

MECHANOCHEMICAL SYNTHESIS OF SALICYLIC ACID-FORMALDEHYDE CO-POLYMER CAPABLE OF BINDING HEAVY METAL IONS

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ABSTRACT. A mechanochemical synthesis of a co-polymer of salicylic acid and formaldehyde is reported. New IR absorbance bands were found after the mechanochemical synthesis and they were attributed to the formation of a salicylic acid – formaldehyde co-polymer.

Dislocation deformation along slide planes in the salicylic acid structure occurs in the course of mechanochemical activation causing no essential changes in the more stable hydrogen bonds net. The weaker inter-layer bonds in the acid structures are broken during the activation, but are restored soon after the completion of the process. Polycondensation reaction occurs as the result of mechanochemical process of a salicylic acid – formaldehyde mixture. The polymer obtained is a chelating agent capable of binding ions of Pb^{2+} , Cu^{2+} and Fe^{3+} . A comparison was made of the ion exchange capacity and metal ion sorption capacity of the mechanochemically polymer obtained with that synthesized using the conventional “wet” method.

Introduction

Selective separation of ionic species from aqueous solutions is of growing industrial and ecological importance in many processes including those dealing with heavy metal ion separations or selective removal of toxic constituents from chemical, electrochemical, tanning, metallurgical and other industrial effluents. Discharge of these streams without adequate purification or after minimal treatment may cause harm to the environment, which is either difficult or very expensive to remedy.

One of the most applied approaches to the treatment of aqueous solutions containing ions of heavy metals is using polymers capable of effectively chelating metal ions. In spite of the existence of a wide range of such polymers, their binding capacitance remains low and their production is often relatively costly.

Mechanochemical synthesis has become a widely used method for preparing powder solid materials in a large variety of compositions: metals and minerals, ceramics, composites, organic substances etc.¹ The advantages of this approach as compared with traditional “wet” synthetic methods cannot be underestimated: the elimination of the stage of dissolution enables one to exclude the formation of environmentally problematic wastes containing organic solvents; solid phase syntheses are often faster and cleaner than those in a solution; the absence of a solvent allows direct targeting a reactive species to an activated site.

Mechanochemical synthesis generally involves the use of a conventional high energy ball mill to initiate chemical reactions and structural changes.¹ While several possible models explaining the mechanism of mechanochemical activation have been proposed^{1,2} and the elaboration of a commonly accepted theory is still far from the completion, practical applications of the approach are continuing to increase. The number of publications dedicated to mechanochemistry is growing by the factor of ten every year starting from the seventies of the previous century.^{3,4}

Another attractive feature of the mechanochemical synthesis in planetary ball mills is the relatively easy achievement of nano-state of the material being milled.⁵

The milling action influences the reaction kinetics in a reacting powder mixture as a result of the intimate mixing and refinement of the grain structure to the nanometer scale, allowing the reaction to occur during the actual milling. Chemical reactions, which normally require high temperatures, can thus be activated in the course of room temperature milling. The resulting product is formed as individual nanometer sized grains in a by-product matrix in relatively short time.

While mechanochemical methods have been successfully applied to metallurgical, mineral and composite systems, their use for the synthesis of organic materials is more limited. Thus, Braga *et al.* performed a series of mechanochemical acid-base reactions for obtaining hybrid organic-organometallic materials.⁶ Margetić has studied a "Highspeed vibrational milling" (HSVM) method on various groups of chemical reactions, such as Diels-Alder and 1,3-dipolar cycloadditions, Reformatsky, Prato and Bingel reactions and others.⁷ Grigorieva *et al* used mechanochemical milling for the immobilization of organic acids by esterification and etherification.⁸ In the current work mechanochemical activation is applied to the polycondensation of salicylic acid with formaldehyde. The product is a polymer powder having pronounced layered tube structure.

The choice of the precursors for the synthesis was determined by their availability. Another advantage of the monomer reagents was the bactericidal activity of the salicylic acid, which should persist in the polymer. The classic "wet" synthesis of the co-polymer is well known, but it must be interesting to compare it to the mechanochemical method.

Experimental

Mechanochemical activation experiments were performed in a planetary ball mill (Retsch, PM100) at the rotation velocities of the drums in the range of 100-650 rpm and the rotation velocity of grinding jars of 200-1300 rpm. The duration of an activation cycle varied from 10 sec to 10 min. 10 mm stainless steel or agate grinding balls and 125 mL stainless steel or agate jars were used for grinding. Mixtures for mechanochemical activation contained salicylic acid (Aldrich, ACS $\geq 99.0\%$) and formaldehyde (Aldrich, ACS reagent, 37% in water) in the molar ratio 1:1 (0.1 mol of salicylic acid 0.1 mol of formaldehyde were sealed in the grinding jar and placed into the mill).

Infrared spectra were measured on FTIR System Spectrum BX (Perkin Elmer) with the use of standard KBr tablet samples. SEM images were taken by Scanning Electron Microscope JEOL JSM – 35 CF. Samples for SEM were prepared as follows: gold coating was sputtered (on an SPI module Sputter Coater) on a powdered sample placed on a double side carbon tape.

Measurement of ion capacity exchange

Samples of 0.15 g polymer were contacted with 25 ml of 0.1 M NaOH solution at 25°C for 24 hours. The excess of base in the supernatant liquid was determined by conductometric titration with 0.1 M HCl solution (Table 1).

Absorption capacity of Pb²⁺ ions

Absorption capacity of Pb²⁺ ions was measured polarographically on a Dropping Mercury Electrode according to the following procedure:

Sample of 0.01 gr of the polymer product were placed in 21 mL of the water solution containing 30 ppm of Pb(NO₃)₂ in the presence of ~0.15 M supporting KCl. The solution was stirred for 24 hours and the residual lead concentration was

measured by Differential Pulse Voltammetry (DPV) on Static Mercury Dropping Electrode (SMDE). A typical voltammogram is given in Fig. 5.

Absorption capacity of ions Cu^{2+} , Fe^{3+}

A 0.01 g polymer sample was placed in a continuously stirred flask with 20 mL of 10 ppm solution of Fe^{3+} (Cu^{2+}) for 24 hours at 25° C. The content was then filtered and the residual concentration of metal ions was measured in a UV-Vis spectrophotometer in the visible range (Table 1).

Metal ion sorption capacity of a polymer synthesized according to conventional “wet” methods (continuous stirring of 1:1 mole salicylic acid: formaldehyde mixture for 4-29 hours at 80°C in the presence of acid, Table 2) was measured for the comparison.

Results and Discussion

1. Mechanochemical activation of individual reagents

Most solid organic acids exist in the form of dimers or polymers so that their reactivity can increase in the course of mechanochemical activation due to the breaking of hydrogen bonds. Solid monocarbon acids have layered structure,⁹ where individual molecules form cyclic dimers having rather stable hydrogen bonds between the carbonyl and hydroxyl groups of two molecules.¹⁰ Such dimers are connected into flat nets because of electrostatic interaction. According to Leiserowitz,⁹ packages of the nets are fixed together due to inter-plane interactions of two types (Fig. 1).

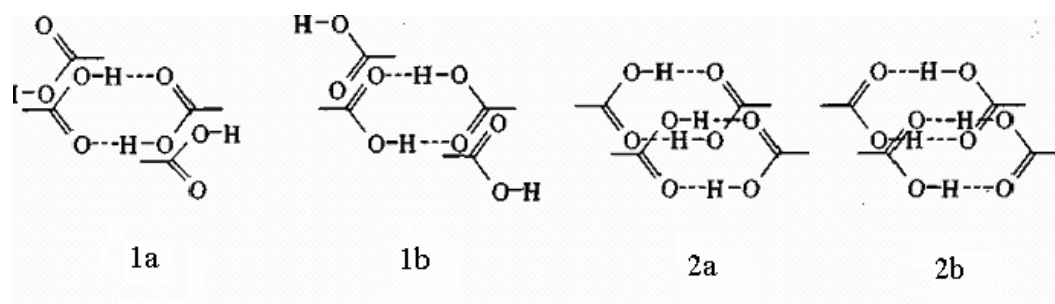


Fig.1. Formation of the layered structure of monocarbon acids due to the electrostatic interaction vertex-to-vertex (1a, 1b) and side-to-side (2a, 2b)

In the dimeric structure of the salicylic acid the carboxylic groups are in the close vicinity with the massive phenyl ring so that the C-H...O distance is ~3.5 Å. Therefore the molecules of salicylic acid are connected not only by hydrogen bonds –C-O-H...O forming the dimers, but also by the “side-to-side” C-H...O bonds (type 3a and 3b in Fig. 1). Such a structure forms rather dense layered packing.⁹

The absorption caused by the OH valent vibration of monocarbon acids appears as a broad band having some poorly pronounced maxima in the range of 2500-3350 cm^{-1} . The main maximum is observed at about 3000 cm^{-1} and a better defined secondary band at *ca.* 2650 cm^{-1} is considered characteristic.¹⁰⁻¹² The genuine shape of this characteristic band is concealed by the very strong valent absorption of CH_3 and CH_2 groups having sharp maxima at 2955, 2920, 2870, 2850 cm^{-1} .

Bands at 940 and 1430 cm^{-1} are attributed to deformation vibration and the latter band is also related to C-O valent vibration. The band at 1710 cm^{-1} and the shoulder at 1690 cm^{-1} are assigned to the antisymmetric vibrations of C=O.

In the current study IR absorption spectra of salicylic acid before and after the activation were measured (Fig. 2.)

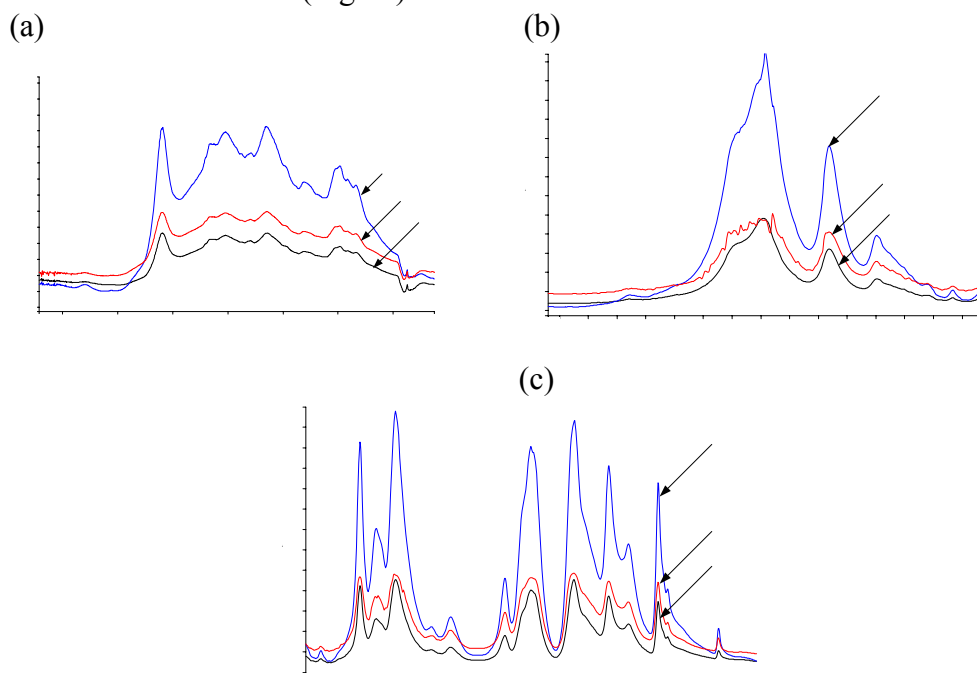


Fig 2. IR absorption spectra of salicylic acid before and after the activation (a) 3600-2700 cm^{-1} , (b) 1800-1500 cm^{-1} , (c) 1500-1100 cm^{-1} .

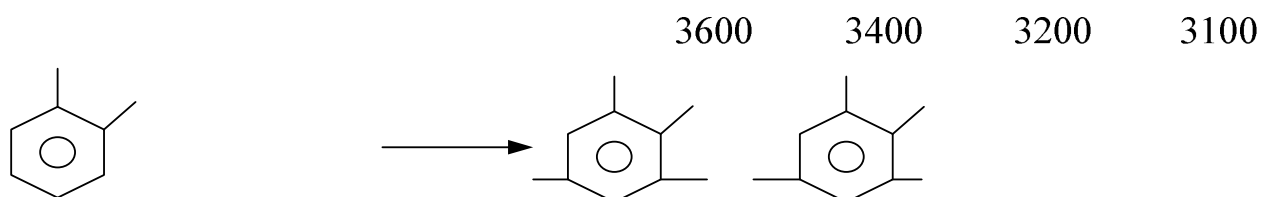
A series of absorptions at 3050 - 2350 cm^{-1} corresponds to the OH- valent vibrations of the acid dimers; the band at 1690 cm^{-1} , the shoulder at 1700 cm^{-1} are attributed to the valent vibrations of C=O; and the bands at 1330 and 1290 cm^{-1} belong to the carboxylic group.¹⁰⁻¹² All these bands grow after 65 seconds of mechanochemical activation (Fig. 2).

From the comparison of IR spectra of the “raw” and the activated acid is obvious that hydrogen bonds are not broken after the activation. Therefore, the crystal structure is not affected by the activation and no polymer destruction takes place. That is, the solid carbon acids stay intact during the mechanochemical activation and thus can be used as monomer precursors for polycondensation processes.

Presumably, mechanochemical activation causes dislocation deformation along slip planes while relatively stronger hydrogen bonds structure is preserved. The weaker interlayer bonds get broken in the activation process and quickly restored soon after it.

2. Mechanochemical synthesis in the system “salicylic acid – formaldehyde”.

The scheme of the polymerization reaction is given below (MCA = mechanochemical activation):



Samples were taken after several sequential activation runs (Table 1).

Table 1. Ion exchange capacity of the obtained polymer for different activation

parameters

| # | Activation time (sec) | Drum Rotation velocity (rpm) | Ion exchange capacity (mmol H ⁺ / 1 gr of polymer) | Absorption capacity of Pb ²⁺ ions (mmol / 1 gr of polymer) | Absorption capacity of Cu ²⁺ ions (mmol / 1 gr of polymer) | Absorption capacity of Fe ³⁺ ions (mol / 1 gr of polymer) |
|---|-----------------------|------------------------------|---|---|---|--|
| 1 | 10 | 100 | | 4.7 | 1.9 | 0.12 |
| 2 | 20 | 100 | 4.8 | 3.9 | 1.1 | 0.10 |
| 3 | 80 | 100 | 4.5 | 3.1 | 1.2 | 0.08 |
| 4 | 240 | 200 | 4.0 | 5.1 | 2.9 | 0.13 |
| 5 | 360 | 200 | 2.7 | 4.7 | 2.4 | 0.12 |
| 6 | 540 | 200 | 3.7 | 2.7 | 3.0 | 0.07 |
| 7 | 600 | 650 | 5.2 | 4.3 | 0.3 | 0.11 |
| 8 | 1320 | 650 | 3.8 | 3.5 | 1.3 | 0.09 |

IR spectra of the synthesized polymer are given in Fig. 3.

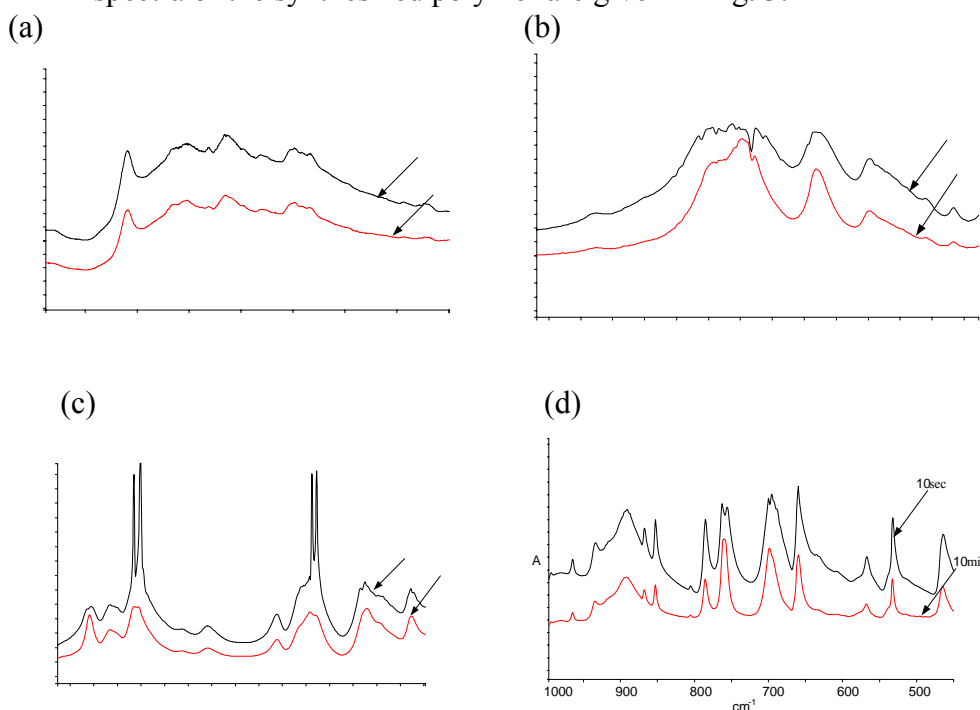


Fig. 3. IR spectra of the synthesized polymer at different activation time (a) 3400-2000 cm⁻¹, (b) 1800-1500 cm⁻¹, (c) 1500-1200 cm⁻¹, (d) 1000-450 cm⁻¹

Starting from 10 seconds of activation, two changes are observed: (1) the absorptions of carboxylic groups (ν (OH) 3250-2450 cm⁻¹; ν_{as} (C=O) 1735 cm⁻¹) decrease and (2) a new band at ~ 1650 cm⁻¹ appears. This new band can be ascribed to the vibrations of carboxylate ions COO⁻ (Fig. 3b).^{10, 13} Another plausible source to this band is the O-H bond deformation of water molecules formed in the course of activation. An argument to the latter explanation is the growth of the bands in the range of 3550-2800 cm⁻¹.¹⁴ The intensity of acid O-H valent vibrations at 3410 and 3350 cm⁻¹ does not change in the first seconds of activation, but sharply decreases after 80 seconds and appears again in the 10th minute of activation.

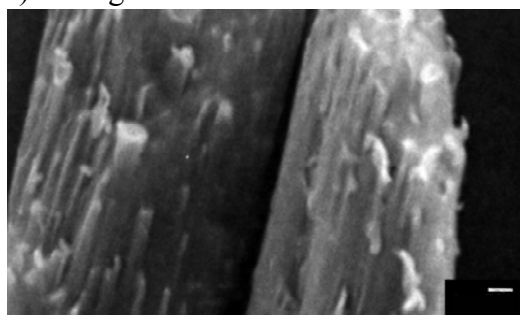
After 80 second activation (Fig. 3b) the band of COOH group of the salicylic acid completely disappears, but a broad band with the maximum at 1640 cm⁻¹

remains. This latter band can be of carboxylate ions or it may be caused by the deformation vibrations of water formed in the process, or be a superposition of both carboxylate and water deformation. The valent band of water in the range 2800-3550 cm^{-1} decreases as well.

The changes in the IR spectra of the formaldehyde-salicylic acid system provide an evidence of the mechanochemical polycondensation caused by the activation process. The mechanochemical reaction starts practically from the very beginning of the activation and is completed in approximately 2 minutes. No new absorptions as compared to those after 2 minutes are observed for longer activation times.

The polymer is obtained in the form of layered tube powder (Fig. 4). The tubes are $\sim 1 \mu\text{m}$ diameter. We are planning to perform a further optimization of the parameters of the mechanochemical activation and to find ways to control the polymer particles sizes.

a) enlargement x5400



b) enlargement x8600



c) enlargement x400

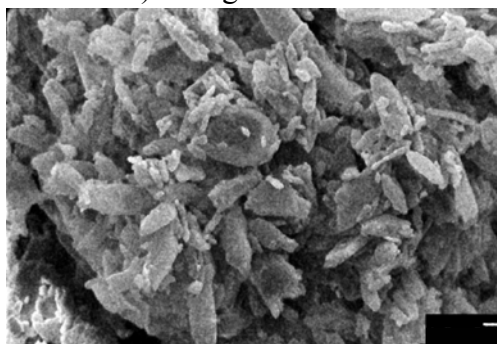


Fig. 4. SEM images of Salicylic acid-formaldehyde copolymer after 22 minute synthesis.

3. Measurement of ion exchange capacity

The measurements of ion exchange capacity demonstrate that the polymer, obtained by the mechanochemical activation (Table 1 and Fig. 6) contains approximately the same amount of active acidic groups as the polymer, synthesized by the conventional “wet” method (Table 2). The mechanochemically synthesized polymer has even a bit higher capacity: 2.7-5.2 mmol of H^+ per gram as compared to 2.4-4.8 mmol H^+ per gram for the “wet” synthesis.

4. Absorption capacity of Pb^{2+} ions

The residual lead concentration was determined by the area of the voltammetric peak at 0.36 V vs. Ag | AgCl reference relatively to peak areas of calibration lead solutions.

The sorption capacitance values for Pb^{2+} ions were in the range 2.7-5.1 mmol / 1 gr of polymer for the mechanochemically synthesized chelator (Table 1), while the appropriate values for the “wet” synthesis lay in the range 2.4-4.1 mmol / 1 gr of polymer (Table 2). Therefore, the polymer obtained by the mechanochemical method has higher Pb^{2+} ion sorption capacitance as compared to that obtained by the conventional synthesis.

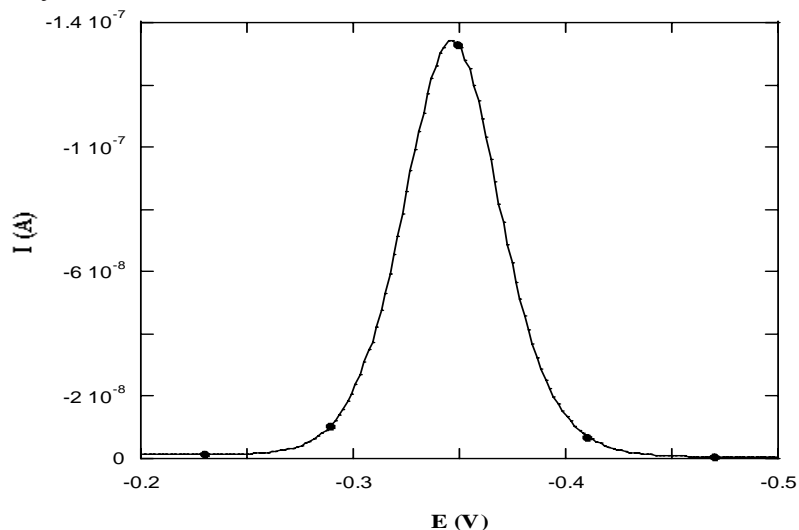


Fig. 5. DPV voltammogram of the residual Pb^{2+} after 2.5 hour sorption by a polymer sample

5. Absorption capacity of ions Cu^{2+} , Fe^{3+}

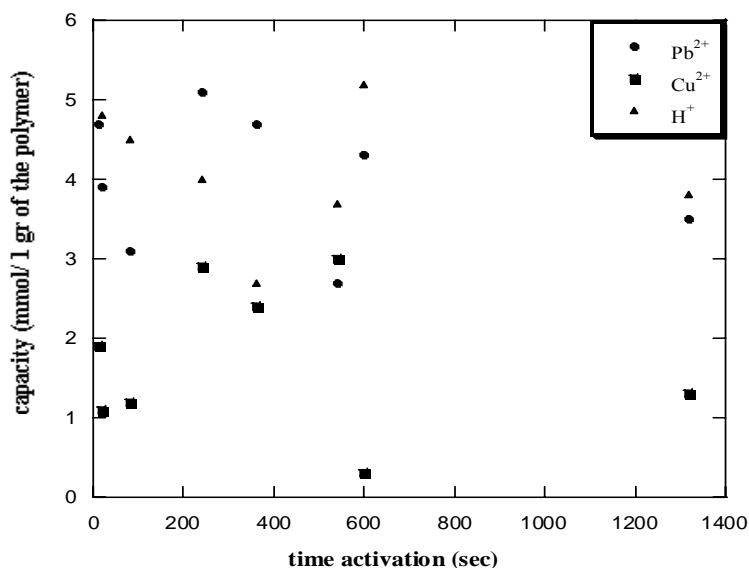


Fig. 6. Dependence of the Cu^{2+} , Pb^{2+} and H^+ sorption capacity of the polymer on the activation time.

Sorption capacity for the metal ions for the MCA polymer is in the range of

0.07-0.13 mol/ 1 gram of polymer for Fe³⁺, 0.3-3.0 mmol/ 1 gram of polymer for Cu²⁺ and 2.7-5.1 mmol/ 1 gram of polymer for Pb²⁺. That is, the chelating capability of the MCA polymer is the same (or even higher) as for the polymer, obtained by the longer and more complicated “wet” synthesis.

Table 2. Ion exchange capacity of the “wet” polymer for different parameters of synthesis

| # | Synthesis time (hours) | Ion exchange capacity (mmol H ⁺ / 1 gr of polymer) | Absorption capacity of Pb ²⁺ ions (mmol / 1 gr of polymer) | Absorption capacity of Cu ²⁺ ions (mmol / 1 gr of polymer) | Absorption capacity of Fe ³⁺ ions (mol / 1 gr of polymer) |
|---|------------------------|---|---|---|--|
| 1 | 4 | 4.4 | 3.5 | 4.2 | 0.013 |
| 2 | 7.5 | 4.1 | 3.5 | 3.1 | 0.020 |
| 3 | 14 | 3.7 | 3.3 | 2.6 | 0.020 |
| 4 | 16 | 2.4 | 3.7 | 3.7 | 0.022 |
| 5 | 18 | 3.4 | 2.8 | 4.2 | 0.021 |
| 6 | 19 | 4.8 | 4.1 | 3.2 | 0.014 |
| 7 | 29 | 3.5 | 3.2 | 2.8 | 0.018 |

As can be seen from Table 1 and Fig. 6, the maximal sorption capacitance for all the studied ions is obtained for the 240 sec activation and 200 rpm drum rotation velocity.

Conclusion

Mechanochemical activation has been used for the polycondensation of a novel layered tube polymer.

The analysis of IR spectra show the decrease and complete disappearance of the formaldehyde carbonyl vibration intensities after 20-80 sec activation and water valent and deformation bands appear instead. These changes witness the process of polycondensation, where a chemical bond between the salicylic acid and formaldehyde is formed.

The obtained polymer binds 3-5 mmol of H⁺ per gram, 2.7-5.1 mmol of Pb²⁺ per gram and 0.3-3.0 mmol of Cu²⁺ per gram and 0.07-0.13 mol of Fe³⁺ per gram.

The optimal activation parameters for the salicylic acid-formaldehyde copolymer synthesis are 240 sec activation time and 200 rpm drum rotation velocity.

The obtained polymer can be used for the purification of water. These preliminary results are promising and can be improved by the further optimization of technologic parameters of the mechanochemical synthesis.

The mechanochemical polymerization of salicylic acid with formaldehyde demonstrates the applicability of this approach to the synthesis of novel sorbents in the hetero-phase and solid-phase setups.

Acknowledgements:

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