APPLICATION OF MICROCRYSTALLINE CELLULOSE/POLYANILINE COMPOSITE FOR REMOVAL OF FOOD DYE TARTRAZINE FROM AQUEOUS SOLUTIONS

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Polyaniline (PAN) and microcrystalline cellulose/polyaniline composite (MCC/PAN) were synthesized by the chemical oxidative *in situ* polymerization of aniline using ammonium peroxodisulphate as an oxidizing agent in aqueous hydrochloric acid solution. The obtained samples were characterized by infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and X-ray diffraction (XRD).
The adsorption properties of the synthesized sorbents for the food dye tartrazine (TZ) were investigated under static model conditions. These materials were evaluated according to various parameters (contact time between the adsorbent and the adsorbate, dye concentration, and adsorbent mass). The obtained kinetic data of adsorption were described by pseudo-second order kinetic equations. The MCC/PAN composite proved to be a better adsorbent material compared to PAN due to its higher adsorption capacity (q = 99.0 mg g^{-1}), which can be explained by the combination of the adsorption properties of the two materials and the morphology of the composite.

Keywords: polyaniline, composite, tartrasine, adsorption, polymerization

Introduction. Industrialization and the increase in the production and consumption of goods and products are factors that affect the quality of the environment. Bright goods and colorful advertising attract more attention, which causes excessive use of synthetic dyes in various industries (dye production, food, leather, textile, printing, pulp and paper, cosmetics, pharmacy). The chemical classification of dyes unites them into separate classes depending on the structure of molecules, methods of production and chemical properties. In particular, anionic (direct, acidic and reactive) and cationic (basic) synthetic dyes are distinguished [1]. Incomplete treatment of wastewater from dyes has a harmful effect on the aquatic environment due to their toxicity, non-biodegradability, and effect on photosynthesis.

Therefore, it is important to remove synthetic dyes from wastewater to preserve the environment. Among the existing methods, adsorption is considered one of the most promising due to its simplicity and ease of operation. An important task among researchers is to search and select the most promising adsorbents from available and inexpensive materials. Natural biopolymer materials, which include cellulose, are attracting increasing attention in wastewater treatment due to their low cost, biodegradability and biocompatibility. Polymers, in particular polyaniline are also widely studied as adsorbents for the removal of heavy metals and organic compounds [2–7]. PAN as an adsorbent for the removal of anionic and cationic dyes can be used due to the presence of amine- and imine- functional groups in its polymer chains. There is growing interest in the synthesis of polymer nanocomposites. For example, composites based on cellulose and polyaniline have demonstrated high adsorption capacity for dyes [8, 9].The objectives of this study were: synthesis and characterization of PAN and MCC/PAN nanocomposite, comparison of their efficiency for removing anionic food dye using tartrazine as an example, study of adsorption isotherms and kinetic models.

Results and discussion. PAN and the MCC/PAN composite (7 wt. % MCC) were obtained by in situ oxidative polymerization of aniline using ammonium persulfate (APS) as an oxidant with a molar ratio of An:APS = 1:1.1 (composite in the presence of an appropriate amount of MCC) in an acidic medium (HCl). The obtained samples were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and X-ray diffraction (XRD). The prepared samples were used to study the adsorption properties of the food dye tartrazine from model aqueous solutions. The influence of various operating parameters (contact time, initial dye concentration and mass of the adsorbent used) was investigated.

Aniline polymerizes in the presence of MCC particles and attaches to these particles, as a result of which they become wrapped in polyaniline fibers, thus forming a composite that has a fibrillar morphology (Fig. 1), while PAN has a granular one. The size of polyaniline chains grown on MCC particles is in the nanometer range.

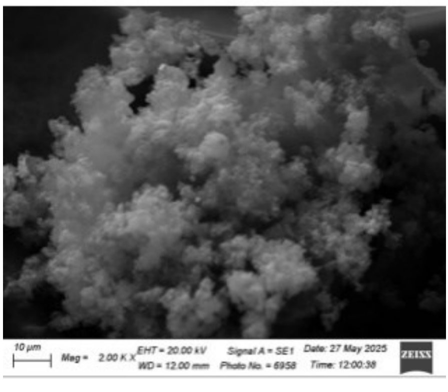

Fig. 1. SEM image of MCC/PAN composite.

As shown in Fig. 2, PAn is characterized by the presence of a broadened peak and an amorphous halo and, and small peaks at 2θ angles of 20.6, 22.7, and 25.6 can also be distinguished, indicating the formation of a small amount of the crystalline phase of emeraldine salt.

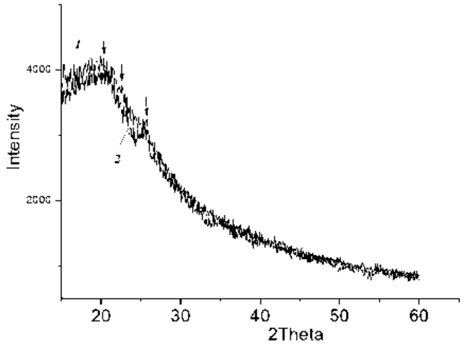

Fig. 2. XRD pattern of PAN (*1*) and MCC/PAN composite (*2*).

Fig. 3 shows the kinetic curves of tartrazine removal (50 mg L^{-1}) from an aqueous solution by PAN and MCC/PAN composite. The kinetic curve reaches a plateau in ~120 min for PAN and ~90 min for its composite, and the dye removal in 150 min is 90.8 % and 99 %, respectively. PANn synthesized in an acidic medium (HCl) is in the form of an emeraldine salt, respectively, protonated amino- and imino- groups are the adsorption centers of negatively charged tartrazine molecules. The worse performance for the PAN sample can be explained by its partial aggregation, which leads to a weakening of its adsorption properties due to the reduction (blocking) of active sites for dye adsorption. The obtained experimental data are in good agreement with the pseudo-second order kinetic model.

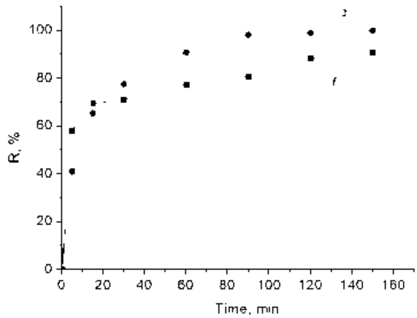

Fig. 3. Removal percentage of TZ by PAN (*1*)
and MCC/PAN composite (*2*) (m_{ads} = 0.01 g, C_{tz} = 50 mg L^{-1}).

Conclusions. The MCC/PAn composite prepared by in situ oxidative polymerization of aniline using ammonium persulfate as an oxidant showed better adsorption capacity for tartrazine compared to polyaniline. The maximum adsorption capacity was 99 and 90.8 mg g^{-1} (25 °C), respectively. The adsorption kinetics were fast, reaching equilibrium at the investigated dye concentration (50 mg L^{-1}) was 90–120 min. The adsorption kinetic data corresponded to a pseudo-second order equation.

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