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Tytuł rozprawy doktorskiej: Sorpcja pestycydów na zeolitach i kompozytach zeolitowych modyfikowanych surfaktantami kationowymi i niejonowymi

PhD Thesis title: Sorption of pesticides on zeolites and zeolitic composites modified with cationic and nonionic surfactants

PhD Thesis abstract

In an era of industrialization and a pressing need for environmental sustainability, the quest for effective water purification techniques remains at the forefront of scientific inquiry. This doctoral thesis presents a comprehensive study on the utilization of fly ash-based adsorbents shedding light on their characterization, and adsorption mechanisms in the context of pesticide removal from aqueous solutions.

The investigation commenced with an extensive review of existing literature, critically examining the state of knowledge concerning the adsorption of pesticides on synthetic zeolites and mesoporous silica materials. This foundational review validates the efficacy of synthetic zeolites, both unmodified and surface-functionalized, as effective materials for the removal of pesticides from water. Moreover, it elucidates the significance of selecting appropriate adsorption isotherms and the limitations of fitting kinetic models, emphasizing the need for analytical techniques like FTIR, SEM, and TGA/DTA to discern adsorption mechanisms.

Experimental studies focus on the modification of zeolites and zeolite-carbon composites using cationic and nonionic surfactants, further utilization of modified and unmodified adsorbents for the adsorption of four pesticides 2,4-dichlorophenoxyacetic acid (2,4-D), 2-methyl-4-chlorophenoxyacetic acid (MCPA), carbendazim, and simazine, as well as on the regeneration of used adsorbents.

Zeolite types A and X, as well as zeolite-carbon composites incorporating zeolite types A and X, produced through the transformation of fly ashes, were subject to modification using cationic (hexadecyltrimethylammonium bromide) and nonionic (Triton X-100) surfactants. The unmodified and modified materials underwent characterization employing techniques such as FTIR, BET, TG/DTA, SEM as well as TEM, XPS, and pHpzc analysis. Then, the initial screening tests of 24 unmodified and modified adsorbents were performed to identify the most efficient adsorbents for subsequent experiments. Consequently, X-FA and X-C, along with their modified counterparts, were chosen for further investigations. The doctoral thesis also thoroughly examines factors influencing pesticide adsorption, including initial pH, concentration, and competitive adsorption. Experimental data are systematically

fitted to multiple adsorption models, elucidating the most suitable models for each pesticide and adsorbent combination. Finally, the study evaluates the potential of thermal and ethanol regeneration methods, demonstrating the effectiveness of both methods.

The study investigated surfactant's modification in zeolites and zeolite-carbon composites. It revealed that surfactants exclusively bind to the external surface of the adsorbent due to their size. The proposed mechanisms of modification include cation exchange, electrostatic forces, hydrogen bonding, and hydrophobic effects. Moreover, the results highlight the efficacy of modifications in enhancing adsorption capacities. The presence of a cationic surfactant leads to a significant increase in the adsorption capacity of 2,4-D and MCPA, whereas carbendazim and simazine exhibit the highest affinity for unmodified zeolite-carbon composites. Furthermore, the sorption mechanism is complex, with physical sorption playing a dominant role. This is primarily attributed to the electrostatic interactions between the protonated binding sites on the adsorbents and the negatively charged pesticide molecules. Adsorption was proven to be a rapid process, with most of the pesticide adsorbed within the first 60 seconds, and it was most effective at higher initial concentrations. Finally, the study demonstrates the effectiveness of ethanol in the regeneration of HDTMA-modified zeolite-carbon composites. Thermal regeneration, although limited due to the high thermal stability of pesticides, remains a viable option for regenerating adsorbents with carbendazim and simazine adsorbed.

In conclusion, this doctoral thesis advances our understanding of fly ash-based adsorbents and their role in sustainable water purification. Future work on these materials should significant emphasis is placed on perfecting granulation techniques for adsorbents, ensuring robustness, and stability. Additionally, dynamic adsorption experiments are proposed to encompass a broader spectrum of real-world conditions, including varying wastewater compositions, pH, temperature, and the presence of particulate matter.