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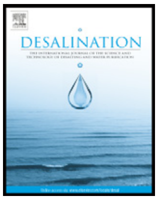

Removal of calcium ions from aqueous solutions by sugar cane bagasse modified with carboxylic acids using microwave-assisted solvent-free synthesis

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ABSTRACT

Removal of Ca(II) from aqueous solutions was potentially achieved using two new naturally benign sorbents. They were obtained via modification of sugar cane bagasse (SCB) with tartaric acid (TA) and citric acid (CA) using microwave-assisted solvent-free synthesis. The highest percentages of surface loading were realized under optimize conditions of mass ratio of SCB and TA or CA, microwave radiation power and time of radiation. Changes in spectral band positions of binding sites of SCB and its modified forms (SCB-TA and SCB-CA) were characterized using FT-IR before and after calcium ions sorption. Also, changes in surface morphology were explored in parallel, using scanning electron microscope (SEM). Moreover, for obtaining maximum Ca(II) removal, batch experiments were carried out at different parameters including hydrogen ion concentration, initial Ca(II) concentrations, mass of the sorbent and finally shaking times. Results of sorption isotherms were better fitted with the Langmuir model ($r^2 = 0.959$ and 0.995 for SCB-TA and SCB-CA, respectively). In addition, the kinetics data were best fitted with the pseudo-second-order type. Applications of the new natural sorbents for lowering hardness and consequently conductivity and total dissolved solids (TDS) in different water samples was superior compared to the cation exchange resin Dowex 50W-X8.

1. Introduction

Calcium is the most abundant mineral in the human body. It is important for intracellular metabolism, bone growth, blood clotting, nerve conduction, muscle contraction and cardiac functions [1,2]. However, there is a significant protective association between drinking-water calcium levels and colorectal [3] gastric [4] and breast cancer [5]. Determination of calcium and other alkali-earth ions in aqueous media is of both scientific and technological relevance. This determination is particularly difficult because of the complex matrix. For solving this problem, there are many methods for detection of calcium [6–9]. Solid phase extraction technique (SPE) has become known as a powerful tool for separation and removal of various inorganic and organic analytes [10–12]. Increasing attention has been focused on removal of metal ions from aqueous solutions using benign natural sorbents such as agricultural wastes to overcome the environmental pollution [13,14]. Sugar cane bagasse (SCB) is a representative example of these sorbents. It is a fibrous residue of cane stalks left over after the crushing and extraction of the juice from the sugarcane. About 54 million dry tonnes of bagasse is produced annually throughout the world [15]. The huge quantities of the remaining sugarcane bagasse are burnt in the fields or on the road, and the pollution caused by burning agricultural residues has been a serious problem. Thus, there is an urgent need to find suitable applications for this waste. Moreover, it was found that, SCB is an abundant, inexpensive, and promising industrial waste with cellulose-lignin polymeric structure. However, direct using of the natural sorbents to act as metal ion sorbent from aqueous solution is limited. So, pre-modification using organic chelating agents are important to increase their metal uptake capacity and selectivity as well [16]. In the last few years, there are several studies of modification of SCB using conventional synthetic methods [17,18]. Microwave heating is today a mature technique which finds wide applications. Recently, microwave energy has been widely used in several fields of applications on both research and industrial processes [19]. This technique did not include the organic solvent, trying to minimize the use of hazardous chemicals and develop environmentally acceptable method to prepare chelating agents from easily available agricultural residues. In particular, microwave heating arises from the direct interaction of matter with electromagnetic energy and it offers a number of potential advantages over conventional heating [20]. The main advantage of using microwave heating is that the treatment time can be considerably reduced, which in many cases represents a reduction in the energy consumption as well. The main goal of this manuscript is performing a benign modification process. This includes the use of SCB as a natural sorbent, TA and CA as benign modifiers – keeping in mind that Ca(II) can strongly bind to carboxylate groups incorporated either aliphatic or aromatic carboxylic acids [21,22]– and an environmentally friendly

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microwave-assisted solvent-free synthesis instead of conventional synthetic routes [17,18]. The benign sorbents thus produced, SCB-TA and SCB-CA, were optimized for removal of calcium ions, as the main determinant of water hardness [23], under different controlling parameters along with the validation of their efficiencies for lowering the hardness of natural water samples.

2. Experimental

2.1. Materials and methods

All chemicals and reagents used were of analytical grade and were purchased from E. Merck, India/Germany. Sugar cane bagasse (SCB) was obtained from Abou-Korkas Sugar Factory, El-Minia, Egypt. Citric and tartaric acids were purchased from Aldrich Chemical Company (Milwaukee, WI, USA). Dowex 50W-X8 was purchased from BDH (England). Water samples including: Nile River water (NRW) and ground water (GW) was collected from El-Minia governorate, Egypt. Doubly distilled water (DDW) was obtained from our lab.

2.2. Instrumentation

The infrared spectra of SCB and its modified phases before and after Ca(II) sorption were obtained using FT-IR model 410 JASCO (Japan). Scanning electron microscope (SEM) analysis obtained using JSM-5400 LV JEOL (Japan). A Fisher Scientific Accumet pH-meter (model 825) calibrated against two standard buffer solutions at pH 4.0 and 9.2 was used for all pH measurements. Atomic absorption measurements were performed with Aquanova-Genway spectrometry. Microwave oven (Sharp REM20) emitting 2.450 MHz microwave frequency.

2.3. Modification of SCB with tartaric and citric acids using microwave technique

SCB was first washed thoroughly with distilled water to remove the dust particles, then soaked over night in 0.1 N NaOH solution and again washed well with DDW. SCB was then soaked in 0.1 N CH_3COOH for a period of 2–3 h to remove the traces of NaOH [24,25]. It was thoroughly washed again with DDW till the wash water became colorless and then filtered, well dried, powdered and sieved before use. The average particle size was 0.75 mm. Then, 1 g of the previous treated bagasse was irradiated for 10 min with 10.0 mmol of tartaric acid (TA) and 15 min with 10.0 mmol of citric acid (CA) in a glass watch using a microwave oven. The products, sugar cane bagasse loaded with tartaric acid (SCB-TA) and sugar cane bagasse loaded with citric acid (SCB-CA), were then washed with hot water (60 °C) to remove the residues and excess acids and left to dry for 30 min.

2.4. Factors controlling Ca(II) extraction using SCB-TA and SCB-CA phases

The percentage extraction of Ca(II) using SCB-TA and SCB-was were determined in triplicate under static conditions by the batch equilibrium technique. 100 mg of each of the phases was added to a 100 μl of 0.1 M of the Ca(II); the total volume was completed to 50 ml by DDW at pH range 1.0–10.0 in a 100 ml measuring flask. For the pH adjustment, solutions of 0.1 M HCl and 0.1 M NaOH were used. This mixture was mechanically shaken for 25 and 10 min with SCB-TA and SCB-CA, respectively at room temperature to attain equilibrium. The phases were separated by filtration and washed with DDW; the unretained metal ion in the filtrate was determined by complexometric EDTA titration [26]. The equation of percentage extraction could be obtained as follows:

$$\%\ \text{Extraction} = (C_i - C_f/C_i) \times 100.$$

Where C_i is the initial concentration of Ca(II) and C_f is its final concentration.

The effect of the contact time on the Ca(II) extraction was determined under the same batch conditions for different shaking periods (5, 10, 15, 20, 30, 45, 60, 90 and 150 min) at the pH of the highest Ca(II) extraction (pH = 6.0) [26]. The effects of Ca(II) concentration (10.0–100.0 μmol) and weight of the phase (15.0–150.0 mg) on extraction efficiency were also systematically investigated.

3. Results and discussions

3.1. Microwave studies

The details of the reaction conditions (power and time) on yield percentage are provided in Table 1. It could be seen from Table 1 that, the microwave radiation synthesis gives good percentage of surface loading (% Yield) at a short reaction time compared to conventional methods [17,18]. Thus, for the synthesis of SCB-TA, the yield could reach to 70.4, 70.0 and 70.6% with a power of 20, 30 and 40 W microwave radiation for 20, 10, and 1 min, respectively. On the other hand, for the synthesis of SCB-CA, the yield could reached to 56.0, 56.3 and 56.0% with a power of 20, 30 and 40 W microwave radiation for 45, 15, and 3 min, respectively. It could also be found that the reaction time became shorter with the increase of the microwave power. According to the data in Table 1 it could be concluded that, the optimum power and time adequate for the microwave synthesis of SCB-TA and SCB-CA were 30 W, 10 min and 30 W, 15 min, respectively. Based on the result obtained on studying the effects of mass ratio of both SCB and TA or CA Table 2, we have selected the 1 g SCB:1.5 g TA (10 mmol) and 1 g SCB:2.2 g CA (10 mmol) SCB:CA as the optimum mass ratio for modification.

3.2. Characterization of the new sorbents (SCB-TA and SCB-CA)

3.2.1. FT-IR spectra

Bagasse consists mainly of cellulose, hemicellulose, lignin and other minor components. The FT-IR spectra of SCB and also SCB-TA and SCB-CA before and after sorption of Ca(II) were performed to determine the vibration frequency changes in their functional groups within the range of 4000–400 cm^{-1} Fig. 1. The spectral measurements support the complex nature of the examined adsorbent. The

Table 1
The reaction conditions for the synthesis of SCB-TA and SCB-CA phases as a function of radiation power and time at fixed mass ratio, 1 g SCB:1.5 g TA (10 mmol), 1 g SCB:2.2 g CA (10 mmol).

Phase	Power (Watt)	Time (min)	% surface loading (%Yield)[a]
SCB-TA	20	10	67.5
	20	20	70.4
	20	30	65.9
	30	2	48.8
	30	5	57.6
	30	10	70.0
	30	12	Carbonization
	40	1	70.6
	40	2	65.3
SCB-CA			
	20	20	53.7
	20	30	55.7
	20	45	56.0
	20	50	Carbonization
	30	15	56.3
	30	20	44.4
	40	1	49.2
	40	2	49.2
	40	3	49.2
	40	4	40.0

[a] Percentage of surface loading (%Yield): Mass of TA or CA in g loaded on 1 g of SCB multiplied by 100.