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Adsorption of poly(acrylic acid) on the surface of microporous activated carbon obtained from cherry stones

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HIGHLIGHTS

- Microporous activated carbon (CSDA) obtained by direct activation of cherry stones was prepared.
- Adsorption of anionic poly(acrylic acid) – PAA on CSDA surface was examined.
- Solution pH and PAA molecular weight influence on surface properties of activated carbon were determined.
- The most favourable conditions for polymer removal from water solution were specified.
- PAA amounts adsorbed on the CSDA surface were compared with those obtained for different metal oxide systems.

GRAPHICAL ABSTRACT

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ABSTRACT

The adsorption properties of microporous activated carbon (CSDA) obtained by direct activation of cherry stones in relation to low-molecular weight poly(acrylic acid) – PAA were examined. The solution pH influence and molecular weight of the polymer were examined. The PAA adsorbed amounts were correlated with the solid surface charge density and zeta potential of the solid particle in the polymer presence. The obtained results indicated that the highest adsorption on the activated carbon surface is exhibited by PAA with lower molecular weight at pH 3 (it reaches the level of 25 mg/g). Thus, under such conditions the CSDA is the most efficient adsorbent for poly(acrylic acid) removal from aqueous solution. The polymeric adsorption layer at pH 3 is composed of more coiled macromolecules (low degree of PAA carboxyl groups dissociation) which are electrostatically attracted to the positively charged solid surface. It was also proved that applied low-cost activated carbon can be used for removal of undesirable low-molecular polymers from wastewaters.

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1. Introduction

Synthetic water-soluble polymers are used in a great variety of practical applications. Their presence in the aqueous medium leads to the modification of physicochemical properties of colloidal systems (i.e. emulsions, suspensions, foams, aerosols, fumes). Their action is manifested through changes in solution viscosity (gelation and thickening agents), as well as through impact on the dispersion system stability (processes of emulsification, stabilization, flocculation, flotation) [1–5].

Two main kinds of polymeric substances are used: non-ionic (its functional groups do not undergo dissociation in aqueous solutions, i.e. poly(ethylene glycol), poly(ethylene oxide), poly(vinyl alcohol), polyvinylpyrrolidone) and ionic (whose macromolecules contain ionized groups, i.e. poly(acrylic acid), poly(methacrylic acid), poly(ethylene imine), poly(vinyl amine), poly(vinyl pyridine)). The ionic polymers are often called polyelectrolytes and in this class of chemical compounds three types can be distinguished: polyacids (anionic polyelectrolytes), polybases (cationic polyelectrolytes) and polyampholytes.

One of the most important polymers from the anionic class is poly(acrylic acid) – PAA. The industrial synthesis of this polymer proceeded by radical polymerization of acrylic acid. Its chains have one carboxyl group per each monomer unit. PAA is characterized by weak acidic properties – its carboxyl groups dissociate with the increasing solution pH [6,7].

Poly(acrylic acid) finds a widespread usage in different practical fields as a dispersing agent in food processing, cosmetics production (personal care products, detergents) [8–11], medical and pharmaceutical applications (drug delivery systems, oral suspensions, bioadhesives) [12–15]. This is a result of PAA very low-toxicity and biocompatibility with human muscle tissue. Additionally, PAA is used in paper making technologies, as well as in pigments and paint formulations [16,17]. On the other hand, poly(acrylic acid), especially its high-molecular weight forms, play a role of destabilizer (flocculent) in water treatment technologies and mineral processing [18–20].

Copolymers of PAA with other polymers (i.e. polyacrylamide, poly(vinyl alcohol), poly(ethylene oxide), carrageen, chitosan) show ability of hydrogels formation. Such superabsorbents are used in agriculture [21], medicine [22] and catalysis [23].

Due to the common use of poly(acrylic acid) its presence in wastewaters is observed. Rather poor biodegradability of this macromolecular compound makes that its fast removal from the aqueous phase is necessary [24,25]. Among the known methods of separation of undesirable organic substances from solution (filtration, membrane processes, ionic exchange, oxidation reactions) the adsorption process is one of the most important [26–30].

Adsorbents are classified as porous and non-porous. The first group include activated carbons, silica gels, molecular sieves (zeolites), porous glasses, hydrated alumina and other metal oxides. The representatives of the non-porous adsorbents are for example barium sulfate and graphite soot.

Activated carbons are widely used for removal of pesticides, detergents, aliphatic and aromatic hydrocarbons, phenols and their derivatives, heavy metals, bacteria, viruses, dyes and low-molecular weight organic compounds in the processes of water and wastewater treatment [31–33].

Their another important application is the purification of industrial waste gases through the adsorption of SO_2, SO_3, H_2S, CS_2, NH_3, NO_x and other toxic compounds [34–36].

In the present study the adsorption properties of activated carbon (CSDA) obtained from cherry stones in the process of direct activation, in relation to low-molecular weight poly(acrylic acid) was determined. On the basis of adsorption and electrokinetic data, the mechanism of polymer chains binding with the solid surface was proposed. The pH conditions assuring the most effective polymer removal from water solution (corresponding with the greatest PAA adsorption) were specified. Moreover, the determined PAA adsorption amounts on the CSDA surface were compared with those obtained on the surfaces of different metal oxides (both single and mixed), silica and porous glass.

The applied activated carbon is a low-cost adsorbent obtained from plant waste material. For this reason, it is competitive to other adsorbents which are much more expensive. Moreover, understanding of the mechanism of interactions between the macromolecules and carbon surface groups will enable selection of appropriate method for the preparation and modification of activated carbons for effective removal of polymeric substances.

2. Experimental

2.1. Activated carbon preparation and its characterization

In the first step, the starting cherry stones (CS) were air-dried at 110 °C for 24 h, next kernels were separated and shells were crushed and sieved to a grain size between 1.2–1.6 mm. Thus the prepared precursor was subjected to direct activation process (DA) – a simultaneous pyrolysis and activation of the carbonaceous material. This process was carried out in the quartz tubular reactor heated by a horizontal resistance furnace. Activation was carried out at a temperature of 900 °C, under a stream of carbon dioxide (Linde Gas) at a flow rate of 0.250 dm^3/min, for 40 min. After the activation process, the final product (CSDA) was subjected to two-step washing procedure, with a hot 5% solution of hydrochloric acid (*Avantor Performance Materials Poland S.A.*) and hot demineralised water and finally was dried at 110 °C to constant mass. The schematic representation of activated carbon preparation is placed in Fig. 1.

The adsorbent was milled and next washed with doubly distilled water to achieve the supernatant conductivity about 2 μS/cm (conductivity meter CDM 83, *Radiometer*). In such a way, the mineral matter deposited on the adsorbent surface was removed.

The solid BET surface area, pore volume and average pore diameter were determined by the use of nitrogen adsorption/desorption method (Accelerated Surface Area and Porosimetry ASAP 2405 Analyzer, *Micrometritics Inc. USA*).

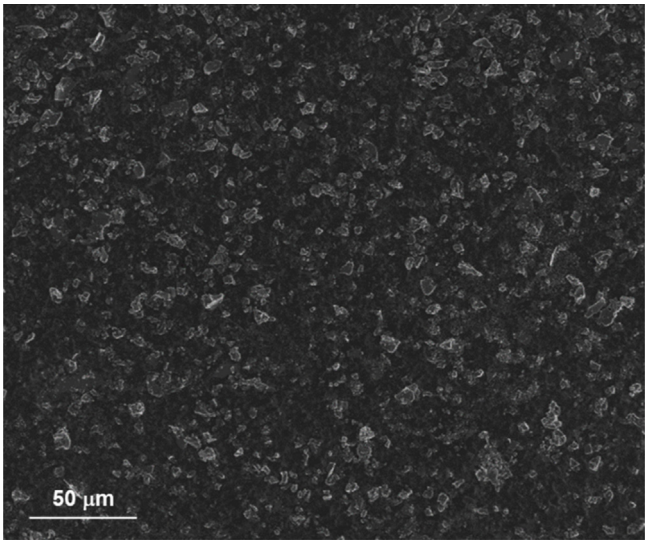

Fig. 1. SEM image of activated carbon particles (after milling) dispersed in PAA 2 kDa solution (pH 3).