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Utilization of fruit processing industry waste as green activated carbon for the treatment of heavy metals and chlorophenols contaminated water

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ABSTRACT

Plum stones, as a part of industrial and municipal organic waste, were used as a precursor for preparation of a low-cost activated carbon. Engineered, thermochemically-modified adsorbent was used to remove lead (Pb^{2+}), cadmium (Cd^{2+}), nickel (Ni^{2+}) and chlorophenols from an aqueous solution. The characterization of the medium was performed using standard instrumental analysis. Additionally, the assessment included the influence of pH, adsorbent dosage, temperature, contact time and initial metal concentration on the separation efficiency in the batch-operational mode. With optimal working conditions, the process efficiency of over 95% was accomplished. The equilibrium and kinetic studies of adsorption were done. The pseudo-second order model described the adsorption kinetics best. The maximum adsorption capacity of the engineered adsorbent for Pb^{2+}, Cd^{2+} and Ni^{2+} ions was calculated from the Langmuir isotherms and found to be 172.43 mg g^{-1}, 112.74 mg g^{-1} and 63.74 mg g^{-1}, respectively. Preliminary results indicate a strong affinity of the separation medium for chlorophenols. Thermodynamic parameters such as Gibbs energy, enthalpy and entropy were calculated. Regeneration of the saturated adsorbent was conducted, with diluted phosphoric acid produced as a waste stream, during the washing of the adsorbent after activation. Based on the desorption study results, the activated carbon was successfully regenerated in 3 cycles. Mutual influence of ions was analyzed in multicomponent systems. The real system production and operational costs analysis confirmed a possibility for a successful implementation of the highly efficient, eco-friendly engineered adsorbent in the field of cost-effective wastewater treatment.

1. Introduction

The increasing concentration of heavy metals in the water is mainly due to the wastewater discharges from industries. The methods that are most commonly used to remove metal ions and organic compounds from wastewaters are various conventional methods, such as chemical precipitation, filtration, flocculation, ion exchange, electrochemical treatments, etc. (Wang et al., 2015; Sadeek et al., 2015). The major disadvantages of these methods are their insufficient selectivity, production of waste sludge, which requires further treatments, high operating costs and various technical limitations, especially when the concentrations of the pollutants are low (Kang et al., 2016). In recent years, more and more attention is paid to non-conventional methods of wastewater treatment. This period of human history is considered the beginning of the development of adsorption with different lignocellulosic waste materials, or the application of biologic waste materials for the removal of pollutants from aqueous solutions (Lu and Gibb, 2008; Mouni et al., 2011). Attractiveness of this technique can be seen through the constant increase in the number of published

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scientific papers in this field, which only confirms the complexity and multidisciplinary nature of this approach (Gadd, 2009). Additionally, in the following years Serbia should solve Chapter 27 on the Environment (negotiating chapters of the European Union), and in that respect, low-cost green technologies for the treatment of wastewaters are of crucial importance.

Various plant materials, being easily accessible, economically and environmentally friendly, are gaining increasing importance as precursors for the production of cheaper activated carbon with specific structure and properties. Some of the plant materials that have been successfully used for this are: forest biowaste (Kim et al., 2015), pine cone (Özhan et al., 2014), blue jacaranda and plum stones (Trevino-Cordero et al., 2013), grape processing wastes (Saygılı et al., 2015), Brazilian pine-fruit shell (Royer et al., 2009), pistachio nut shells (Nowicki et al., 2015), cherry/sweet cherry kernels (Pap et al., 2016), apricot stones (Soleimani and Kaghazchi, 2008), hazelnut husks (Imamoglu and Tekir, 2008), oil palm shell (Tan et al., 2008), corncob (Sych et al., 2012), tomato processing solid waste (Saygılı and Güzel, 2016), coffee grounds (Reffas et al., 2010), wooden precursors (Largitte et al., 2016; Hajati et al., 2015), sea-buckthorn stones (Mohammadi et al., 2010).

The aim of the research presented in this paper was the selection, synthesis, characterization and efficiency evaluation of an alternative adsorption medium for the separation of inorganic ions and organic pollutants from model solutions and real wastewater samples. The main source of biomass used for production of activated carbon was lignocellulosic material (plum stone), as a waste byproduct of fruit processing industry. The activated carbon was prepared by thermochemical conversion. In order to minimize the operating costs, which is one of the main challenges of most research studies, the preparation process of activated carbon was conducted in the complete absence of inert atmosphere. Carbonization was performed in a furnace exposed to air, without the application of any inert gases. The resulting activated carbon has been characterized by numerous instrumental analyses: elemental analysis, Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX) and Brunauer, Emmett and Teller (BET) technique. As a part of this study, the impact of the variability of different process parameters (pH value, the amount of adsorbent, contact time of the adsorbent with an aqueous solution, temperature and the initial concentration of adsorbate) on the separation efficiency of adsorbate from aqueous solutions in a batch mode has been examined. After determining the most important characteristics of the activated carbon and optimal process parameters, the kinetic, equilibrium and thermodynamic studies of adsorption on this separation medium were conducted in a batch mode. The mutual influence of ions has been analyzed in multicomponent systems. The affinity of the adsorbent towards chlorophenols has been examined as well. A detailed analysis of the production cost and the application of activated carbon, obtained in the analysis of real samples, showed the possibility of successful implementation of the media produced in the field of separation technology for wastewater treatment.

The purpose of this work was to evaluate the possibility of using fruit processing industry waste as renewable, low cost and sustainable adsorbent for the removal of heavy metals and chlorophenols from wastewaters. These results may provide a solution for cleansing and reuse of this type of waste, which can reduce its disposal cost, finally resulting in the protection of the environment from pollution by organic and inorganic pollutants.

2. Material and methods

When using green activated carbons, the preparation and implementation costs are as important as the properties of the obtained adsorbent. Therefore, the characteristics of activated carbon should be identified during the production process and optimum operation conditions should be determined carefully.

2.1. Sample preparation and analysis of inorganic and organic pollutants

The chemicals employed in the experiment, 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 all of analytical grade and supplied by Fisher Scientific. Stock solutions were prepared and diluted to the required concentrations using deionized water (EASYpure® II Reservoir Feed Water Purification System). The Pb^{2+}, Cd^{2+} and Ni^{2+} content in the supernatant was measured using flame atomic absorption spectrometry (FAAS, model Thermo Scientific S Series) with an air-acetylene flame.

The chlorophenols used in this research (2,4 – dichlorophenol, 2,4,6 – trichlorophenol, 2,3,4,6 – tetrachlorophenol and pentachlorophenol) and brominated phenols surrogate standards (2,4-dibromophenol and 2,4,6-tribromophenol) were purchased from LGC Standards - Dr. Ehrenstorfer GmbH. After each experiment, chlorophenols and bromophenols were derivatized to acyl derivatives directly, in the water samples with acetic anhydride, under basic conditions. The investigated compounds were extracted using liquid-liquid extraction technique, with dichloromethane as solvent. The chlorophenols (in the form of acyl derivatives) were quantitatively analyzed against the internal surrogate standards, using gas chromatography–mass spectrometry (GC-MS, model Agilent 7890B, with HP5-MS capillary column, 30 m × 0.25 mm, film 0.25 μm).

2.2. Untreated lignocellulosic biomass

Plum (*Prunus domestica* L.) is a fruit tree from the plum family (*Prunoidae*), which is widespread in Serbia and belongs to the group of trees that are frequently found in orchards and tree-lined streets. The seeds of the fruit have no practical application and, when separated from the fleshy part, they must be collected and transported to a landfill site. Since the stones are rich in organic carbon, their use for production of powdered activated carbon is examined in this paper. The average production of plums in Serbia amounts up to 600 000 t y^{-1}. Stone weight is 20% of the total weight of the fruit. Accordingly, it can be calculated that approximately 120 000 tons of this vegetable waste is produced annually. The basic characteristics and the appearance of this raw material after grinding are shown in Table 1 and Fig. 1.

2.3. Activated carbon preparation

Local plum stones were collected from a fruit plantation located in Novi Becej, province of Vojvodina (Serbia) and washed in water prior to peel separation. The plum stones (kernels and shells) were crushed in a mechanical mill and dried for 2 h at 105 °C. The milled raw materials were impregnated with 50 wt% H_3PO_4 aqueous solution at a ratio of 2.66:1 (weight). This corresponds to 1 kg of stones impregnated with 2 L of 50 vol% acid. The mixture of the raw material and activating agent was allowed to stand for the next 24 h at room temperature (22.0 ± 1.0 °C) and then the suspension was filtered to remove the residual acid. Subsequently, impregnated samples were placed in ceramic crucibles, air dried at room temperature for 2 h and then introduced into an electric furnace. During the first phase of carbonization the samples were heated at a rate of 10 °C min^{-1} to 180 °C and held at this temperature for