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Efficient removal of priority, hazardous priority and emerging pollutants with *Prunus armeniaca* functionalized biochar from aqueous wastes: Experimental optimization and modeling

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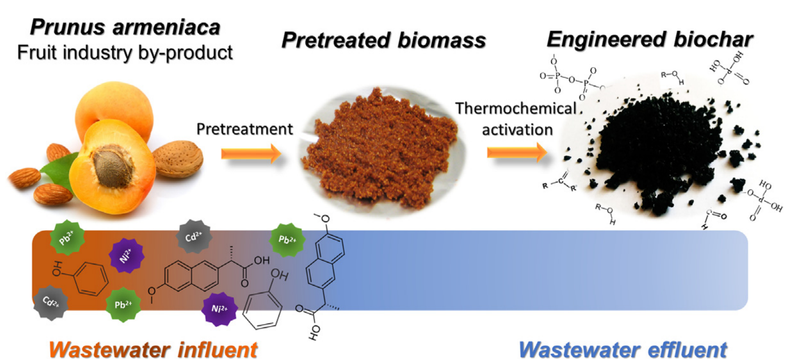
HIGHLIGHTS

- Engineered biochar for heavy metals and organic micropollutants removal was studied.
- Production cost and properties suggest that it can be a promising green adsorbent.
- The adsorption capacity with 179.48 mg g^{-1} mainly depends on the surface chemistry.
- Adsorption mechanisms were detailed analyzed.
- A novel biochar could be applied into slurry reactor wastewater treatment systems.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper investigates the ability of the phosphoric acid functionalized *Prunus armeniaca* stones biochar (AsPhA) prepared by thermochemical activation to remove lead (Pb^{2+}), cadmium (Cd^{2+}), nickel (Ni^{2+}), naproxen and chlorophenols from aqueous wastes. The engineered biochar was characterized using the Scanning Electron Microscopy, Energy-dispersive X-ray Spectroscopy, Fourier Transform Infrared Spectroscopy and Brunauer, Emmett and Teller technique. The batch studies were performed by varying the initial pH of the solution (2–9), adsorbent dosage (0.2–10 g L^{-1}), contact time (5–60 min), temperature (22, 32 and 42 °C) and initial adsorbate concentration (5–500 mg L^{-1}). With the optimal process conditions, the adsorption efficiency was over 95% (100 mg L^{-1}). The results were fitted with three kinetic and three equilibrium theoretical adsorption models. The adsorption process has good correlation with pseudo-second-order reaction kinetics. Adsorption mechanism was found to be controlled by pore, film and particle diffusion, throughout the entire adsorption period. The monolayer adsorption capacities were found to be 179.476, 105.844 and 78.798 mg g^{-1} for Pb^{2+}, Cd^{2+} and Ni^{2+}, respectively. Thermodynamic parameters such as Gibbs energy, enthalpy and entropy were also calculated. Additionally, preliminary results indicated a strong affinity of the biochar for selected organic micropollutants: naproxen and chlorophenols. Based on desorption study results, biochar was successfully regenerated in 3 cycles with diluted phosphoric acid produced as a waste stream during washing of the biochar after thermochemical activation. The experimental results were applied in a two-stage completely stirred tank reactor design. Cost estimation of AsPhA production substantiated its cost effectiveness and adsorption costs of selected pollutants were 5 times

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lower than with the commercial activated carbons. Based on the low-cost and high capacity, engineered biochar can be used as a highly efficient eco-friendly adsorbent for removal of heavy metal and organic micropollutants from wastewaters systems.

1. Introduction

Industrial progress has made life more comfortable, but at the same time the natural environment had suffered from the effects of pollutions. The presence of metal ions, chlorophenols and pharmaceuticals in municipal or industrial wastewater and landfill leachate and their potential impact have been a subject of scientific environmental research for a long time (Ghasemi et al., 2014a). Because of their greater stability, they cannot be automatically degraded and removed from the environment (Ciopec et al., 2012).

The heavy metals, such as lead, cadmium and nickel are among the most common pollutants found in industrial effluents in Serbia (Dalmacija et al., 2011). Even at low concentrations, these metals can be toxic to humans. Various industries such as battery manufacturing, printing, metal plating and finishing, generate huge amounts of wastewater contaminated with lead (Fu and Wang, 2011). Cadmium enters into the aquatic systems from the effluents of electroplating, smelting, alloy manufacturing, pigments, plastic, cadmium–nickel batteries, fertilizers, pesticides, mining, pigments and dyes, textile operations and refining (Zouboulis et al., 2004). Nickel have widespread applications in many industrial processes such as mineral processing, paint formulation, electroplating, batteries manufacturing, forging, porcelain enameling (Bhatnagar and Minocha, 2010). Pharmaceuticals and chlorophenols have been recognized as a hazardous class of organic micropollutants due to their extensive use, (eco)toxicity, potential health and long term effects toward aquatic environment (Barbosa et al., 2016).

Many processes have been suggested to remove these pollutants from wastewaters. These processes include chemical precipitation (Grimshaw et al., 2011), ion exchange (Oehmen et al., 2006), coagulation and flocculation (Amuda et al., 2006), complexation (Camarillo et al., 2012), membrane processes (Aydiner et al., 2006), biosorption (Abdolali et al., 2014) and adsorption (Kwon and Jeon, 2012; Trakal et al., 2016; Wang et al., 2015b. The first five conventional separation methods have many disadvantages for instance, the high capital and operational cost, the production of large amount of heavy metal sludge and possible generation of secondary pollutions resulting in high disposal costs (Albadarin et al., 2012). In contrast, biosorption and adsorption technique is one of the preferred methods due to its simplicity as well as the availability of wide range of sorbents (Ghaedi et al., 2015). The cost of adsorption technology application can be reduced, if the adsorbent is cheap. So, there is a constant search for alternate "low-cost" adsorbents, as technologically optimal and cost effective solutions. Adsorption on activated carbons and biochars is still regarded by far more advantageous due to their high specific surface area and pore volume, relatively "low-cost" and simplicity of designs. Conventional adsorbents such as granular or powdered activated carbons are not always popular for the wastewater treatment as they are not economically viable and technically efficient (Delgado et al., 2012; Li et al., 2010). In recent years growing research interest in the production of "low-cost" and highly efficient biochar based adsorbents has been focused on the relatively cheap and effective raw materials with a high carbon and low inorganic content, for like biomass waste materials, such as agriculture residues, fruit industry waste and various solid organic substances. Biochar is a pyrogenic carbon material produced by combustion of biomass under oxygen limited conditions (Mohan et al., 2014). Techniques have been developed to produce engineered biochars with enhanced adsorption ability. The engineered biochars are prepared through either surface modification of pristine materials or direct pyrolysis of pretreated biomass feedstocks (Wang et al., 2015a, 2015c). A number of studies have been reported for heavy metal ions and some organic micropollutants removal by using different biochar, such as rice straw (Han et al., 2013), empty fruit branch (Mubarak et al., 2013), digested dairy waste (Inyang et al., 2012), agriculture wastes (Mandal et al., 2017), *Cocos nucifera* L. (Wu et al., 2017), apple pulp (Depci et al., 2012), tamarind wood (Acharya et al., 2009), peach stone (Duranoĝlu et al., 2010), cherry and plum kernels (Pap et al., 2016, 2017), etc. Detailed analysis of the efficiency in removal of chlorophenols from aquatic systems using biochar has not been published yet.

In this study, *Prunus armeniaca* stones lignocellulosic biomass derived from fruit industry by-product has been used for engineering biochar as a new adsorbent for removal of Pb^{2+}, Cd^{2+}, Ni^{2+} ions, chlorophenols and naproxen from aqueous solution. These substances were selected from those presenting a significant risk to or via the aquatic environment, using the approaches outlined in Annex II of Directive 2008/105/EC and NORMAN List of Emerging Substances (EU, 2008; NORMAN Network, 2011). Biochar functionalization was performed by thermochemical conversion at 500 °C with 50 vol% phosphoric acids. A detailed characterization of the AsPhA was performed through various instrumental analyses. The influence of several important operating parameters, such as initial pH of water media, AsPhA dosage, contact time, temperature and initial adsorbate concentration were studied in batch mode. Furthermore, the adsorption kinetics, equilibriums and thermodynamics of Pb^{2+}, Cd^{2+} and Ni^{2+} ions were also investigated. The desorption study showed that filtrate may recover up to 95% of the adsorbate. Completely stirred tank reactor (CSTR) has ability to provide the best contact between powdered biochar and water to be treated consequently. This study was performed to enhance knowledge about the adsorption capacity of the AsPhA in a CSTR, for heavy metals contaminated graphic industry wastewaters. The knowledge of this evolution will help operators to manage the powdered biochar in order to optimize its utilization. For the first time, the cost involved in AsPhA preparation was calculated to account the cost effectiveness. In addition, engineered biochar shows a great affinity toward chlorophenols and naproxen, which allows its successful implementation in the field of green separation technology for specific organic residues wastewater treatment.

2. Methods

2.1. Materials, equipment and detection methods

All chemicals and reagents used were of analytical reagent grade. Lead nitrate ($Pb(NO_3)_2$), cadmium sulfate octahydrate ($3CdSO_4 \cdot 8H_2O$), nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), concentrated hydrochloric acid (HCl), ammonium hydroxide (NH_4OH) were supplied by Fisher Scientific. Stock solutions were prepared and diluted to the required concentrations using deionized water (EASYpure® II Reservoir Feed Water Purification System). In order to make standard solution for experiments, the stock solution containing naproxen was prepared dissolving naproxen standard (Fisher Scientific) with 10 mL of deionized water and then 10 mL acetonitrile (HPLC grade, Sigma-Aldrich, Germany). After that 10 mL of 0.05% CH_3COOH, 250 mL of glacial CH_3COOH (Zorka Pharma), diluted in volumetric flask of 500 mL filled with milli-Q water, and another 10 mL of acetonitrile were added. Aqueous solution is then transferred in volumetric flask and filled