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Hardness removal from waters by using citric acid modified pine cone

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ABSTRACT

In this study, an effective cation exchanger was developed from the pine cone by citric acid modification and its hardness removal properties from the waters were investigated. For this purpose, ground pine cone samples were subjected to a citric acid modification following NaOH saponification. Both of the raw (RPC) and modified pine cone (MPC) samples were subjected to standardized hardness removal tests by shaking with hard waters. These tests showed that citric acid modification significantly increases the cation exchange capacity of the pine cone. Most suitable size fraction of pine cone was determined as -16 + 30 mesh ($600\ \mu m < x < 1200\ \mu m$). Also, citric acid modified product obtained from this fraction was used in a continuous system to remove hardness from water. The results of this study showed that the MPC can be used for hardness removal from waters as a cheap, durable and environment-friendly material. Finally, regeneration experiments showed that the MPC can be used for hardness removal from water repeatedly by a simple HCl regeneration.

1. Introduction

A considerable amount of pine cone can be obtained from forested areas. Pine cones significantly contain cellulose, hemicellulose and lignin. Also, it contains little amounts of xylose, arabinose and some extractable compounds. Due to it has a woody structure, pine cones are evaluated as fuel or fire initiator on a large scale. There is no important industrial usage of the pine cone. In some researches, it has been reported that some extraction products obtained from pine cones can be used as medicine or fungi toxic agent [1].

In a few last decades, a lot of studies on the production of ion exchange resin from plant residues have been made. Especially, it can be said that studies mainly focused on the ion exchanger production from agricultural wastes. The main goals of these studies are to obtain cheaper and environment-friendly ion exchanging materials. In fact, most of the commercial ion exchangers are produced from petroleum derivatives. Some environmental and health risks can occur during both production and usage of ion exchangers obtained from petroleum derivatives. For example, although carcinogenic effects of some petroleum derivatives are well known, ion exchangers obtained from these derivatives are widely used for drinking water treatment. So, it can be said that production from the natural sources is an important issue.

It has been showed that treating agricultural materials with polyacids (citric, tartaric, phosphoric i.e.) at a mildly elevated temperature enhanced their metal ion sorption capacity [2,3]. By such a treatment, some extra carboxyl groups can be introduced to the material by forming ester linkages. Some agro-industrial materials have been modified with commercial phytic acid, which is an organic polyphosphoric acid [4]. A research group has extensively studied on the ion exchanger production from cellulose based agricultural by-products such as soybean hull, peanut shell and corn cob by using the citric acid modification [5–12]. Some other lignocellulosic materials modified by citric acid such as sugar beet pulp [13], lemon [14,15], leaves [16], grass [17], barley straw [18], soybean straw [19], bagasse [20] and paper [21] have been investigated for heavy metal removal from aqueous solution. In fact, similar ion exchangers can be used to remove water hardness mainly originated from calcium and magnesium cations. This situation is also important due to use of natural ion exchanging material against the resins obtained from petroleum derivatives for softening of drinking water. Nevertheless, there are only a few studies on the usage possibility of the natural material based ion exchangers for removing of Ca and Mg hardness from the waters. Junior et al. [22] have studied Ca^{2+} and Mg^{2+} removal from aqueous solutions by using mercerized cellulose and mercerized sugarcane bagasse grafted with EDTA dianhydride. In another study, removal of calcium ions from aqueous solutions by sugarcane bagasse modified with tartaric and citric acids using microwave-assisted solvent-free synthesis has been investigated [23]. Also, it can be considered that the pine cone having woody structure is more

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suitable than the cellulose based agricultural by-products to obtain an ion exchanging material. Especially in a continuous ion exchanging system, some physicochemical properties of the material such as water retention and swelling capacities and mechanical strength are to be important characteristics. According to these characteristic properties, the pine cone can be considered as the more suitable material than the most of agro-industrial materials for production of an ion exchanger depending on relatively high lignin content.

The main objective of this study is to obtain an ion exchanger from the pine cone by using the citric acid modification and to investigate its hardness removal abilities from the waters. For this purpose, citric acid modification method described by Marshall et al. [2] was used to prepare an ion exchanger from the pine cone. This modification method was applied to different particle size fractions of the pine cone. Obtained citric acid modified pine cone samples having different granulation were subjected to standardized batch hardness removing tests to determine most suitable particle fraction. Finally, the most suitable modified product was tested to observe hardness removal properties in a continuous system. Also, reusability properties of the material were tested by a regeneration study.

2. Materials and methods

2.1. Materials

Open cones of the 2-year-old pine tree (*Pinus nigra*) were collected from a plantation in Elazığ, Turkey. The cones were washed with distilled water (water/cone weight ratio: 20) three times to remove impurities such as soil and leaf. Rough moisture of wet cone scales was removed by air blowing and then they were dried by heating in an oven at 50 °C for 24 h. Cone axis were separated and removed from seed scales of the cones by pulling with a nipper. The cone scales were shredded by a blender and ground by a ball mill. Ground samples were sieved through a series sieves to obtain different particle fractions (–8 + 16 mesh, –16 + 30 mesh, –30 + 50 mesh, –50 + 100 mesh and –100 mesh). Finally, all fractions were again dried in an oven at 50 °C for 24 h.

In the study, tap water obtained in our laboratory was used for hardness removal experiments. This tap water comes from deep wells located in the Elazığ city (Turkey) and it contains high hardness in varying levels. For that reason, hardness analyses (total, calcium and magnesium hardness) were made before every experiment group.

2.2. Modification of pine cone

Modification of pine cone was carried out in two stages using the method reported by Marshall et al. [2] and Wong et al. [3]. First is extraction with NaOH solution and the second is an esterification with citric acid. In order to see the effect of particle size fraction, modified products obtained were subjected to a standardized hardness removing test by shaking of hard water-modified pine cone mixture.

100 g of the pine cone sample having different particle size fractions were placed in 2 L of 0.1 M NaOH solution in a PE jar of 5 L. The slurry was shaken at 200 rpm for 1 h at room temperature. The mixtures were poured onto a perforated ladle and rinsed with distilled water. The obtained solids were added to 2 L of distilled water in a jar and shaken at 200 rpm for 1 h to remove the excess base. The washed pine cone samples were poured onto the perforated ladle, rinsed and added to 2 L of distilled water. This procedure was repeated until no pH variation in the washing water could be detected. These products are nominated as saponified pine cone samples. Saponified pine cone samples were exposed to blowing air in order to remove excess humidity. Then, they were dried in an oven at 50 °C for 24 h. Then, they were subjected to a standardized citric acid esterification procedure the conditions of which are an optimal of the study conducted by Marshall et al. [6] in order to see the effect of saponification and citric acid modification conditions. For this purpose saponified cone samples were mixed with a 0.6 M concentration of citric acid in a ratio of 1.0 g material to 7.0 mL citric acid. Samples completely imbibed the citric acid solution within a couple of hours. The citric acid-saponified cone mixtures were dried for 24 h at 50 °C. The dried mixtures were then heated at 120 °C for 90 min. Modified products were added to distilled water in a water/solid ratio of 20 and shaken at 200 rpm for 1 h to remove unreacted acid. The mixtures were poured onto the perforated ladle, rinsed and added to new distilled water. This procedure was repeated to ensure the complete removal of unreacted citric acid. The presence of citric acid in washing waters was tested by adding 0.1 M lead (II) nitrate solution [6]. Washing was terminated when no turbidity from lead (II) citrate was observed. The modified cone samples were coarsely dried by air blowing and then in an oven at 50 °C until constant weight and final products are referred to as citric acid modified pine cone.

2.3. Standardized hardness removing tests

In order to see the effect of particle size and citric acid modification on hardness removing properties of pine cone, both of raw pine cones (RPC) and modified pine cone (MPC) samples were subjected to standardized hardness removing tests. For this purpose, 0.5 g of samples was added to 100 mL of tap water having high hardness in a 250 mL of Erlenmeyer flasks. The flasks were agitated on an orbital shaker at 200 rpm and at room temperature for 12 h. After the shaking period, mixtures were filtered through a blue ribbon filter paper and the supernatant fractions and tap water samples were analyzed for determining the hardness. Uptake values were calculated from the difference between the hardness of initial and final solutions. All experiments were carried out in duplicates and the mean values were used for further calculations. Thus, the most suitable particle size of modified pine cone samples was determined.

2.4. The characterization of materials

After determining the most suitable particle size fraction of modified pine cone from standardized hardness removing tests, some of its chemical and physicochemical characteristics were analyzed comparatively with raw pine cone having same granulation. The pH of materials in water medium was measured. For this purpose, 1 g of material was placed into a conical flask containing 100 mL of water and it was shaken at 100 rpm for 24 h. Then, the pH of the suspension was measured. In addition, the suspension was filtered and material was dried at 50 °C and weighed. Thus, matters soluble in water were determined. For determining of matters soluble in HCl, the same steps were conducted using 0.1 M HCl solution instead of water.

The material was dried at 105 °C until constant weight to determine the moisture content. The mechanical moisture content was calculated from the weight loss. The same material was burned at 600 °C for 4 h in a muffle furnace. The ash content was calculated from weight loss. Bulk densities were determined by a tamping procedure [24].

Copper ion sorption capacity of material was measured. For that reason, 1.0 g of material was added in 100 mL of 10 mmol/L solution buffered with 0.07 mol/L sodium acetate and 0.03 mol/L acetic acid to maintain the constant pH of 4.8. The amount of sorbed copper was measured using an atomic absorption spectrophotometer (Perkin Elmer AA400).

For determination of water retention capacity, dry material was soaked either in water or in 0.1 M $NaNO_3$ for 16 h at 4 °C and centrifuged for 1 h at 5000 rpm. The supernatant was carefully removed and was weighed [25]. The swelling capacity was measured by the bed volume technique. Dry material was weighed in a glass cylinder and left overnight at 25°°C in an excess of either water or 0.1 M $NaNO_3$ and volume change of material was determined [26].