Separation and Purification Technology 363 (2025) 132297

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Natural polymers as stability modifiers of suspensions containing carbonaceous materials obtained by microwave-assisted chemical activation of waste cornelian cherry stones

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A R T I C L E I N F O

Editor: Dr. B. Van der Bruggen

Keywords:
Waste cornelian cherry stones
Nanostructured activated biocarbons
Thermochemical conversion of lignocellulosic biomass
Protein-based carbonaceous composites
Hydrolyzed collagen
Plant-based phytokeratin

A B S T R A C T

The cornelian cherry (*Cornus mas L.*) stones were used as a precursor for the preparation of activated biocarbons for cosmetic applications. The microwave-assisted chemical activation with the use of phosphoric acid and potassium carbonate was applied. The resulting carbonaceous materials (CS_P and CS_K) are characterized by a well-developed specific surface area (600 – 800 m^2/g) and micro/mesoporous structure with a mean pore diameter of about 2 nm. Their adsorption properties towards hydrolyzed collagen and phytokeratin were checked within the pH range 3–10, and the stability of protein-containing and protein-free suspensions was determined spectrophotometrically. To explain the adsorption and stability mechanisms in the examined systems the solid surface charge and electrokinetic measurements were additionally performed. The surface and electrokinetic properties of both carbon adsorbents were found to be quite similar, e.g. pH_{pzc} points of 6.4 and 8.2, and the pH_{iep} values of 3.5 and 3.6, for samples CS_P and CS_K, respectively. It was shown that the greatest amounts of both proteins were adsorbed in the case of H_3PO_4-activated biocarbon (587 mg/g at pH 6 for collagen and 585 mg/g at pH 3 for phytokeratin, so very close to their pI values of 5.4 and 3.5, respectively). These systems also exhibit the highest stability among all tested suspensions, as indicated by the smallest aggregate sizes of 23.8 and 21.4 μm, respectively. Such behaviour is highly desirable for cosmetic formulations containing activated biocarbon with adsorbed layers of proteins acting as active agents.

1. Introduction

The Cornelian cherry, or *Cornus mas L.*, is a valuable fruit-bearing plant from the Cornaceae family. It is a deciduous, small shrub or tree reaching a height of 2–5 (up to 9 m) meters. The fruits are drupes of dark-red, sometimes light-red or yellowish-pink color, mainly elliptical or cylindrical, sometimes pear-shaped, ranging from 10 to 15 to 35 mm in length, smooth or slightly granular, sweet-tart in taste. The stone is elliptical or spindle-shaped, almost smooth. All parts of the plant have medicinal properties. Cornelian cherry raw material has antiscorbutic, antidiabetic, antipyretic, anti-inflammatory, bactericidal, general strengthening, choleretic, and diuretic effects. Fresh and dried fruits are used for anemia, inflammatory diseases of the gastrointestinal tract, deficiency of vitamins C and E as well as metabolic disorders. In Georgia, a fixative drug "Schinpani" (dense extract of wild cornelian cherry and pear fruits) has been created, which has undergone clinical trials and received approval for use. The drug made from cornelian cherry pulp in the experiment accelerated protein digestion and showed bactericidal properties against microorganisms of the dysentery group [1–3].

Waste material from cornelian cherry processing, such as stones, can be used to production of activated biocarbons. In this way, such a type of biomass will be utilized and the resulting pyrolysis product will be

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https://doi.org/10.1016/j.seppur.2025.132297
Received 6 January 2025; Received in revised form 21 February 2025; Accepted 25 February 2025
Available online 25 February 2025
1383-5866/

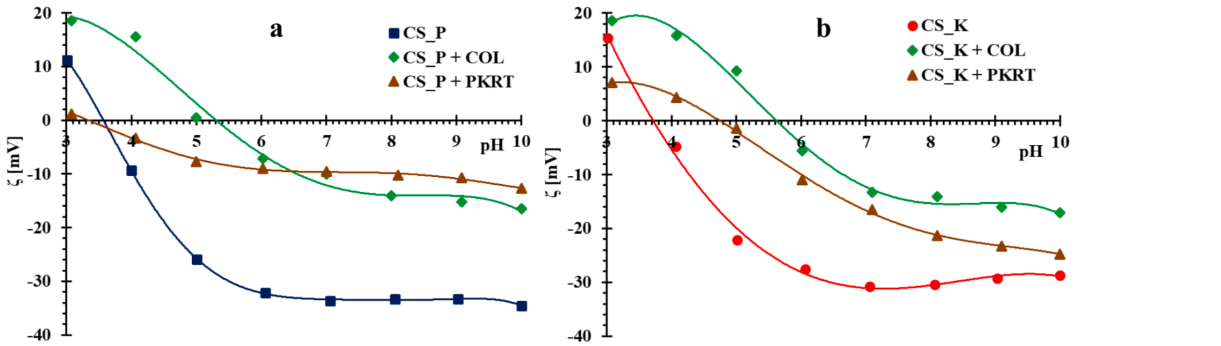

Fig. 13. Zeta potential of CS_P (**a**) and CS_K (**b**) particles dispersed in an aqueous solution as a function of solution pH in the absence and presence of proteins.

biocarbon the maximal adsorbed amounts were 585 mg/g for phytokeratin and 587 mg/g for collagen, respectively. In the analogous systems in the case of CS_K material, the adsorption levels are: 409 and 462 mg/g, respectively. The stability of CS_P suspensions containing both biopolymers is relatively high, when their adsorption reaches considerable levels, specified below. The decrease in suspension stability is accompanied by an increase in the size of the aggregates formed. The densely packed adsorption layers of protein molecules assuming their native conformation guarantee effective steric repulsion between solid particles dispersed in an aqueous solution. The surface charge density and zeta potential values determined for activated biocarbons systems confirmed the adsorption of proteins and indicated the specific conformation of their macromolecules in the surface layer. In the course of the conducted research, it was proven that systems with optimal composition for cosmetic applications were obtained, i.e. those that showed significant adsorption of the active substance (protein) at pH suitable for skin and hair care and were very stable. The best in this aspect turned out to be CS_P activated biocarbon with adsorbed collagen at pH 6. It is worth mentioning that we have already successfully attempted to introduce the tested activated biocarbons modified with hydrolyzed COL into cosmetic products for body and hair care, such as solid shampoo and bar soap (in cooperation with companies "SPA-Vita product" and ZELENAHA).

CRediT authorship contribution statement

Małgorzata Wiśniewska: Conceptualization, Methodology, Validation, Formal analysis, Resources, Writing – original draft, Writing – review & editing, Supervision. **Teresa Urban:** Methodology, Investigation, Data curation, Writing – original draft, Writing – review & editing. **Iwona Ostolska:** Validation, Investigation, Writing – original draft, Visualization. **Karina Tokarska:** Investigation, Resources, Data curation. **Victoria Paientko:** Formal analysis, Investigation, Resources, Visualization. **Alla Kustovska:** Investigation, Data curation, Writing – original draft. **Vita Vedmedenko:** Investigation, Data curation. **Natalia Kurinna:** Investigation, Data curation. **Piotr Nowicki:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing – original draft, Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: The authors Vita Vedmedenko and Natalia Kurinna are sole entrepreneurs employed by the companies "SPA – Vita product" and ZELENAHA. The remaining Authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Acknowledgments

The authors would like to thank the Association of Perfumery and Cosmetics of Ukraine (APCU) for the support.

Data availability

Data will be made available on request.

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