FACULTY OF AGRICULTURE, UNIVERSITY OF BELGRADE

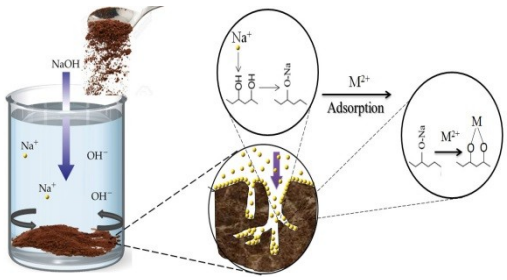
Tatjana D. Šoštarić, doktorska disertacija

Heavy metals removal from aqueous solution by biosorbent based on apricot stones waste biomass

Abstract

In this doctoral thesis, use of apricot (*Prunus armeniaca* L.) stone endocarp as possible biosorbent for the removal of Cu(II), Zn(II) and Pb(II) ions from aqueous solution was examined. Apricot stones are from "Vino Župa" Inc. Aleksandrovac where it is classified as a waste product from fruit processing. In order to get biosorbent with highest sorption performances this waste material was treated with solution of NaOH. In a series of

experiments optimal modification parameters were determined (initial concentration 1mol/L NaOH; solid/liquid ratio 1:20; contact time 180 minutes) and modified material was obtained (KKM). Characterization and comparison of both material, native (KK) and modified (KKM), was performed. Results of chemical analysis as well as FT-IR spectra, showed that disintegration of hemicellulose occurs as a result of alkaline treatment



(decrease of hemicellulose content from 19.23% in KK to 3,52% in KKM; FT-IR spectrum shows loss of 1730 cm^{-1} peak in KKM, that shows -C=O group in hemicellulose). FT-IR and SEM analysis showed that with alkaline treatment wax and oils are removed from the surface of the biomatirial. Point of zero charge also rose as a consequence of alkaline treatment. Concentration of total acidic groups is higher in KK than in KKM (1.619 mmol/g and 0.317 mmol/g, respectively), while in KKM total concentration of basic groups is higher than in KK (0.309 mmol/g and 0.037 mmol/g, respectively). Results of porosimetry confirmed that after alkaline treatment pore volumes increased in KKM (from 218 to 270 mm^3/g), as well as pore diameters (from 393 to 468 nm) and porosity (from 25 to 30%). KKM was examined as a biosorbent for removal of Cu(II), Zn(II) and Pb(II) ions from water solutions. Parameters that affect biosorption were triald (pH, contact time, concentration of biosorbent, granulation)

and optimum values for each parameter were established: pH=5,0; contact time 120 minutes; solid/liquid ratio 0,1g/50mL; granulation <0,8mm. During sorption of metal ions by KKM, release of alkali and earth alkali cations occurred and results showed that cation exchange capacity is 5 times higher in KKM (29,51 meq/100g) than in KK (6,72 meq/100g). Bonding mechanism of investigated metal ions to KKM is complex, hence in lower initial concentrations it is conducted by ion exchange between metal ions and Na ions, while at higher initial concentrations this is not the only mechanism. Results showed that sorption capacity is higher in KKM than in KK and the experimentally obtained results fit well with Freundlich isotherm model for all three metal ions. Experimentally obtained kinetic results fit well to pseudo-second order model. Although temperature affect is not very high still contributes to increase of sorption capacity for all three investigated metal ions.

In order to establish efficiency of KKM as a biosorbent in complex systems similar to real effluents, mutual influence of metal ions was investigated in binary and ternary systems. As a result of competition between ions for active sites on KKM surface antagonism exist. The affinity of the target metals to the KKM surface was in descending order: Pb(II)>Cu(II)>Zn(II). For practical application KKM biomass was immobilized in sodium alginate. To get compact granules suitable for real systems bentonite was added as a bonding agent. Obtained granules were investigated in batch system and in real effluents. Suggested model of conversion and modification of apricot stones, as a waste material from food industry, in to efficient biosorbent for investigated heavy metals from water solutions, also contributes to environment protection through sustainable management and care for food industry waste.

Kew words: waste biomass, *Prunus armeniaca* L., lignocellulosic biomaterials, biosorption, heavy metals

Scientific area: Biotechnical Science

Scientific sub-area: Biotechnology

UDC number: 628.4.042+634.21]:628.35(043.3)