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Production of Struvite from Beverage Waste as Phosphorus Source

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In this work was investigated the influence of pH on the synthesis of struvite using cola beverage waste as source of phosphorus. The process was operated in a batch reactor. The reaction time was 20 minutes, and the chemicals $MgCl_2.6H_2O$ and NH_4Cl were used in the experiment, with a molar ratio of Mg^{+2}:NH_4^+:PO_4^{3-} = 1:1:1. The products were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), surface area (BET), thermogravimetric analysis (TGA) and infra-red (IR). From the results was verified the formation of a crystalline phase at pH 9.5, with a surface area of 6.59 $m^2 g^{-1}$ and a particle size of about 0.25 μm.

Keywords: *struvite, characterization, beverage waste, phosphorous*

1. Introduction

Struvite ($MgNH_4PO_4.6H_2O$) is a crystalline solid with equal molar concentrations of magnesium, ammonium and phosphorus and it has been used as slow-release fertilizer[1] and as reagent for the preparation of magnesium phosphate cement materials[2,3]. The struvite precipitation process is an attractive method because it can remove and recover simultaneously P and N from wastewater[4], decreasing the environmental impact as the eutrophication[5]. Different sources of phosphorus and nitrogen have been used for struvite production such as swine wastewater[6], leather tanning wastewater[7], waste sludge[8], poultry wastewater[9], municipal landfill leachate[10] and synthetic form[11]. The formation of struvite normally occurs in alkaline medium, and the optimal pH value for struvite crystallization is reported in the range 8.0-11.0[12,13]. Magnesium chloride ($MgCl_2$) has been widely used as a Mg source because of it quick dissociative nature, resulting in short reaction time[14,15].

Although several works are reporting the use of different sources of phosphorous to synthesize the struvite, there are no studies concerning the evaluation of waste from the cola beverage as phosphorous source, since this beverage present high content of phosphorous[16,17]. In this sense, the main objective of this work was to investigate the influence of pH on the characteristics of struvite particles obtained by precipitation using cola beverage waste as phosphorous source. The materials were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), surface area (BET), thermogravimetric analysis (TGA) and infra-red (IR).

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2. Experimental

The sample used in this work was a cola beverage with shelf life expired obtained from a local beverage industry. The sample was maintained at 4 °C until the analysis. The experimental system consisted of a simple glass batch reactor (11 × 11 × 17 cm) with a total volume of 2.0 L. The agitation of the reaction media was carried out using a paddle with diameter of 7.5 cm and height of 2.5 cm. The working volume of the reactor was 1.0 L, which was operated at 20 °C under agitation of 200 rpm. Analytical grade chemicals ($MgCl_2.6H_2O$, NH_4Cl and NaOH) were used as received. In order to eliminate carbon dioxide dissolved in the beverage sample, a vigorous mechanical stirring was carried out by 5 hours before the experiments. The amounts of $MgCl_2.6H_2O$ and NH_4Cl used in the tests were calculated according to the concentration of PO_4^{3-} present in the sample of beverage, considering a molar ratio of 1:1:1 (Mg^{+2}:NH_4^+:PO_4^{3-}). In this work, the concentration of total PO_4^{3-} was determined by ascorbic acid colorimetric method[18]. The solution was prepared by dissolving amounts of cola beverage, magnesium chloride (1M) and ammonium chloride (1M), respectively, in the batch reactor. Afterwards, the pH of solution was adjusted to the desirable value (8.5, 9.0 and 9.5) by adding a 4M NaOH solution. All the reaction runs were carried out during 20 minutes. The suspension was centrifuged, and the precipitate was washed with distilled water and dried at 50 °C for 6 hours

Nanopowder was characterized by X-ray diffractometry (XRD) (equipment Bruker D8 Advance, with Cu Kα radiation). The average nanocrystallite size was determined through X-ray diffraction (and reflection) line broadening using the Scherrer equation[19]: $D = K.\lambda / (\beta.\cos\theta)$, where D is the crystallite size, K is the Scherrer constant (0.90), λ is

the wavelength of the X-ray radiation (0.1542495 nm for Cu-Kα), and β is the peak width at half height and finally θ corresponds to the peak position (in the current study, 2θ = 20.84). The morphology of particles was examined by atomic force microscopy (Agilent Technologies 5500 equipment). Thermogravimetric analysis (TGA) was carried out on Q500 analyzer (TA instruments) using a heating rate of 10 °C/min^{-1} at an air flow rate of 50 mL/min^{-1}. The BET surface area was obtained from nitrogen adsorption isotherms at 77 K, conducted on an ASAP 2020 system, at a relative pressure (P/Po) from 0 to 0.99.). IR spectra were recorded on a PerkinElmer FT-IR Spectrum spectrophotometer in the region of 600-3900 cm^{-1}, using KBr pellets.

3. Results and Discussion

The concentration of phosphorus in the cola beverage sample was 415 mg $PO_4^{3-}L^{-1}$, decreasing its value to 12 mg PO_4^{3-} L^{-1} after the struvite production for all experimental conditions, implying in a reduction of 97% of the initial phosphorus content. Removal of phosphorus ranging from 55 to 98% in different experimental conditions has been reported using liquid swine manure[20]. Recovery efficiency of phosphorus between 80 and 90% was achieved in the treatment of sludge digester liquors[21].

The analysis of XRD was used to characterize the synthesized powders (Figure 1). It was verified the formation of amorphous solids at runs carried out at pH 8.5 and 9.0 (Figure 1a). However, at pH 9.5 (Figure 1a), was verified the formation of crystalline struvite. The formation of struvite was indicated by location of the peaks, corresponding to reference database lines for struvite (Figure 1b). By applying of Scherrer equation, the average nanocrystallite size was about 55 nm. Several authors have been reported that the formation of crystalline struvite is verified in a narrow range of pH, which is closely related to the raw material characteristics. By example, for struvite precipitation using swine wastewater as raw material, different values of pH such as 8.0-8.5[22], 8.5[23], 9.0[8], 8.9-9.25[24], 9.5-10.5[25] were reported. The narrow range of pH for synthesis of crystalline struvite is because maintaining the pH above the optimum point occurs the formation of $Mg_3(PO_4)_2$ instead of struvite, whereas at pH below the optimum range promotes the increase of H^+ in the solution inhibiting the struvite crystallization[22].

The identification of struvite phase obtained at pH = 9.5 was confirmed by thermogravimetric analysis (TGA) (Figure 2a). According to the chemical structure of struvite ($MgNH_4PO_4.6H_2O$), the theoretical mass loss under heating should be 51.42%, due to mass losses of water (44.08%) and ammonium (7.3 4%). From Figure 2a it is seen that the mass loss was about 50%, that is very close to the theoretical (51.42%) and similar to those reported by other researchers (51% and 52.49%)[11,26]. AFM image (Figure 2b) indicated that the struvite particles obtained at pH = 9.5 presented quasi-spherical shape with size of about 0.25 μm, which are formed by agglomeration of nanocrystals.

The N_2 adsorption-desorption curves were of type IV with H3-type hysteresis loop (in accordance with IUPAC classification)[27] at relative pressure > ca. 0.3, as shown in Figure 3. The shape of the isotherms suggested that the sample obtained at pH = 9.5 presented basically mesoporous structure. It was confirmed by analysis of pore size distribution (see insert in Figure 3), which was unimodal, and showed spectra of pore diameter in the mesopous region, according to the IUPAC classification[27]. Therefore, struvite had mesopores, most likely due to the interparticles and out-of-order porosity. The results of surface area and total pore specific volume (at P/Po = 0.99) were 6.59 m^2.g^{-1} and 0.0254 cm^3.g^{-1}, respectively.

The identification of single-phase struvite obtained at pH = 9.5 was also confirmed by IR spectroscopy (Figure 4). The band at 2970 cm^{-1} was the antisymmetric stretching vibration of NH_4 groups. The broad band between 2500 and 2200 cm^{-1} was assigned to water-phosphate H bonding. HOH deformation of water was at 1680 cm^{-1}, and the bands

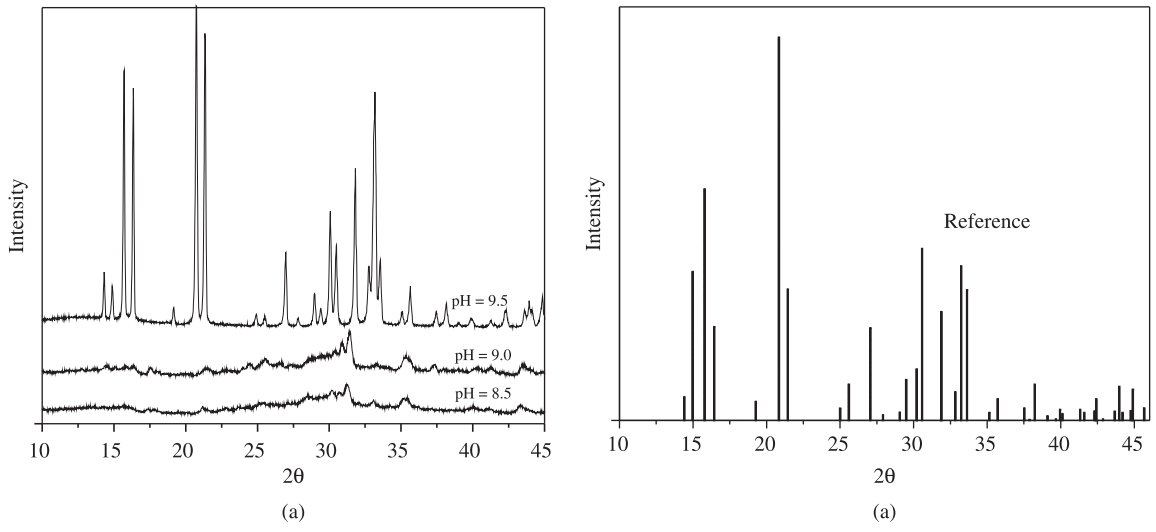

Figure 1. XRD analysis of (a) samples obtained at different pH values, and (b) reference struvite (JCPDS Card No 1-077-2303).

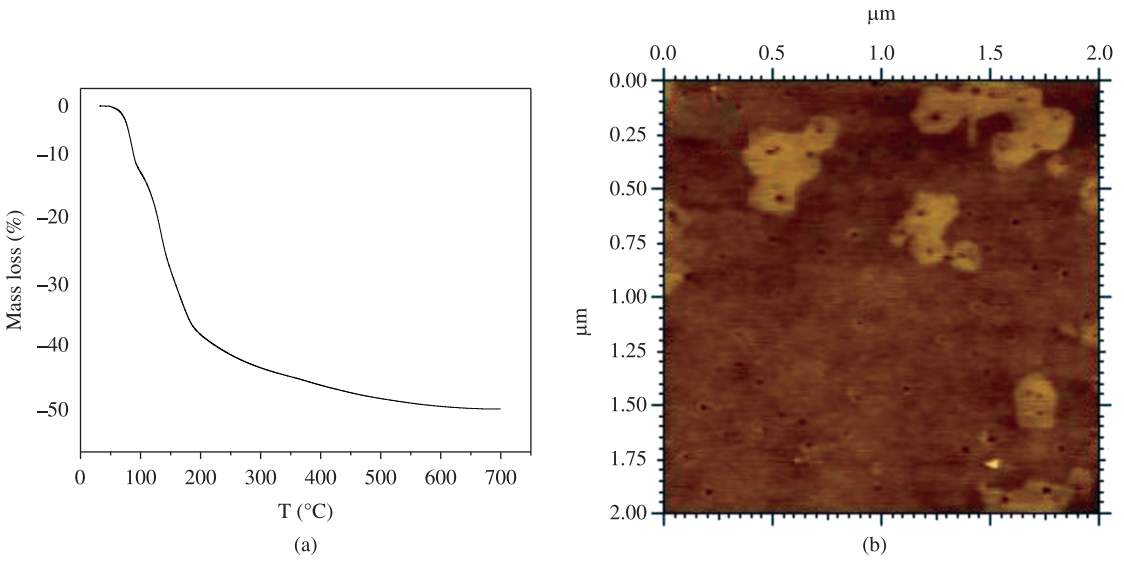

Figure 2. (a) TGA pattern and (b) AFM image of struvite sample obtained at pH 9.5.

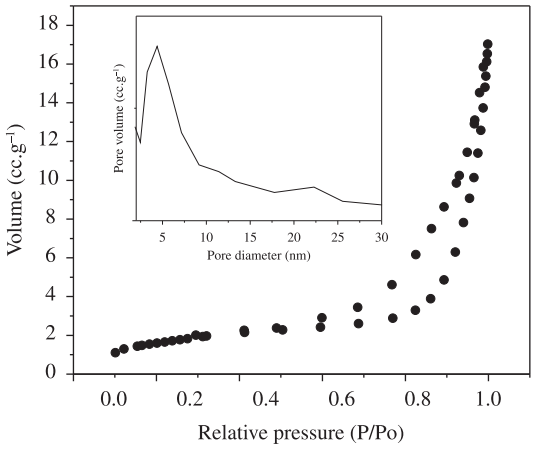

Figure 3. N_2 ad/desorption isotherms and pore size distribution of struvite sample obtained at pH 9.5.

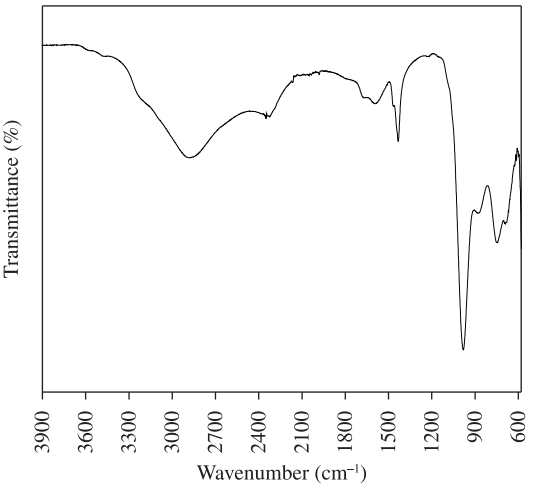

Figure 4. IR data of struvite sample obtained at pH 9.5.

seen over the range of 1600 to 1400 cm^{-1} were those of the HNH deformation modes of HN_4. The band of PO_4 unit was observed at 1006 cm^{-1}[28]. Water-water H bonding were observed at 760 and 695 cm^{-1}, whereas ammonium-water H bonding was observed at 890 cm^{-1}[28].

4. Conclusions

This study investigated the phosphorus removal and recovery from cola beverage waste by struvite crystallization process. From the results was verified that pH influenced the crystalline struvite precipitation, where the pH 9.5 showed to be the most suitable for the synthesis. The recovered solids at pH 9.5 presented a pure and crystalline phase, with a particle size in the micrometric scale. Thus, the struvite can be produced from waste of cola beverage industries.

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