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STUDY ON SORPTION CHARACTERISTICS OF CITRIC ACID MODIFIED RAPE-SEED PELLET CONSIDERING THE CHEMICAL PRE-TREATMENT PROCESSES

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The ground rape-seed pellet was pre-treated then reacted with citric acid which resulted in a rape-seed citrate having ion exchange capacity. The effects of pre-treatment steps (including extraction of fatty substances by organic solvent, moreover acidic and alkali treatment of the rape-seed pellet) on the ion binding capacity of the materials were investigated. The capacity was determined for three cations (copper, zinc and nickel) separately, from aqueous solutions in batch mode of operation.

Based on the experimental results it was found that the highest ion exchange capacity for all the cations was obtained by the process involved the pre-treatment combining of extraction and alkali treatment followed by the reaction with the citric acid.

Keywords: Ionic liquid, organic synthesis

Introduction

The removal and recovery of heavy metals, which are the main source of water pollution, are important in protecting the environment and human health. That is why strict environmetal protection legislation, public environmental concerns and express of conventional disposal methods provide incentives for developing novel techniques for heavy metal wastewater treatment.

Several kinds of agricultural waste have natural deionising property [1]. The possibility of producing low cost adsorbents gained from agricultural waste enhanced many researchers' interest. In the last few years, several products with deionising characteristics were prepared from agricultural materials. Including sawdust [2], sugar-cane bagasse [3], wheat-husk [4], the corn-cob [5], rice husk [2], soya husk [6], tobacco [7], peanut husk pellet [8], orange wastage [9], banana peel [10], etc. These papers showed that different chemical treatments could be used successfully for improving the sorption capacity or the chemical characteristics of biological polymers – like the fibres containing starch or cellulose. However, because the combination of the wastage has various composition, the optimal producing methods and features (capacity, , stability, etc.) might be very different. Their inadaptability is caused by the lack of this information. Unlike the deionising synthetic resins which have petrol-chemical origins and used in water treatment, these wastage are biodegradable and more affordable.

Searching for the possible raw materials, then turning them into value-added products and investigating the product-characteristics is a very significant field of research nowadays.

In this research we used the rape-seed pellet as a new possible adsorbent material. The rape-seed pellet is pressing wastage proceeded from the production of biodiesel. This lignocellulose based remainder is originated from the 65% of the rape-seed used for the production. Currently, they are used for energetic and foraging purposes.

The ground rape-seed pellet is submitted to a proceeding process containing combined pretreatment and citric acid modification, and it resulted in a rape-seed citrate with ion exchange characteristics. The effects of the dissolvent extraction and the acidic and alkali pretreatments for the formation of the adsorption efficiency of citric acid modified rape-seed is studied. The adsorbents produced in different combinations were classified according to their adsorption efficiency showed with three metal ions (copper, zinc and nickel), typically found in sewage-water.

Materials

The rape-seed pellet is provided by the Öko-Line Hungary Ltd. (Hungary). The ingredients of the rape-seed pellet is presented in *Table 1*. The pellet has been ground to 0–1 mm particle size of the powder. The humidity of the raw material is 7 (w/w)% in average. The citric acid and any other chemicals were supplied by Spektum 3D Ltd and Scharlab Hungary Ltd (Hungary).

Table 1: The ingredients of rape-seed pellet, based on the weight of the total solid substance (TSS)

Components	(w/w)%
glucan	6.0
xilan	3.4
arabinan, galactan, mannan	4.4
cellulose	6.0
hemicellulose	7.8
lignin	9.7
protein	32.5
ash	5.8
hexane extractives	17.2

Treatments

Solvent extraction

Solvent extraction with hexane was carried out in a Soxhlet extractor. Keeping the 21.5 ml/g hexane: dry rape-seed ratio, the extraction filter is filled with rape-seed and measured the needed amount of hexane into the extractor's test-tube. A spherical condenser is put on and heating is started. The extraction treatment has been carried out for an hour and it has been completed by this time. The extracted fibre was dried room at temperature for having the rest of the hexane evaporated, than we dried it to constant weight on 105 °C. We suspended the dry fibre half an hour for in distilled water (sugars) setting the dry-substance content on 10%, than we filtrated and washed it in triple amount of water. We dried it to constant weight and stored it in a desiccator.

Acidic and alkaline treatment

One (w/w)% NaOH and H_2SO_4 solution was poured into a screw topped bottle setting the dry-substance content on 10%, in which we put the dry material and kept it at room temperature for a week, shaking it once a day. By the end of the treatment period we filtrated the substance, than washed it in distilled water to make it free from acid and alkali. The fibre we gained was dried at 105 °C and stored in a desiccator.

Modification with citric acid

In laboratory scale citric acid solution was mixed with powdered rape-seed pellet using 10 ml/g citric acid solution/rape-seed ratio. The mixture was dried at 60 °C until the weight became constant, resulting a hard, bulky material. The product was then ground and sieved to provide the suitable particle size, which means greater contact surface area for the thermochemical reaction. Then the sample was placed in an oven to dehydrate at 60 °C for 24 h. That way all surface moisture was removed. Then the temperature is increased to 120 °C and kept 120 minutes, while the thermochemical reaction is completed *(Fig. 1)*, [12-13]. In the end of the process the not reacted citric acid is removed from the surface of the particles by washing with water and then the rape-seed citrate is dried. The applied reaction parameters are determined with utilizing full factorial experimental plans.

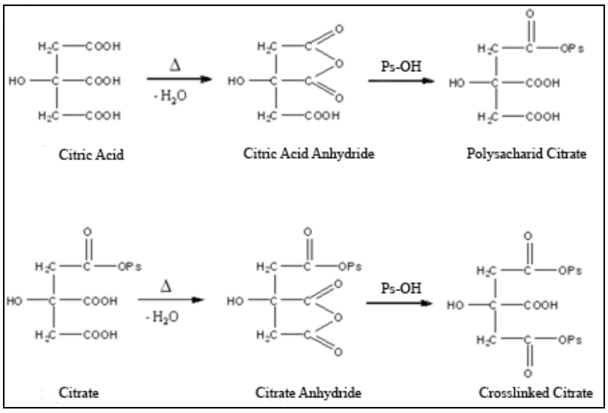

Figure 1: Thermochemical reaction of polysaccharide and citric acid

Determination of sorption efficiency

The evaluation of produced sorbent samples is based on their binding capability of Cu(II), Zn(II), Ni(II). 1 g sample with 200–400 μm particle size was put into 100 ml 30 mM $CuSO_4$ or $ZnSO_4$ or $NiCl_2$ solution, where the pH=4.5 was adjusted by acetic acid – sodium acetate puffer. The mixture was stirred for 24 h, at 130 rpm and 25±3 °C with a magnetic stirrer. When the contact time was over, the solid material was filtered, the Cu, Zn, Ni content of the filtrate has been determined with ICP.

The sorption capacity was determined as follows:

$$q = \frac{V(C_0 - C_e)}{M} \quad (1)$$

where:

V – the volume of the solution (l)
M – weight of the sorbent sample (g)
C_0 – initial concentration of the solution (mg/l)
C_e – final concentration of the solution (mg/l)
q – the binded mg Cu (II)/Zn(II)/Ni(II) / g sorbent

The sorption capacity can be expressed in the following form:

$$q\,\% = \frac{q}{C_0 V} 100 \qquad (2)$$

where:

q% – the binded Cu(II)/Zn(II)/Ni(II) content in % of its initial quantity / g sorbent

Results

It can be seen in *Fig. 2* that the modification of untreated rape-seed with citric acid had a positive effect on the binding of the metal ions.

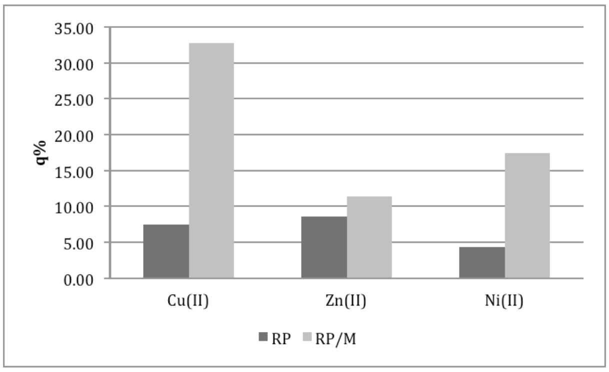

Figure 2: Adsorption effectiveness of the untreated (RP) and citric acid modified rape-seed (RP/M) in the case of metal ions

In *Fig. 3*, the inclination of the pre-treated samples (without citric acid modification) can be observed against copper, zinc and nickel ions.

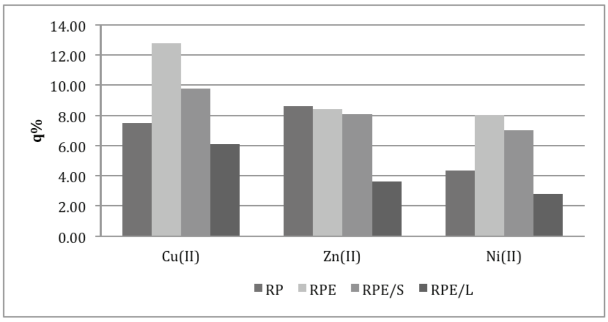

Figure 3: The adsorption effectiveness of the pre-treated rape-seed in the case of metal ions (RP – rape-seed without pre-treatment; RPE – extracted rape-seed; RPE/S – extracted and acidic treated rape-seed; RPE/L – extracted and alkaline treated rape-seed)

Although the dissolvent extraction improved the fibre's ability to bond in the case of copper and nickel, we did not observed significant changes with zinc. After the pressing procedure in the production of bio-diesel, there were some triglycerides left in the pellet (Table 1). This material (Table 1) was supposed the features of the lignocellulotic structure. With its extraction, the active surface can be increased.

Because of the significant improvement of the quality that was gained by extraction, the acidic and alkaline treatment was not performed as a separate treatment, but connected to the previous one. These washes damaged our results in hexane extraction. It is to be mentioned though, that the adsorption results received through acidic treatment were higher than in the case of untreated rape-seed. The combination of extraction-alkaline can be classified as an unsuccessful treatment, as its results did not even reach the results of the untreated base material.

Concluding these results it can be proved that, among all the pre-treatments we made, the extraction performed with hexane was only significant, while the treatments widened the procedure and the time of the adsorbent production unnecessarily.

The materials gained by this procedure were further modified by citric acid. So the previously produced materials can be considered as the core of the ion changing substance on which we built the ion changing function group. Because these cores had already had adsorption capacity and they were very different, *Fig. 4* only shows the ability to bond the metal ions gained with citric acid, to avoid any misunderstanding.

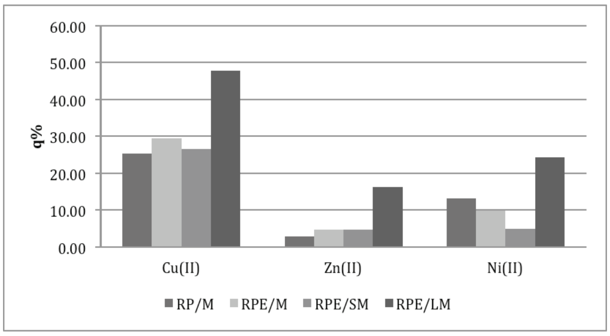

Figure 4: The effect of citric acid modification for the adsorption efficiency of the properly pre-treated rape-seed in the case of copper, zinc and nickel ions (RP/M – rape-seed modified with citric acid; RPE/M – extracted and citric acid modified rape-seed; RPE/SM – extracted and acidified, citric acid modified rape-seed; RPE/LM – extracted and lixiviated, citric acid modified rape-seed)

In the case of all the three examined ions we experienced that the effect of the modification was almost the same at the extracted (RPE/M) and extracted and acidified (RPE/SM) samples, as at the citric acid modified samples (RP/M). This is very interesting concerning the extracted material, because its core had previously showed better results than the untreated one. On the basis of this research, the citric acid reaction is less effective with the extracted core than with the untreated rape-seed. Presumably, the specific surface increases thanks to the extraction but the number of the reactive groups decreased. The failure of the acidic pre-treatment and modification can be explained with the fact that in the presence of acid, the number of the negative charged places decreased remarkably [2]. This restricts the natural sorption characteristics and the number of the reactive places that are able to make ester bonds.

In the case of alkaline treated samples, the modification was significantly efficient (~50 % Cu). At the previous analysis (Fig. 3) its core showed the worst results. On the basis of these, the reactivity of the extracted and alkaline treated and prepared core was the the highest. Its metal ion bonding capability gained by the modification was always higher than in the case of untreated core (with cooper ions appr. +23%, with zinc ions appr. +14%, with nickel ions appr. +11%). The extraction and the NaOH treatment contributed to the formation of the reactive construction, therefore a large number of carboxyl group was built in with citric acid modification.

Summarizing the results of the pre-treatments and modifications, under the given circumstances, the best values of the metal ion bond can be reached by the extracted, alkaline pre-treated citric acid modified rape-seed *(Table 2)*. In *Fig. 5* the results of all the modifications can be seen together.

Table 2: Amount of the metal ion bond by extracted, alkaline treated, citric acid modified rape-seed in the given research circumstances

RPE/LM	q	q %
Cu^{2+}	101.9 mg/g	53.9%
Zn^{2+}	42.3 mg/g	20.0%
Ni^{2+}	47.5 mg/g	27.1%

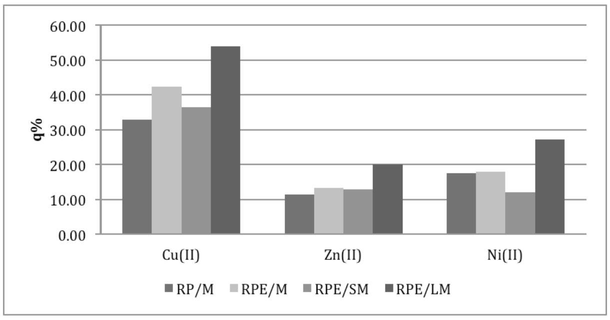

Figure 5: The adsorption efficiency of the pre-treated and modified rape-seed in the case of copper, zinc and nickel ions (see explanation of the symbols at Fig. 4)

The efficiency of the NaOH treatment had been discussed in many studies [2, 5, 6, 10, 11]. The experiences are rather dissimilar as they depend on the different raw materials and treatment circumstances. In the case of smaller capacity enhancement it is not recommended to apply the pre-treatments as it increases the time of production and the costs. Apart from the quantity data it is worth considering the changes in quality. For instance, the un-extracted fibres leaked some brown pigments into the solutions during the 24 hours bound, which changed the solutions' colour significantly. The same problem occurred during the treatment of soya husk [6]. So the extraction of the unwanted ions was done, however some other organic contamination appeared in the solution. This did not occurred in the case of the treated fibres.

Summary

The ground rape-seed pellet was extracted by hexan and pre-treated by NaOH and H_2SO_4 in order to improve the natural adsorption characteristics of the rape-seed. From these procedures, the best metal ion bond was gained with the extracted rape-seed.

In the case of the citric acid modification of the pre-treated substances the number of the sorbent bound metal ions enlarged, regardless the type of the pre-treatment. The degree of the efficiency of the modification was the highest in the case of extracted, citric acid modified alkaline treated core.

Considering the results of the pre-treatments and the modification, the best metal ion bounds results can be reached by the extracted, citric acid modified alkaline pre-treated rape-seed, under the given circumstances.

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