UNIVERSITY OF BELGRADE
TECHNICAL FACULTY IN BOR
CHAMBER OF COMMERCE AND
INDUSTRY OF SERBIA

PROCEEDINGS

IMPRC
INTERNATIONAL MINERAL PROCESSING & RECYCLING CONFERENCE

XIII International MINERAL PROCESSING and RECYCLING CONFERENCE

Editors:
Grozdanka Bogdanović
Milan Trumić

Belgrade, Serbia, 8 – 10 May 2019

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APRICOT SHELLS AS BIOSORBENT FOR CU(II) IONS: DETERMINATION OF OPTIMAL ALKALINE TREATMENT CONDITIONS

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ABSTRACT – The apricot stones (KK) were investigated as biosorbent of copper ions from aqueous solution. The rigidity of lignocellulosic compact molecular arrangement, induce the necessity of its modification. The aim of this paper was to establish optimal parameters of KK modification in order to improve low-cost biosorbent with improved biosorption characteristics. The modification parameters were: initial NaOH concentration, contact time and biomass/base solution ratio. After sets of experiments, the optimal modification parameters for copper removal were found to be: initial concentration of modification agent 1.0 mol/L NaOH, solid/liquid ratio 1:20 and 180 minute of contact time.
The results show that modified apricot shells doubled the binding affinity toward copper ions, and could be used as an efficient low-cost biosorbent, promoting more sustainable production and to stop waste disposal at landfill sites.

Key words: apricot shells, biosorption, Cu(II) ions, modification.

INTRODUCTION

The waste utilization of fruit processing industries has become one of the greatest challenges in world nowadays. Apricots have a significant role in Serbia's fruit production, but average annual production of 30,063 t (Statistical Office of the Republic of Serbia 2018) generates approximately 1,879 t apricot stone waste. Although apricot shells can be used for active carbon production and seeds can be used in food or pharmaceutical industry, most of the apricot stone waste ends up in landfill sites. In order to minimize this type of waste, apricot shells could be used as a biosorbent for removal of different types of pollutants. Because of all mentioned and faced with local environment pollution problems apricot shells was chosen for sorption experiments in the present study. This lignocellulosic biomass fulfils the criteria of unconventional sorbent: it is abundant, cheap and it is waste.

Since preliminary experiments showed that native apricot shells have low affinity

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toward copper ions [1], need for modification of this material has been emerged. In order to get better biosorption performances alkaline modification has been applied. It is well known that this type of treatment has a significant impact on swelling of cellulose fibres causing the hydrogen bond breakage. Due to realising of OH groups cellulose becomes more reactive. Also this type of treatment removes superficial impurities waxes and fats and consequently functional groups become more accessible [2].

In order to get biosorbent with improved biosorption characteristics, raw apricot shells were object of alkaline treatment. Focus of this study was to investigate the optimal parameters of modification, which have effect on chemical, structural and morphological changes of this lignocellulosic material, in order to get biosorbent with improved sorption characteristics..

MATERIALS AND METHODS

Untreated biomass (KK)

Apricot stones were obtained from juice Factory from the Rasina district of Serbia. They were manually separated from kernels and only shells were used for further experiments. Shells were grinded in mill (KHD Humbolt Wedag AG, Germany) and sieved at particle size less than 0.3 mm.

Metal solution preparation

Initial copper solution with concentration of 1g/L were prepared by dissolving precise amount of $Cu(NO_3)_2 \times 3H_2O$ in deionized water.

Adsorption experiments

The removal of copper ions was investigated with differently obtained biosorbents. Batch experiments were carried out when 0.2 g of each obtained sorbent was put in 100 ml glass flask, left on orbital shaker at constant rate (250 rpm/min) for 120 min. The pH value of metal solution was 5.0. After sorption experiment suspension were filtered and residual meal concentration in filtrate were determined by usage of atomic adsorption spectrophotometer. The biosorption capacity was calculated by using the following equation:

$$q_e = \frac{V\ (C_i - C_e)}{m} \quad (1)$$

Where q is the biosorption capacity - amount of adsorbed metal ions (mg/g); C_i is initial metal concentration while C_e is equilibrium metal concentration (mg/L); V is volume (L) and m is mass sample (g).

Determination of optimal modification parameters

In order to design biosorbent with best adsorption performance, the effects of three modification parameters on the rate of adsorption process were observed by varying initial concentration of modified agent (NaOH), ratio between KK and NaOH solution and contact time between modified agent and KK.

Effect of initial NaOH concentration

The first set of experiments was conducted with different initial NaOH concentration: 0.25; 0.5, 1.0; 2.0; 3.0 and 4.0 mol/L. Contact time between base and KK was 120 minute and ratio between them was 1:20. Each obtained biosorbents were rinsed with distilled water until neutral reaction. After drying we tested each of this individual sorbents through set of sorption experiments previously described in section 2.3.

Effect of m/V ratio

Next set of experiments was conducted with different ratio between KK and base: 1:20; 1:40; 1:60; 1:80 and 1:100. Contact time was 120 minute and initial NaOH concentration was 1 mol/L as it was chosen from first set of experiments.

Effect of contact time

The final set of experiments was conducted by varying the contact time between KK and base: 30, 60, 90, 120, 180, 240 and 300 minute. The ratio between solid and liquid phase of 1:20 were applied and initial NaOH concentration was 1 mol/L due to previous set of experiments.

RESULTS AND DISCUSSION

In this section, results of investigation of optimal modification parameters have been presented with the focus if chemical treatment onto raw biomass was sufficient to produce the desired effect (improved biosorption characteristic). According to literature, effects of initial base concentration, contact time and temperature have major effects on results of alkaline treatment [2]. In this paper effect of temperature was not the object of study and all experiments were done on room temperature. Ratio between liquid and solid phase were examined, instead.

Effect of initial concentration of modified agent - NaOH

Native apricot shells (KK) has been modified with different initial concentration of NaOH solution and the results are presented at Figure 1.

As concentration of NaOH rise from 0.25 to 1 mol/L biosorption capacity has risen from 8.4 to 10.6 mg/g, too. However, with further increase of NaOH concentration biosorption capacity started to decrease. The reason for this could be that severe concentration of alkaline effects lignocellulosic structure causing loss of functional groups due to hydrolyses of hemicellulose and depolymerisation of lignin [1]. Similar results were obtained when modified poplar sawdust were used for removal of Cu(II) ions in biosorption experiments by Šćiban [2].

Furthermore, each modified sample (KKM) was tested if it was washed properly: the idea was to test if any deposition of hydroxi groups into the pores of the biosorbent, had occurred. This would lead to sorption false results. In accordance with this the final pH value of solution after biosorption experiments was measured and results are presented in Table1.

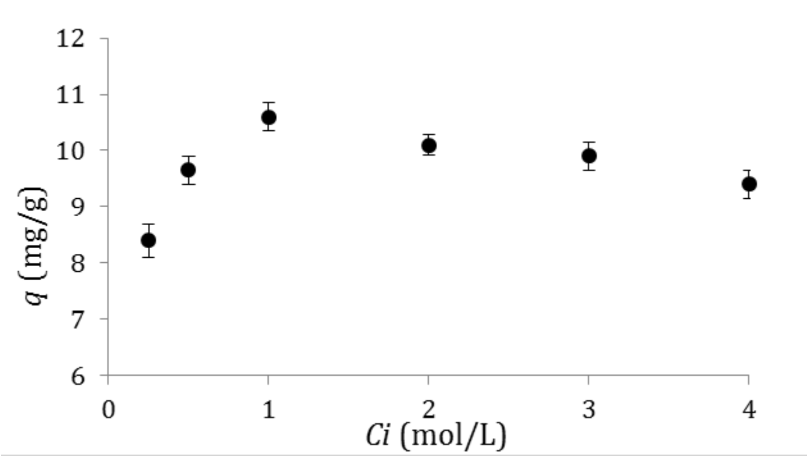

Figure 1. Effect of initial concentration of NaOH onto sorption capacity: m/V = 1:20, contact time was 120 min and concentration of Cu(II) solution was 60 mg/L

Table 1. Change of pH value after Cu(II) ions adsorption by native biomass modified at different NaOH concentration: initial pH value was 5.00

NaOH concentration (mol/L)	0.25	0.50	1.0	2.0	3.0	4.0
pH_f	4.25	4.27	4.28	4.31	4.30	4.37

As can be seen from Table 1 it is evident that there wasn't any noticeable change in pH value of residual solution after biosorbent experiments. This means that the material was washed thoroughly during alkaline treatment and most importantly it means that the increase of biosorption capacity is due to higher porosity and functional groups accessibility of modified biosorbent KKM [1]. Therefore, initial concentration of 1 mol/L of modified agent NaOH was chosen for further experiments.

Effect of ratio between KK and base during the modification process onto biosorption capacity

In order to exam if the ratio between solid (KK) and liquid (NaOH) phase have impact on biosorption capacity, the sorption experiments were conducted by varying the m/V ratio from 1:20 to 1:100. The results are presented at Figure 2.

Figure 2 show that the solid/liquid ratio doesn't have any effect on biosorption capacity of obtained material. In order to get economical and eco-friendly biosorbent m/V ratio of 1:20 was chosen for alkaline treatment. Table 2 shows that after each set of biosorption experiments finale pH value stays unchangeable.

Table 2. Change of pH value after each sets of biosorption experiments: pHi = 5.00

m/V	1:20	1:40	1:60	1:80	1:100
pH_f	4.28	4.25	4.32	4.25	4.24

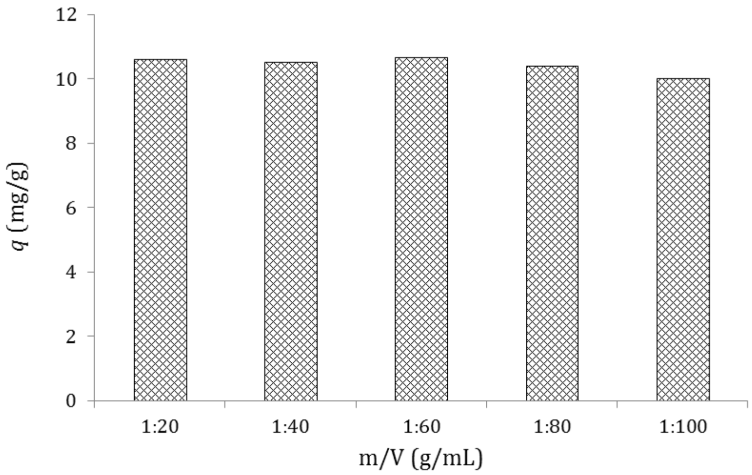

Figure 2. Effect of ratio among KK and NaOH on biosorption capacity towards Cu(II) ions: initial concentration of NaOH was 1mol/L; contact time:120 min, and metal concentration was 60 mg/L

Effect of contact time between KK and NaOH onto biosorption capacity

The effect of treatment time on biosorption capacity of KKM toward Cu(II) ions was investigated in order to determine the necessary time for best results. The obtained results are presented on Figure 3.

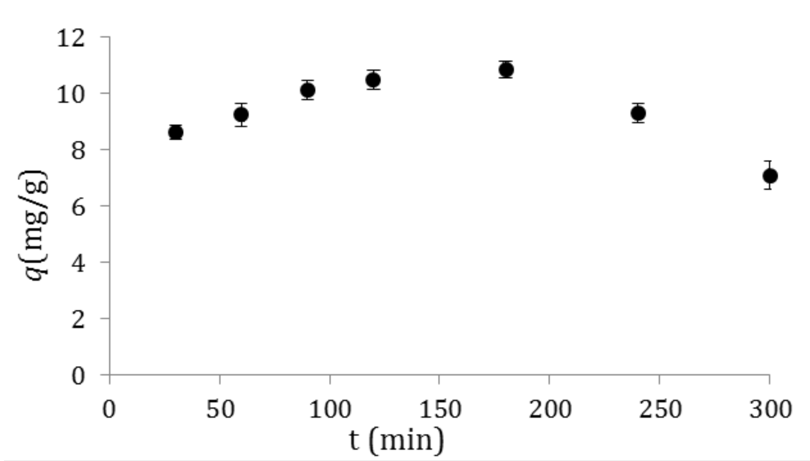

Figure 3. Effect of alkaline treatment time on biosorption capacity of KKM: concentration of NaOH was 1mol/L; m/V= 1:20, concentration of Cu(II) solution was 60 mg/L

Prolonging the contact time between KK and alkaline solution from 30 to 180 minute, biosorption capacity increases from 8.6 to 10.9 mg/g, respectively. However, afterwards biosorption capacity decreases for almost 40 %. If the contact time is longer than 180 minute, the lignocellulosic biomass become more disturbed which causes the biomass to be chemically altered and not suitable for copper ions bonding: the number of active sites becomes lower. As in previous experiments final pH values of solution were measured and the results are presented in Table 3.

Table 3. Change of pH value after biosorption experiments where contact time between KK and NaOH was varied: pHi = 5.00

Contact time (minute)	30	60	90	120	180	240	300
pH_f	4.31	4.24	4.22	4.20	4.25	4.16	3.98

As can be seen from Table 3 final pH value of residual solution after biosorption experiments doesn't varied till 180 minute, while after this point it starts to decrease slightly: after 300 minute it is pH < 4.0. Contact time of 180 minute was chosen as time on which modification will be occurred.

Considering all previous experiments the chosen optimal parameters of KK modification are: initial concentration of modified agent is 1.0 mol/L NaOH, solid/liquid ratio is 1:20 and 180 minute of contact time among KK and NaOH. After alkaline treatment, treated biomass was washed thoroughly in distilled water, filtered and left in oven for 24 h at 50 °C. Obtained material was label as KKM.

The effect of alkaline treatment on native apricot shells biomass onto biosorption capacity toward Cu(II) ions is presented at Figure 4. It is evident that alkaline treatment doubled the value of biosorption capacity due to physical and chemical changes of this lignocellulosic biomass as it was later profoundly presented [1].

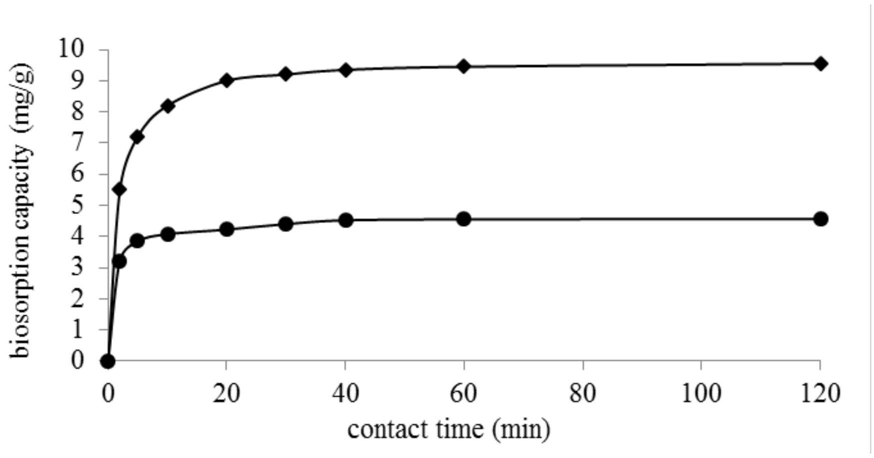

Figure 4. Difference in biosorption capacity between KK and KKM

CONCLUSION

The presented study demonstrates that alkaline modification has significant effect on biosorption performance of rigid native lignocellulosic biomass. Throughout set of experiments the optimal parameters of modification were establish: initial concentration of modified agent is 1.0 mol/L NaOH, solid/liquid ratio is 1:20 and 180 minute of contact time. Acquired biosorbent KKM achieve to double the value of biosorption capacity of native biomass. As apricot shells are widely available in the Republic of Serbia as an agricultural waste, biosorbent made of this type of biomass has twofold significance: economical solution for wastewater treatment and preventing the waste from going to lendfill.

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