

Preparation of Spherical Nanocellulose Based/Amino Acid Composite Adsorption Materials and Its Application

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Abstract: With the development of industry, a large amount of heavy metal ions are discharged into the environment, causing serious damage to water bodies and natural ecosystems. Cellulose is the main chemical component of forest resources and a renewable biomass resource. Its high-value conversion has been extensively studied. In recent years, spherical nanocellulose has gradually gained attention as a novel nanocellulose with great potential in chemical modification, biomedical, and other fields. The adsorbents composed of spherical nanoparticles exhibit excellent adsorption performance and have been widely studied in recent years. Using spherical nanocellulose could prepare all-biomass cellulose/amino acid spherical nanomaterials with high functional group density for adsorption, medical, catalytic, analytical chemistry, corrosion, and photochromic applications. In this study, corn straw was transformed into spherical nanocellulose with a cellulose II crystal structure by using NaOH/urea/thiourea solvent system via a bottom-up approach. Through sodium periodate oxidation and glutaraldehyde grafting, tri-aldehyde spherical nanocellulose-based adsorbent materials that could be modified by various of functional groups were successfully prepared. Two representative amino acids were introduced into the pre-modification platform of tri-aldehyde spherical nanocellulose adsorbent, and two all biomass spherical nanocellulose adsorbents, whose namely cellulose/L-lysine (CTNAP-Lys) and cellulose/L-cysteine (CTNAP-Cys) were effectively prepared. Detailed studies were conducted on the microstructure, chemistry, and crystal structure of two adsorbents, in addition the adsorption mechanisms of CTNAP-Lys for Cr(VI) and CTNAP-Cys for Cu(II) were researched. The results shows that pre-modified platform of spherical nanocellulose adsorbent was successfully prepared, and the surface aldehyde group content up to 1.85 ± 0.07 mmol/g. Two all-biomass spherical nanoadsorbents namely CTNAP-Lys and CTNAP-Cys were prepared, those exhibit two important characteristics, a spherical nanoparticle morphology and cellulose II crystal structure, which significantly enhanced their adsorption performance. The adsorption capacity of CTNAP-Lys adsorbent for Cr(VI) is 361.69 mg/g, and the adsorption mechanism involved three synergistic processes: electrostatic interaction between protonated amino groups and Cr(VI), chelation of amino and carboxyl groups with Cr(VI)/Cr(III), and partial reduction of Cr(VI) to Cr(III) by amino groups. The adsorption capacity of CTNAP-Cys adsorbent for Cu(II) is 252.38 mg/g, and the mechanism involved three synergistic processes: electrostatic interaction between deprotonated thiol and carboxyl groups and Cu(II), chelation of thiol and carboxyl groups with Cu(II)/Cu(I), and partial reduction of Cu(II) to Cu(I) by thiol groups.

球状纳米纤维素基/氨基酸复合吸附材料的制备与应用

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摘要: 随着工业的发展,大量的重金属离子被排放到环境中,对自然生态系统造成了极为严重的影响。纤维素是林木资源的主要化学成分,是一种可再生生物质资源,其高值转化被广泛研究。近年来,球状纳米纤维素作为一种新型纳米纤维素逐渐受到关注,其在化学修饰、生物医学等领域具有很大的应用潜力。由球形纳米粒子组成的吸附剂表现出优异的吸附性能,近年来得到广泛研究。以球状纳米纤维素为基底,可制备出具有高官能团密度的全生物质纤维素/氨基酸球形纳米材料,可用于吸附、医学、分析化学、腐蚀和光致变色应用。本研究以玉米秸秆为原料,利用 NaOH/尿素/硫脲溶剂体系,通过自下而上的方法将玉米秸秆转化为具有 II 型纤维素结晶结构的球状纳米纤维素。通过高碘酸钠氧化、戊二醛接枝对球状纳米纤维素进行表面改性,成功构建了可被多种吸附功能官能团改性的三醛球状纳米纤维素吸附材料预改性平台。分别将两种具有代表性的氨基酸引入三醛球状纳米纤维素吸附材料预改性平台,成功制备了两种全生物质球形纳米吸附剂,即纤维素/L-赖氨酸 (CTNAP-Lys) 和纤维素/L-半胱氨酸 (CTNAP-Cys)。详细研究了两种吸附剂的微观形态及化学和晶体结构,以及 CTNAP-Lys 对 Cr(VI) 和 CTNAP-Cys 对 Cu(II) 的吸附机理。结果表明,成功制备了表面醛基含量高达 $1.85 \pm 0.07 \text{ mmol/g}$ 的三醛球状纳米纤维素吸附材料预改性平台;成功制备了 CTNAP-Lys 与 CTNAP-Cys 吸附剂,其微观形貌上表现出两个重要特征,即球形纳米粒子形态和纤维素 II 晶体结构,显著提高了其吸附性能。CTNAP-Lys 吸附剂对 Cr(VI) 的吸附容量为 361.69 mg/g ,其吸附机理为三种作用的协同吸附,分别为:质子化氨基与 Cr(VI) 之间的静电作用、氨基和羧基对 Cr(VI)/Cr(III) 的螯合作用、部分 Cr(VI) 被氨基还原为 Cr(III); CTNAP-Cys 对 Cu(II) 的吸附容量为 252.38 mg/g ,其吸附机理为去质子化的巯基和羧基与 Cu(II) 之间的静电作用、巯基和羧基对 Cu(II)/Cu(I) 的螯合作用、部分 Cu(II) 被巯基还原为 Cu(I) 三种作用的协同吸附。