were of analytical grade.

2.2. Preparation of Ni–ZVI-MBC

The paper mill sludge was collected from dewatering unit of pulp and paper mill and detailed characterization of paper mill sludge is provided elsewhere [21]. The Ni–ZVI-MBC was synthesized from the paper mill effluent treatment plant (ETP) sludge in three steps. Initially, paper mill ETP sludge was pyrolyzed at 700 °C [21] and the resultant biochar was used for the preparation of ZVI-MBC by impregnation of ZVI particles on paper mill sludge biochar surface. The detailed procedure for ZVI and ZVI-MBC preparation is stated elsewhere [1]. Briefly, the preparation of ZVI was carried out by reduction of $FeSO_4$ to Fe(0) using $NaBH_4$ solution as a reducing agent (Eq. (1)). The $NaBH_4$ solution was dropwise added into the flask containing $FeSO_4$ solution resulting in the formation of ZVI as black precipitate:

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0 + 3H_2BO_3^- + 6H_2 + 12H^+ \quad (1)$$

The preparation of ZVI-MBC was performed by impregnation of ZVI on biochar-cetyltrimethylammonium bromide (CTMB) complex (5 g of biochar in the CTMB solution of known concentration (0.1–0.8%). To prepare ZVI-MBC, 5 g of biochar-CTMB complex was added into the reaction mixture containing ZVI and stirred vigorously at 1000 rpm for 30 min. 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.

For the preparation of the Ni–ZVI-MBC, the doping of Ni was performed on the ZVI-MBC surface. A solution (50 mL) of nickel chloride ($NiCl_2{\cdot}6H_2O$) of desired concentration (0.1–1.0 wt%) was prepared and 5 g of ZVI-MBC was added in the solution. The mixture was ultra-sonicated for 20 min at 25 °C and the solid residue was separated from the liquid by centrifugation at 1000 rpm. The solid residue was washed several times with ethanol to prevent the oxidation of the ZVI particles. After washing, the solid residue was dried at 105 °C for 2 h to obtain Ni–ZVI-MBC. The Ni–ZVI-MBC was stored in air-tight container for further use.

The synthesis of Ni–ZVI was performed by impregnation of Ni on ZVI surface as per the above procedure without the addition of biochar-CTMB complex in reaction mixture.

2.3. Characterization of Ni–ZVI-MBC

The synthesized Ni–ZVI-MBC was characterized for the surface area, porosity, surface functional groups, surface morphology and crystal structure. The BET surface area and porosity of the Ni–ZVI-MBC was analyzed using N_2 adsorption–desorption isotherm at 196 °C using a Micromeritics ASAP 2010 apparatus. The surface functional groups of the Ni–ZVI-MBC was analyzed using FTIR spectrometer where the dried Ni–ZVI-MBC sample was mixed with the dried KBr in a ratio of 1:30 and FTIR spectra was recorded at a resolution of 4 cm^{-1} in the region of 4000–400 cm^{-1}. The surface morphology of the Ni–ZVI-MBC was determined using scanning electron micrograph (SEM). The crystal structure of Ni–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.