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ORIGINAL PAPER

Novel effective dye sorbents: synthesis and properties of 1,2,3-triazole-modified thiacalix[4]arene polymers based on click chemistry

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Abstract By introducing 1,2,3-triazole-ester groups on thiacalix[4]arene based on click chemistry and then ammonolysis with ethylenediamine, diethylenetriamine or triethylenetetramine, three novel 1,2,3-triazole-modified thiacalix[4]arene polymers were conveniently prepared in "4+2" condensation mode in ideal yields. The structures of polymers **4a–4c** were confirmed by elemental analysis, FTIR and ^{1}H NMR spectra. The surface morphologies of polymers **4a–4c** were investigated by SEM micrographs. The M_n of novel polymers **4a–4c** indicated approximately 18–20 calixarene units in each polymer molecule. The dye adsorption abilities of polymers **4a–4c** for series of organic dyes (alizarin green, orange I, neutral red (NR), Congo red (CR), orange G (OG), crystal violet, Victoria blue B and methylene blue) were studied by solid–liquid adsorption experiments. The adsorption experimental results implied that they had excellent adsorption abilities for tested organic dyes. The highest adsorption percentage reached 97 % for OG. The best saturation adsorption capacities for NR and CR were as high as 1.282 and 1.407 mmol/g, respectively. These novel polymers possessed stable adsorption abilities in the scopes of pH 5–9 and had good reused properties after desorption. The adsorption mechanism proposed that not only dipole interaction, electrostatic interaction and hydrogen bonding interaction, but also the π–π stacking interaction plays important role in binding dyes.

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Introduction

Dyes are widely used in various industries including textiles, leather, dyestuffs, papers, etc. However, serious water pollution is brought about by wastewaters in these industries [1, 2]. In order to remove the dyes from wastewaters, many conventional treatment methods, such as precipitation [3], extraction [4], adsorption [5, 6], membrane filtration [7] and photodegradation [8] have been developed. Among these wastewater treatments, much attention has been paid to adsorption due to its providing selective separation and recovery of dyes from the effluent mixtures. As a result, the design and synthesis of novel absorbent for dyes is the crucial task in this research field. Recently, some researches focused on the supramolecule-based hosts for binding dyestuff effectively. For example, the synthesis and dye complexation abilities of some calixarene-based derivatives and polymers were described by Yilmaz et al. [9–11], Memon et al. [12, 13] and Diao et al. [14], respectively. Our group also reported series of calixarene derivatives and polymers with high binding properties for aniline derivatives [15, 16], and organic dyes [17–19]. These literatures suggested that the structures of calixarene skeleton, the sizes of cavities and the influences of intermolecular acting forces produced by different functional groups played important roles in binding dyes.

Thiacalix[4]arene, of which the phenyl groups are bridged by four sulfur atom, possesses excellent structural flexibility and exhibits outstanding recognition ability for organic molecules, anions and cations [20–22]. Moreover, its flexible cavity might be favorable for adjusting its shape