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# Modified softwood sawdust as adsorbent of heavy metal ions from water

Marina Šćiban *, Mile Klašnja, Biljana Škrbić

*Faculty of Technology, University of Novi Sad, Novi Sad, Serbia and Montenegro*

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**Abstract**

The sawdust of deciduous softwood–poplar, and coniferous softwood–fir, have been found to possess some adsorption capacities for heavy metal ions. Their adsorption capacities can be increased by previous treatment with a sodium hydroxide solution. Adsorption capacities of alkali modified adsorbents were higher than for unmodified ones from 2.5 to 5 times for copper ions, and about 15 times for zinc ions. Also, for modification can be used solution of sodium carbonate, but that alkaline solution is less efficient than sodium hydroxide solution. The 1% sodium hydroxide solution is suggested for modification of softwood sawdust. It was established that the ion exchange is not only adsorption mechanism, than microprecipitation of metal-hydroxide in the pore liquid was happened, too. At the same time, the leaching of organic matters from modified softwood sawdust were less than from unmodified ones for about 7% for poplar and 23% for fir.


*Keywords:* Adsorption; Copper; Zinc; Softwood sawdust; Alkaline treatment

## 1. Introduction

Several inexpensive materials have been studied for the adsorption of heavy metal ions from water [1]. The lignocellulosic waste materials are accomplished requirements for good adsorbent—they possess some adsorption capacities and they are locally available and have a low cost. Different lignocellulosic materials have different adsorption capacities for individual metal ions [2].

For the increase of the adsorption capacities of these adsorbents, and the improvement to their usage, some methods of their previous treatment have been used. Deshkar et al. [3] treated *Hardwickia binata* bark with formaldehyde in acidic medium, to prevent leaching of organic coloured matter from it. Seki et al. [4] treated *Populus jezoensis* bark with a hot water, 1% NaOH solution and an ethanol:benzene mixture. They established that alkaline solution markedly decreased, and other solvent had not significant influence on bark adsorption ability. Also, Rios et al. [5] established that alkaline modification of oat and wheat straw either in no degree or only slightly increased their adsorption capacities. On the other hand, when a virgin granular activated carbon was treated with 0.1N $HNO_3$, followed by 0.1N NaOH, a dramatic improvement in adsorption quality was observed [6]. The authors explained that phenomenon with the deposition of $OH^-$ group and possible precipitation of metal-hydroxide in the pore liquid.

Sodium hydroxide is a well-known fibre-swelling agent. Degree of change is dependent on time, temperature and alkali concentration [7,8]. Because of that, the aim of this paper was to investigate the influence of alkali pretreatment of softwood sawdust on their adsorption abilities.

## 2. Materials and methods

### 2.1. Wood sample

The sawdusts of poplar and fir, two species of locally available wood, were sieved, and the fraction with particle size between 0.5 and 1.0 mm was used for experiments. Dry matter of poplar and fir sawdust were 93.5 and 92.5%, and surface areas were 1.05 and 3.85 $m^2\,g^{-1}$, respectively. Textural properties (surface area, pore volume, average pore diameter) of adsorbents were obtained via low-temperature nitrogen absorption measurements using a Micrometrics ASAP 2000 instruments.

* Corresponding author. Tel.: +381216350122/366; fax: +38121450413.
*E-mail address:* msciban@uns.ns.ac.yu (M. Šćiban).

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### 2.2. Methods of wood modification

One part of adsorbent was treated with 15 parts of sodium hydroxide or sodium carbonate solution of different concentration. It was kept at 20 °C for 6 h, or at 80 °C for 2 h, and occasionally was stirred. The product was filtered, washed with four-time larger volume of distilled water than volume of solution for modification was, and was dried at 50 °C, overnight. Drying at 50 °C was chosen because severe drying conditions (high drying temperature) might cause a decrease of the number of cellulose based $OH^-$ groups on the lower wood moisture content. That might cause a thermic deactivation of the wood surface [9].

Wastewater from modification and wastewater from rinsing of adsorbent after modification were analysed. The alkalinity and COD [10] in wastewater were measured.

### 2.3. Adsorbate solution

The stock solutions of copper(II) and zinc(II) (0.25 mol $l^{-1}$) were prepared by dissolving $CuSO_4{\cdot}5H_2O$ or $Zn(SO_4)_2{\cdot}7H_2O$ in distilled water. Adsorbate solutions were prepared by dilution of stock solutions with distilled water. pH in adsorbate solution were adjusted to desired values by adding 0.5 mol $l^{-1}$ $CH_3COOH$. All chemicals used were of analytical reagent grade.

### 2.4. Batch adsorption studies

Batch adsorption experiments were carried out by shaking 5 g $l^{-1}$ of wood sawdust with an aqueous solution of Cu(II) ions at pH 4, or an aqueous solution of Zn(II) ions at pH 6. pH in model water was adjusted in accordance with previous investigations [2,5]. In fact, the copper ions precipitate as copper hydroxide at pH 6, which flocks are easy visible, and in that condition the investigation of adsorption phenomena is impossible. After 3 h of shaking, the adsorbent was separated by vacuum filtration through a Gooch G3 crucible.

Concentrations of copper(II) and zinc(II) before and after adsorption were determined on an atomic absorption spectrophotometer (Pye Unicam SP 191). The same instrument was used to determine calcium, magnesium, sodium and potassium ion concentrations in the ion-displacement tests.

Each experiment was carried out in duplicate and the average results are presented.

### 2.5. Adsorption model

To determine the adsorption capacity of adsorbents for Cu(II) and Zn(II) ions, the Langmuir (1) and the Freundlich (2) adsorption models were used:

$$q = \frac{q_m K_L C}{1 + K_L C} \tag{1}$$

$$q = K_F C^{1/n} \tag{2}$$

where $q$ is the amount of Cu(II) adsorbed per specified amount of adsorbent (mmol/g), $C$ the equilibrium concentration (mmol $l^{-1}$), $q_m$ the amount of Cu(II) required to form a monolayer on the surface (mmol $g^{-1}$), $K_L$ the Langmuir equilibrium constant, and $K_F$ and $n$ are the Freundlich equilibrium constants. Computer simulation technique was applied to fit the Langmuir and Freundlich equations for the adsorption data. The accuracy of such fits was estimated in terms of the computed correlation coefficients ($R^2$).

## 3. Results and discussion

### 3.1. Adsorption capacities of unmodified wood sawdust

The adsorption capacities of poplar and fir sawdust for copper and zinc ions were determined by constructing the corresponding equilibrium isotherms (Fig. 1).

The curves on Fig. 1 show that the both adsorbents have a bigger capacity for copper ions than for zinc ones. The adsorption curves for zinc characterize mild rise and sharper one for copper. That reflects a better "affinity" of investigated adsorbent for the copper ions. Because of that, both adsorbent were saturated by a constant amount of copper ions at lower concentration, than for zinc ions. That fact appears that the number of active sites on the adsorbent surface is limited.

The adsorption of copper and zinc ions follow both Langmuir- and Freundlich-type isotherms. Regression analysis of the linearized Langmuir isotherm ($C/q$ versus $C$) and linearized Freundlich isotherm ($\log q$ versus $\log C$) gave the adsorption constants and correlation coefficients ($R^2$) listed in Table 1.

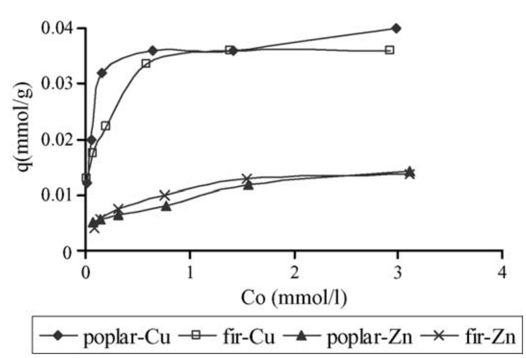


Fig. 1. Adsorption isotherms of Cu(II) and Zn(II) ions onto unmodified poplar and fir sawdusts (sawdust concentration 5 g/l; initial pH: for copper pH 4, for zinc pH 6).

Table 1
Adsorption constants for copper(II) and zinc(II) adsorption by unmodified softwood sawdust

| Adsorbent | Metal | Langmuir constants | | | Freundlich constants | | |
|---|---|---|---|---|---|---|---|
| | | $K_L$ ($l$ mmol$^{-1}$) | $q_m$ (mmol g$^{-1}$) | $R^2$ | $K_F$ ($l$ g$^{-1}$) | $1/n$ | $R^2$ |
| Poplar | Cu | 14.42 | 0.040 | 0.998 | 0.0142 | 0.22 | 0.835 |
| | Zn | 2.596 | 0.015 | 0.971 | 0.0029 | 0.29 | 0.959 |
| Fir | Cu | 13.92 | 0.037 | 0.999 | 0.0129 | 0.22 | 0.952 |
| | Zn | 3.662 | 0.015 | 0.997 | 0.0026 | 0.33 | 0.974 |

Although two kinds of investigated adsorbents are different in the anatomical structure and the chemical composition, they have similar capacities for copper or zinc ions. Because the Langmuir isotherm is slightly better followed adsorption of investigated metal ions than Freundlich one that means the surfaces of unmodified softwood sawdusts are homogenous.

Equal adsorption capacity for zinc ions has e.g. Sphagnum moss peat [11] or hazelnut shell [12]. But, in many cases adsorbent capacities of different adsorbents for copper ions are higher than capacities of adsorbents investigated in this paper, e.g. for oat and wheat straw [5], or barks of different wood [4,13].

### *3.2. Adsorption capacities of wood sawdust modified with sodium hydroxide*

In order to increase the adsorption capacities of adsorbents they both were modified with sodium hydroxide. Fig. 2 shows the adsorption efficiencies of modified adsorbents for copper and zinc, as a function of the alkali concentration and the temperature of modification. Concentration of metal ions before adsorption were about 0.8 mmol $l^{-1}$.

The curves present in Fig. 2 are shown that the use of lower alkali concentration results in significant increase of the adsorption capacity of modified adsorbents. But, if alkali concentration is increased away, that will not cause an increase of adsorption capacities proportionally. The temperature is a significant parameter in wood deacetylation process for pretreatment of lignocellulosic materials with NaOH, prior to pulping [14]. However, the temperature of modification is not a considerable factor for the increase of adsorption capacities of modified adsorbent. On the base of the presented results, it might be suggest no greater concentration of alkali solution for modification than 1%, and treatment at 20 °C.

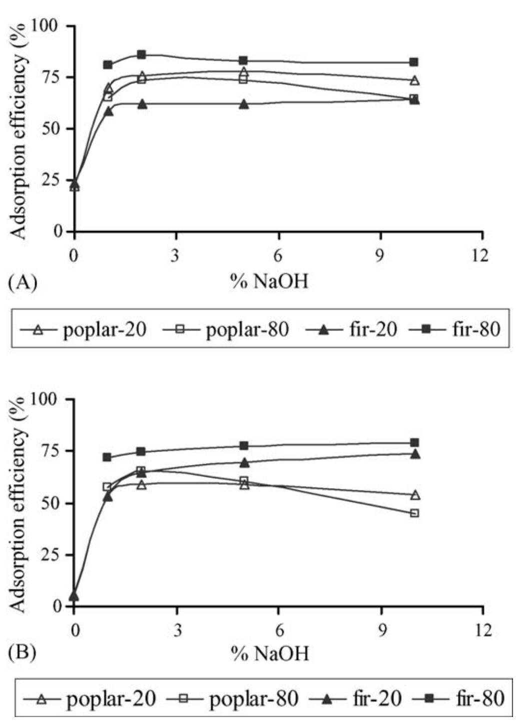


Fig. 2. Adsorption efficiencies of: (A) Cu(II) and (B) Zn(II), by poplar and fir wood sawdusts modified with NaOH solutions of different concentration, at 20 °C for 6 h or at 80 °C for 2 h (initial metal ions concentration 0.8 mmol/l).

Table 2
The influence of modification contact time on adsorption efficiency of poplar sawdust modified with 1% NaOH at 20 °C (initial metal concentration 0.8 mmol/l)

| | Modification contact time (h) | | | |
|---|---|---|---|---|
| | 2 | 6 | 12 | 24 |
| Efficiency of modified adsorbent (%) for | | | | |
| Cu | 75.8 | 75.0 | 74.8 | 77.8 |
| Zn | 55.6 | 54.2 | 54.0 | 55.1 |

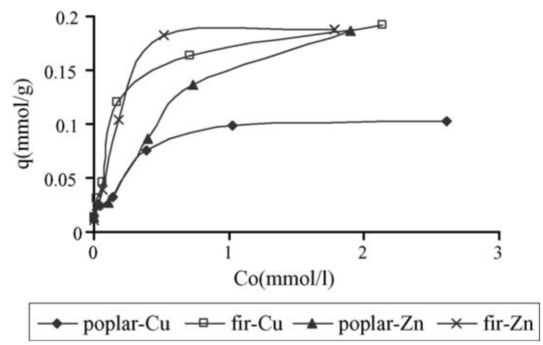


Fig. 3. Adsorption isotherms of Cu(II) and Zn(II) ions onto poplar and fir wood sawdusts modified with 1% sodium hydroxide at 20 °C for 2 h.

The influence of modification contact time on adsorption efficiency was investigated too. The poplar wood sawdust was treated with 1% NaOH, at 20 °C, and different contact time. Concentration of metal ions before adsorption were about 0.8 mmol $l^{-1}$. The results were presented in Table 2.

On the base of the results presented in Table 2 it might conclude that the sufficient contact time for alkaline modification of softwood sawdust is 2 h.

The adsorption capacities of adsorbents modified with 1% sodium hydroxide solution at 20 °C, for 2 h, were determined. The adsorption isotherms for adsorbents modified on that way are presented in Fig. 3, and constants in adsorption models are presented in Table 3.

Alkaline treatment is more effective for coniferous wood sawdust than for deciduous one. Application of alkaline treatment results in very good increase of adsorption capacities of modified

Table 3
Adsorption constants for copper(II) and zinc(II) adsorption by adsorbents modified with 1% NaOH at 20 °C for 2 h

| Adsorbent | Metal | Langmuir constants | | | Freundlich constants | | |
|---|---|---|---|---|---|---|---|
| | | $K_L$ (l $mmol^{-1}$) | $q_m$ (mmol $g^{-1}$) | $R^2$ | $K_F$ (l $g^{-1}$) | $1/n$ | $R^2$ |
| Poplar | Cu | 6.545 | 0.109 | 0.990 | 0.0162 | 0.40 | 0.915 |
| | Zn | 1.674 | 0.242 | 0.931 | 0.0135 | 0.56 | 0.939 |
| Fir | Cu | 9.086 | 0.200 | 0.996 | 0.0234 | 0.49 | 0.938 |
| | Zn | 6.867 | 0.205 | 0.990 | 0.0157 | 0.61 | 0.959 |

adsorbents for both metal ions, especially for zinc. Adsorption curves for zinc characterize sharp rise at lower metal concentration, and that means the better "affinity" of the alkaline modified adsorbents for this ions. On the other hand, the "affinity" of the alkaline modified adsorbents for copper ions are slightly lower than "affinity" of unmodified adsorbents. Adsorption capacities of alkaline modified adsorbents are higher than for unmodified ones from 2.5 to 5 times for copper ions and about 15 times for zinc ions.

Improvement of adsorption capacity of alkaline modified lignocellulosic materials are not a general rule. The modification of juniper wood and bark with 1% NaOH also promotes their adsorption capacity for cadmium ions, for more than three times [15]. However, the modification of kenaf bust or cotton with 1% NaOH do not change their adsorption capacity for copper ions [16]. The same effect was accomplished when the oat and wheat straw modified with 0.1 M NaOH [5]. Treatment of some other lignocellulosic materials, like kenaf core, bagasse, coconut coir and spruce, even decrease their adsorption capacity for copper ions from 40 to 75% [16].

The correlation coefficients for the Freundlich model are smaller than those for the Langmuir model (Tables 1 and 3). Good fit of the Langmuir model indicates monolayer adsorption on the homogenous surface of modified adsorbents. Therefore, the alkaline modification do not cause essential changes on the adsorbent surface, but, obviously improvement the adsorption process. The rinse of wood extractives with a mild alkaline solution causes the liberation of new adsorption sites on the sawdust surface.

### 3.3. Adsorption capacities of wood sawdust modified with sodium carbonate

Investigated adsorbents were modified with sodium carbonate, too. Fig. 4 shows the adsorption efficiencies of adsorbents modified with $Na_2CO_3$ or NaOH solutions, for both heavy metals, as a function of alkaline solution concentration. In adsorption experiments the concentration of metal ions was about 0.8 mmol $l^{-1}$, and contact time was 2 h.

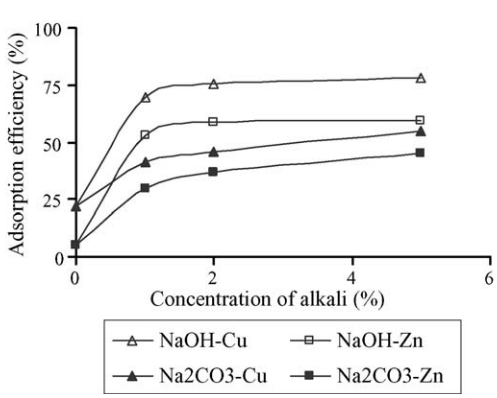


Fig. 4. Adsorption efficiencies of Cu(II) by poplar wood sawdust modified with NaOH or $Na_2CO_3$ solutions of different concentration at 20 °C for 2 h (initial copper concentration 0.8 mmol/l).

The modification with sodium carbonate increases adsorption efficiency of modified adsorbents for both metal ions. The adsorption efficiencies of adsorbents modified with sodium carbonate are higher than for unmodified ones about two times for copper, and about six times for zinc. The curves in Fig. 4 show that the use of sodium carbonate solution for modification is less efficient than the use of sodium hydroxide.

The reason of that is the fact that equal percentage solutions of sodium carbonate and sodium hydroxide contain different quantity of sodium ions and the presumption is that the sodium hydroxide is the main adsorption agents. Particularly, 1 g of sodium carbonate is equal to about 0.75 g of NaOH, and because of that the efficiency of modification with sodium carbonate is less efficient. However, if higher concentration of sodium carbonate solution is applied for modification, the sawdust adsorption efficiencies will not be increased as in case of application of the solution with a corresponding lower concentration of sodium hydroxide.

### 3.4. Adsorption characteristic of alkali modified poplar wood

Textural characteristics of both unmodified and poplar sawdust modified with 1% NaOH at 20 °C for 2 h are presented in Table 4.

Surface area of poplar sawdust modified with 1% NaOH are about three times greater than for unmodified poplar sawdust. But, both these values are more less than surface area of common activated carbons. The average pore volume (for pore with diameter from 1.7 to 300 nm) and average pore diameter of modified sawdust enlarge very slightly related to unmodified sawdust. These results indicate that the anatomic structure of the alkaline modified poplar sawdust was very little changed. Therefore, the changes were happened on the wood sawdust surface only.

Different deacetylation processes notably reduced the water solubility of *O*-acetyl-galactoglucomannans and *O*-acetyl-glucuronoxylans from chemicelluloses, and increased the sorption of these polymers onto cellulose fibers, changing its structure [17]. This phenomenon possibly caused increase of number or the order of the adsorption sites on wood surface, and on that account increased its adsorption capacity.

Ion exchange can be considered as the most predominant mechanism involved in the biosorption processes on microbial cells [18,19]. The involvement of this mechanism in the course of metal ions (in this case copper ions) adsorption onto modified poplar wood sawdust was investigated by following the release of $Ca^{2+}$, $Mg^{2+}$, $Na^{+}$, $K^{+}$ and $H^{+}$ from the adsorbent after the adsorption. The release of metal ions from the control

Table 4
Textural characteristics of unmodified poplar sawdust and sawdust modified with 1% NaOH at 20 °C for 2 h

| Poplar wood sawdust | Surface area ($m^2\,g^{-1}$) | Average pore volume ($cm^3\,g^{-1}$) | Average pore diameter (nm) |
|---|---|---|---|
| Unmodified | 1.05 | 0.0091 | 1.93 |
| Modified | 2.99 | 0.0125 | 3.06 |

Table 5
Release of $Ca^{2+}$, $Mg^{2+}$, $Na^{+}$, $K^{+}$ and $H^{+}$ due to adsorption of $Cu^{2+}$ by unmodified and alkali modified poplar wood sawdust (initial copper concentration 0.3 mmol/l)

| System | Total $Cu^{2+}$ bound (mmol $l^{-1}$) | Amount of cation released[a] (mmol $l^{-1}$) | | | | | $R_{b/r}$ |
|---|---|---|---|---|---|---|---|
| | | $Ca^{2+}$ | $Mg^{2+}$ | $Na^{+}$ | $K^{+}$ | $H^{+}$ | |
| Unmodified [20] | | | | | | | |
| Control (water) | – | 0.1715 | 0.0284 | 0.6870 | 0.2013 | – | – |
| Water with $Cu^{2+}$ | 0.1767 | 0.0700 | 0.0275 | 0.0870 | 0.0118 | 0.0089 | 1.167 |
| Modified | | | | | | | |
| Control (water) | – | 0.2185 | 0.0016 | 0.9348 | 0.0000 | | |
| Water with $Cu^{2+}$ | 0.2901 | 0.0160 | 0.0042 | 0.4435 | 0.0064 | −0.060 | 1.328 |

[a] Difference between metal released by adsorption system and that by the control.

(consisting of adsorbent and double distilled water) was also measured. The net release of metal ions from adsorption system (Table 5) represents the difference between the metal ions content measured in the filtrate after the adsorption and that of the control. Initial concentration of copper ions in adsorption experiments was 0.3 mmol $l^{-1}$.

The $R_{b/r}$ ratio is calculated as:

$$R_{b/r} = \frac{[Cu^{2+}]}{[Ca^{2+}] + [Mg^{2+}] + \frac{[Na^{+}]}{2} + \frac{[K^{+}]}{2} + \frac{[H^{+}]}{2}} \quad (3)$$

Results in Table 5 show that the exchange of potassium and magnesium ions with sodium ions was happened on wood surface during modification. Because of that, during copper ions adsorption with modified poplar wood the sodium ions were predominantly released.

The displacement of $H^{+}$ indicates covalent bonding of the metal ions [18], while the displacement of $Ca^{2+}$, $Mg^{2+}$, $Na^{+}$ and $K^{+}$ indicates ionic bonding of the metal ions [19]. The smaller amount of $H^{+}$ released, in comparison with the other cations released, indicates that ionic bonding was primarily involved in the adsorption process.

For the pure ion exchange mechanism the $R_{b/r}$ ratio has to be equal to unity. When the $R_{b/r}$ value exceeds unity this means that the sum of cations released is smaller than the amount of copper ions bound. In the case of unmodified poplar sawdust, and especially for modified one, it is indicated that the ion exchange is not the only bonding mechanism and that some other mechanisms are involved. Modified poplar sawdust bound more copper ions for about 65% than unmodified one, and at the same time has higher $R_{b/r}$ ratio, which means lower amount of ion exchange. This fact confirms assumption that the deposition of $OH^{-}$ group in the pore of modified sawdust and the precipitation of metal-hydroxide in the pore liquid was probably happened, too.

The pH values in model water before and after adsorption with unmodified and alkaline modified poplar sawdust was measured to verify this assumption. The results of these experiments are presented in Table 6.

After adsorption of copper and zinc ions by unmodified poplar sawdust, the pH in model water slightly decreases. That means that only a small quantity of hydrogen ions release from sawdust during adsorption. On the other hand, pH in model water after adsorption by modified poplar sawdust significantly increases, especially after adsorption of copper ions. Because of that microprecipitation in pore liquid is very possible. However, improvement of zinc adsorption is much better than improvement of copper adsorption although zinc precipitated on pH not earlier than 7, and copper on pH even higher than 5. This means that the microprecipitation is not only reason of improvement of adsorption characteristics of alkaline modified sawdust than liberation of some new adsorption sites are happened, too.

### 3.5. Leaching of organic matter from wood sawdust during adsorption

The leaching of some organic matter from investigated adsorbents into water during adsorption was observed. This results in light yellow colouration of water. The COD in water after adsorption by unmodified poplar sawdust was 31.5 mg $O_2$ $l^{-1}$ and by fir sawdust 82 mg $O_2$ $l^{-1}$. The COD in water after adsorption by poplar and fir sawdust modified with 1% sodium hydroxide solution, were slightly decreased to 29 and 63 mg $O_2$ $l^{-1}$, respectively. That is one more amendment of adsorption features of alkaline modified softwood sawdust.

### 3.6. Wastewater from sawdust modification

Besides the good effects of modification, unfavourable fact is production of high loaded wastewater from the modification process. The wastewater from the modification and the wastewater from rinsing of modified adsorbent, were analysed. The results are presented in Table 7.

Table 6
pH in model water before and after adsorption of Cu(II) and Zn(II) by unmodified and poplar sawdust modified with 1% NaOH at 20 °C for 2 h (initial metal concentration 0.3 mmol/l)

| | pH in model water with | |
|---|---|---|
| | Cu | Zn |
| Before adsorption | 4.20 | 6.08 |
| After adsorption by unmodified poplar sawdust | 4.14 | 5.95 |
| After adsorption by modified poplar sawdust | 5.47 | 6.40 |

Table 7
Analyse of wastewaters from wood sawdust modification with sodium hydroxide

| | COD (mg $O_2$ $l^{-1}$) | Alkalinity (mg $CaCO_3$ $l^{-1}$) |
|---|---|---|
| Solution for modification | 10 | 102250 |
| Wastewater | | |
| Poplar | | |
| From modification | 26270 | 95750 |
| From rinsing | 1338 | 6250 |
| Fir | | |
| From modification | 12377 | 71500 |
| From rinsing | 606 | 5250 |

The modification of wood sawdust produces 15 l of high-polluted wastewater from modification per 1 kg of modified adsorbent, and 60 l of wastewater from rinsing per 1 kg of modified adsorbent. The wastewater from rinsing process is more less polluted than wastewater from modification. The costs for chemicals and equipment for modification, and the costs for treatment of originated wastewaters, are diminished achieved amendment of adsorption features of modified adsorbent. However, considerable improvement of adsorption capacities of modified adsorbents for zinc ions, which were poor adsorbed by unmodified adsorbent, justifies these costs.

## 4. Conclusions

In this paper, the influence of alkaline modification on increase of adsorption capacities of softwood sawdust have been investigated. It was shown that sawdust of deciduous soft wood-poplar and coniferous soft wood–fir, are capable for adsorption of copper and zinc ions from water. The adsorption capacities of these wood sawdusts are almost the same for both metal ions, although these sawdusts are different in chemical composition and anatomical structure.

The treatment with sodium hydroxide solution increases adsorption capacities of modified sawdusts, especially for zinc ions. Alkaline treatment is more efficiency for coniferous wood than for deciduous one. On the base of the results, for modification 1% NaOH solution and contact time of wood sawdust and alkaline solution for 2 h, at 20 °C are suggested. For modification, the sodium carbonate has been able to use, too.

In the case of unmodified poplar wood, and especially for modified one, it was indicated that the ion exchange is not the only adsorption mechanism and that some other mechanisms are involved.

As the product of applied modification process, very loaded wastewater were appeared. However, considerable improvement of adsorption capacities of modified adsorbent for zinc ions, which were poor adsorbed by unmodified adsorbent, justifies the costs for modification and for treatment of wastewater from modification.

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