



Research article

Alkali modified hydrochar of grape pomace as a perspective adsorbent of Pb^{2+} from aqueous solution

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ABSTRACT

Hydrochar produced via hydrothermal carbonization of grape pomace was considered as novel sorbent of Pb^{2+} from aqueous solution. In order to enhance the adsorption capacity, hydrochar was chemically modified using 2 M KOH solution. Both materials were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy and X-ray diffraction technique. Batch experiments were performed to examine the effect of sorbent dosage, pH and contact time. Obtained results showed that the KOH treatment increased the sorption capacity of hydrochar from 27.8 mg g^{-1} up to 137 mg g^{-1} at pH 5. Adsorption of lead on either of the materials was achieved through ion-exchange mechanism, chemisorption and Pb^{2+} - π interaction. The Sips isotherm model gave the best fit with the experimental data obtained for Pb^{2+} sorption using activated hydrochar. The adsorption kinetic followed a pseudo second-order model. Thermodynamic parameters implied that the Pb^{2+} binding for hydrochar surface was spontaneous and exothermic process. Findings from this work suggest that the hydrothermal carbonization is a promising route for production of efficient Pb^{2+} sorbents for wastewater treatment.

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1. Introduction

Over the years, increasing anthropogenic activity and spillage of industrial waters into watercourses have become a worldwide environmental problem. Conventional methods for water purification, such as coagulation/flocculation, chemical oxidation, membrane filtration, adsorption on activated carbon and electrochemical treatment, are oftentimes expensive, polluting, time consuming and mostly ineffective at low concentrations of contaminants (Elaigwu et al., 2014; Iftikhar et al., 2009; Regmi et al., 2012; Kilic et al., 2013). Therefore, there is a growing interest of utilization of novel, low-cost and efficient technologies for wastewater treatment (Harman et al., 2007; Elaigwu et al., 2014).

Due to its cumulative effects, heavy metals in waters are potential threat to the environment, humans and other living organisms (Regmi et al., 2012). One of the most prevalent, toxic metals in industrial effluents is lead (Pb^{2+}) (Milojković et al., 2014; Mohan et al., 2015). It is well known that Pb^{2+} may cause mental, brain

and liver damage, and also can be assimilated and concentrated in animal tissues (Guo et al., 2015; Wang et al., 2015a, 2015b). The adsorption of Pb^{2+} using waste biomass has been confirmed as a simple, inexpensive and efficient method for treatment of polluted waters (Milojković et al., 2014; Wang et al., 2015a; Lu et al., 2012; Guo et al., 2015).

Comparatively, development of new methods for thermochemical conversion of waste biomass into valuable products is on the increase. Biochars derived from lignocellulosic residuals via dry pyrolysis and hydrothermal carbonization (HTC) has been broadly examined for different environmental applications (Sun et al., 2015; Mohan et al., 2015; Xue et al., 2012). The latter conversion procedure offers significant advantages relative to dry pyrolysis, such as mild reaction conditions and high conversion efficiency of wet biomass load (Tan et al., 2015). Produced hydrochars, although with lower porosity and carbon content in comparison to pyrolyzed biochars are very abundant with the reactive oxygen functional groups (OFGs) (e.g., hydroxyl and carboxylic) (Sun et al., 2015). Therefore, hydrochars may represent alternative low-cost and efficient sorbents of heavy metals from polluted waters (Xue et al., 2012; Regmi et al., 2012; Sun et al., 2015). Structure and adsorption capacity of hydrochar depends primarily on the HTC temperature,

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reaction time and feedstock type (Parshetti et al., 2013; Dai et al., 2014).

In order to further enhance heavy metal sorption ability of hydrochars, several studies have investigated different methods of tailoring the hydrochar's surface structure (Jin et al., 2016; Regmi et al., 2012). Thus, activation of hydrochars obtained from peanut hull and *Cymbopogon schoenanthus* L. Spreng, using hydrogen peroxide (H_2O_2), have significantly improved hydrochar's sorption capacities for Pb^{2+} and Cu^{2+} , respectively (Xue et al., 2012; Zuo et al., 2016). Xue et al. (2012) have reported that the Pb^{2+} removal from aqueous solution using H_2O_2 -activated hydrochar was enhanced more than 20 times in comparison to untreated material, while Zuo et al. (2016) have reported an increase of Cu^{2+} removal for 30%.

Also, cold alkali modification of hydrochar using potassium hydroxide solution (KOH) has been proposed as a relatively simple procedure to obtain more efficient hydrochar-based heavy metal sorbents (Regmi et al., 2012; Sun et al., 2015). Regmi et al. (2012) have investigated the removal of Cu^{2+} and Cd^{2+} from the solution using untreated and KOH modified switchgrass hydrochar, while Sun et al. (2015) have examined the efficiency of KOH-activated hydrochars from sawdust, wheat straw and corn stalk as alternative adsorbents of Cd^{2+} and heavy metals from aqueous multi-metal system. Both authors have reported that alkali modification enhances the content of OFGs on hydrochar surface, which subsequently improved metal adsorption capacity of activated hydrochars (Regmi et al., 2012; Sun et al., 2015).

Grape is one of the most common fruit crops in Mediterranean Europe with annual production of about 29 million tones, of which more than 70% is consumed for the production of wine. During winemaking, significant amount of pomace is generated (20–25% from feedstock). Common disposal of this wet biomass on landfill sites may cause serious environmental problems like uncontrolled decomposition, moldering, bad odor spreading and leakage of waste fluids. Therefore appropriate reuse of pomace would contribute to global environmental protection and sustainable development of wine industry.

In this study, for the first time suitability of grape pomace hydrochar (GP-HC) as an adsorbent for Pb^{2+} removal from aqueous solution was investigated. Additionally, inspired by studies of Regmi et al. (2012) and Sun et al. (2015), GP-HC was activated with 2 M KOH. The effect of pH, adsorbent dosage, concentration of the heavy metal, temperature and contact time on the adsorption process of a single component system for both materials was studied, in order to understand its kinetics, thermodynamics and mechanisms of Pb^{2+} removal.

2. Materials and methods

2.1. Chemicals

All the chemicals and reagents used in the present study were of analytical grade. The primary standard solution of Pb^{2+} (2000 mg L^{-1}) was prepared by dissolving the weighed amount of $\text{Pb}(\text{NO}_3)_2 \times 3\text{H}_2\text{O}$ in distilled water. Solutions of various Pb^{2+} concentrations used in experiments were prepared by diluting the primary stock solution with distilled water.

2.2. HTC hydrochar preparation

Preparation of used HC has been described in detail in our previous study (Petrović et al., 2016a). Briefly, about 250 g of the air dried and homogenized biomass (particle size <0.5 mm) was mixed with distilled water at 1:5 ratio and carbonized in 2000 mL autoclave (model 10253, Deutsch&Neumann), at 220 °C 1 h. After a

reaction period and cooling of the reactor to room temperature, solid and liquid products were separated by filtration and collected. The separated HC was then rinsed several times with distilled water and dried at 105 °C in the oven.

Alkali activation was carried out by stirring 5 g of the obtained HC with 500 mL of 2 M KOH solution for 1 h at room temperature (25 ± 0.5 °C). Afterwards, the obtained activated hydrochar (HC_{act}) was filtered, rinsed with distilled water and adjusted to the neutral pH with 0.1 M HNO_3 /KOH solution. During the final step, the HC_{act} was filtered again and dried overnight in an oven at 105 °C.

2.3. Characterization of hydrochar

The point of zero charge (pH_{PZC}) of HC and HC_{act} surface was determined based on the method proposed by Milonjic et al. (Milonjic et al., 1975). More precisely, 0.1 g of HC and HC_{act} were shaken with 50 mL of KNO_3 solution (0.001 M and 0.01 M) for 24 h at 250 rpm. The initial pH values (pH_i) of KNO_3 were adjusted from 2.0 to 12.0 using 0.01 M HNO_3 and/or 0.01 M KOH. After 24 h the suspension was filtered and the final pH was measured (pH_f). The change in pH_f vs pH_i were plotted for the determination of the pH_{PZC} .

Scanning electron microscopy (SEM) was performed using a JSM-6610 (JEOL Inc., USA) in order to analyze the surface structure of HC and HC_{act} before and after Pb^{2+} sorption. All samples were coated with gold, placed on the adhesive carbon disc and recorded.

Spectroscopic analyses were conducted with Thermo Scientific Nicolet iS50 FT-IR spectrometer. The KBr pastilles with 0.8 mg sample and 80 mg KBr have been recorded in transmission mode to identify the chemical functional groups present on the original and Pb-loaded HC_{act} . The spectra were obtained in the range of 4000–400 cm^{-1} .

X-ray diffraction analyses were used to determine the phase composition of HC_{act} before and after Pb^{2+} sorption. Samples were analyzed on the X-ray diffractometer ("PHILIPS", Model PW-1710), with curved graphite monochromator and a scintillation counter. The intensity of diffracted X-ray $\text{CuK}\alpha$ ($\lambda = 1.54178$) were measured on the room temperature at intervals of $0.02^\circ 2\theta$ and time of 1 s, and in the range of 4° – $65^\circ 2\theta$. X-ray tube was loaded with a voltage of 40 kV and current of 30 mA, while the slots to guide primary and diffracted beam were 1° and 0.1 mm.

2.4. Batch adsorption studies

In order to investigate the effect of pH, mass balance, contact time and Pb^{2+} initial concentration batch experiments were performed. The effect of solution pH on the adsorption of Pb^{2+} onto HC and HC_{act} was conducted in the pH range from 2.0 to 7.0. Adsorbent dose of 0.5 g L^{-1} was added to 100 mL volumetric flasks containing 50 mL of standard Pb^{2+} solution (100 mg L^{-1}). All flasks were put on top of a Heidolph Unimax1010 orbital shaker, and shaken at room temperature (25 ± 0.5 °C) for 60 min at 250 rpm. The adsorbents doses of 0.4–4.0 g L^{-1} were agitated with 50 mL of Pb^{2+} solution (100 mg L^{-1}) at pH 5.0 for 60 min in order to investigate the mass balance. Batch kinetic experiments were carried out at different contact times (5–120 min) contacting 0.5 g L^{-1} of HC or HC_{act} and 50 mL of Pb^{2+} solution (100 mg L^{-1}) at pH 5.0. For isotherm studies, 50 mL of lead solutions of different concentrations (40–180 mg L^{-1}) were shaken with 0.5 g L^{-1} HC_{act} for 60 min (250 rpm) at different temperatures (298, 308 and 318 K).

To address the contribution of possible ion-exchange mechanism during Pb^{2+} sorption in obtained filtrates, except Pb^{2+} , the released cations (Ca^{2+} , Mg^{2+} , K^+ and Na^+) were also measured. The content of Ca^{2+} , Mg^{2+} , K^+ and Na^+ released from HC_{act} mixed only

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