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Grafting of aniline derivatives onto chitosan and their applications for removal of reactive dyes from industrial effluents

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ABSTRACT

A series of chitosan-grafted polyaniline derivatives {chitosan-*g*-polyaniline (CS-*g*-PANI), chitosan-*g*-poly(*N*-methylaniline) (CS-*g*-PNMANI), and chitosan-*g*-poly(*N*-ethylaniline) (CS-*g*-PNEANI)} were synthesized by *in situ* chemical oxidation polymerization method. The synthesized copolymers were analyzed by means of Fourier transform infrared (FTIR), and ultraviolet-visible (UV–vis) spectroscopies, thermogravimetric analysis (TGA), and field emission scanning electron microscopy (FE-SEM). These copolymers were applied as adsorbent for removal of acid red 4 (AR4) and direct red 23 (DR23) from aqueous solutions. The adsorption processes were optimized in terms of pH, adsorbent amount, and dyes concentrations. The maximum adsorption capacities (Q_m) for the synthesized copolymers were calculated, and among them the CS-*g*-PNEANI sample showed highest Q_m for both AR4 (98 mg g^{-1}) and DR23 (112 mg g^{-1}) dyes. The adsorption kinetics of AR4 and DR23 dyes follow the pseudo-second order kinetic model. The regeneration and reusability tests revealed that the synthesized adsorbents had the relatively good reusability after five repetitions of the adsorption–desorption cycles. As the results, it is expected that the CS-*g*-PANIs find application for removal of reactive dyes (especially anionic dyes) from industrial effluents mainly due to their low production costs and high adsorption effectiveness.

1. Introduction

It is an unquestionable fact that organic contamination of water is one of the most important environmental problems worldwide. With the growth of mankind, society, and technology the production amounts of wastewater has progressed significantly. The large amounts of wastewater containing various pollutants have been produced by industrial activities [1–5]. Among these, the organic dyes are the most important classes of the pollutants due to their toxic, mutagenic, carcinogenic, and non-biodegradable features. These dyes are widely used in various industries including papers, paints, textiles, leather, and many more [6,7]. Azo class is an important group of synthetic dyes, mainly due to give bright and high-intensity colors [8,9]. In this category, acid red 4 (AR4) and direct red 23 (DR23) are the most important members. The chemical structures of these dyes are shown in Scheme 1. These types of dyes can be incorporated in a number of applications such as cotton and rayon, leather, paper, and to some extent in nylon. These anionic dyes are water-soluble, and generally are polyazo compounds, along with some stilbenes, phthalocyanines, and oxazines [10–12].

Considering these facts, the design and development of more efficient approaches for removal of synthetic dyes from industrial effluents is extremely urgent for coming years. Some conventional approaches including chemical decomposition by oxidation, photodegradation, and microbiological decoloration, employing activated sludge, pure cultures, microbe consortiums and ion exchange on adsorbent resins have been applied for removal of synthetic dyes. However, these approaches are expensive, complex, and less efficient in more cases [13–15].

During the last decades, the photocatalyst degradation of pollutants has received a great deal of research effort. In this approach a semiconductor (*e.g.*, zincoxide (ZnO) and titanium dioxide (TiO_2) as photocatalyst) is incorporated into/onto organic or inorganic matrixe/surface [18,19]. This approach can be efficiently removing the pollutants through photocatalyst degradation. However, in

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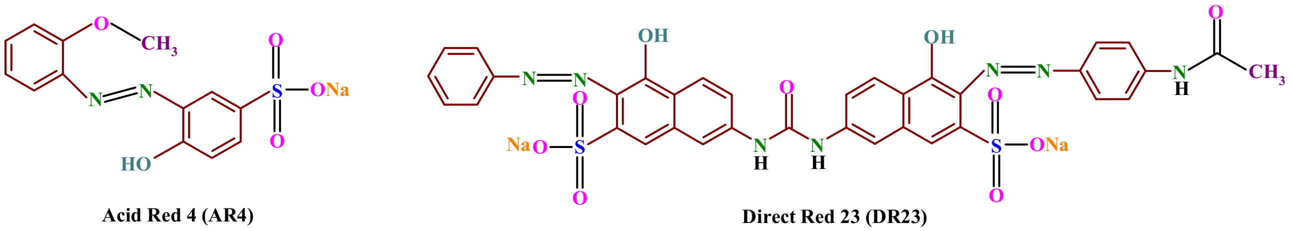

Scheme 1. The chemical structures of acid red 4 (AR4) and direct red 23 (DR23) dyes.

long time, especially in the case of organic materials, the matrix is destructed by reactive species (*e.g.*, $^{\bullet}O^{-}{}_2$, $HO^{\bullet}$ and HOO) which are generated during photocatalyst degradation process. Another traditional approach in this area is adsorption processes, which established as an attractive and low cost option. In this context, adsorption of organic pollutants on activated carbon has been used for a long time. Nevertheless, this method suffers from high cost of activated carbons, and complex and inefficient regeneration process [16,17]. These problems can be circumvented through the use of low-cost and efficient adsorbents such as natural polymers.

Chitosan (CS) is a cellulose-like linear polycationic polysaccharide that produced through the both alkaline deacetylation and enzymatic degradation of chitin (the next abundant polysaccharide after cellulose in nature). Since its introduction in 1859, more and more research effort has been focused on the application of this natural polymer in wide verity of industrial as well as biomedical field [20–22]. Chitosan has number of inherent characteristics including chemical inertness, mild processing conditions, biodegradability, biocompatibility, high molecular weight, high mechanical strength, good film-forming properties, and low cost. In addition, the availability of amine and hydroxyl functional side groups allows the chemical modification through the attachment to small/macromolecules [23,24]. Owing these facts, CS has found a wide range of applications in water treatment. The functional side groups of CS make it as a promising adsorbent for pollutants (*e.g.*, synthetic dyes) through electrostatic attraction or hydrogen bonding [25,26].

However, some drawbacks such as low stability and less defluoridation capacity (DC) of the raw CS restrict its individual application as adsorbent [27]. Some strategies including blending of CS with other organic (*e.g.*, cellulose) [28], and inorganic (*e.g.*, silica gel, alumina, clay, and hydroxyapatite) [29] materials have been applied in order to improve the mechanical strength and to expose the active binding sites to increase the sorption capacity. In this context, polyaniline (PANI) and its derivatives can be considered as promising materials for balding or copolymerization with CS. It is well demonstrated that PANI and its composites can be applied in environmental fields (especially scavenging of negatively charged pollutants such as anionic synthetic dyes from wastewater) due to chelating properties of electron donating groups such as amine, imine, and secondary amino groups on the PANI backbone. It should be pointed out that individual usage of PANIs in adsorption process could be limited by the massive aggregation of polymeric chains. This problem can be overcome by preparing PANI composites or copolymers [30–34].

To the best of our knowledge, no report is available so far on the application of chitosan-grafted polyaniline derivatives for the removal of AR4 and DR23 dyes from aqueous solutions. In this investigation, CS-*g*-PANI, CS-*g*-PNMANI, and CS-*g*-PNEANI were synthesized by *in situ* chemical oxidation polymerization approach. The resultant copolymers were subsequently used for removal of AR4 and DR23 dyes from aqueous solutions. The adsorption processes were optimized in terms of pH, adsorbent amount, and dyes concentrations. The adsorption kinetics, and maximum adsorption capacities (Q_m) for the synthesized copolymers were also investigated. Furthermore, regeneration and reusability of adsorbents were examined.

2. Experimental

2.1. Materials

Aniline (ANI), *N*-methylaniline (NMANI), and *N*-ethylaniline (NEANI) were obtained from Sigma-Aldrich (USA), vacuum-distilled twice, and then stored at −20 °C prior to use. Chitosan (medium molecular weight, extent of deacetylation 75–85%) was purchased from Sigma-Aldrich. Ammonium proxydisulfate (APS) was purchased from Merck (Darmstadt, Germany), and purified through re-crystallization from ethanol at room temperature. Acetic acid (CH_3COOH), hydrochloric acid (HCl), and sodium hydroxide (NaOH) were purchased from Merck, and were used as received. Acid red 4 (AR4; $C_{17}H_{13}N_2NaO_5S$; 50%) and direct red 23 (DR23; $C_{35}H_{25}N_7Na_2O_{10}S_2$; 30%) were supplied from Sigma-Aldrich. All other reagents were purchased from Sigma-Aldrich and purified according to the standard methods.

2.2. Synthesis of CS-g-PANI

The aniline monomer was grafted onto CS by a chemical oxidation polymerization approach. In a typical procedure, CS (2.00 g) was dissolved in acetic acid solution (2% v/v; 50 mL) through constant stirring overnight. At the end of this period, aniline monomer (1.9 mL, 20.7 mmol) was dissolved in HCl solution (1 mol L^{-1}, 120 mL) and added to the above reactor. The mixture was stirred for about 2 h and temperature was reduced to 5 °C. Afterward, APS (0.30 g, 1.3 mmol) was added, the reaction mixture was stirred for about 1 h at 5 °C, and then 5 h at room temperature. At the end of this time, the reaction was terminated by pouring the content of the flask into a large amount of methanol. The resultant product was filtered, washed with methanol several times, and dried in vacuum at room temperature. The resulting crude product was extracted with *N*-methyl pyrrolidinone (NMP) and acetone in order to remove PANI (homopolymer) and PANI oligomers from CS-*g*-PANI copolymer, respectively. The doped dark green powder was obtained after drying in vacuum at room temperature. The CS-*g*-PNMANI and CS-*g*-PNEANI were synthesized by the same method (Scheme 2).

2.3. Adsorption experiments

Adsorption experiments were carried out in glass flasks using a batch technique at 25 °C as follows. For this purpose, adsorbent (CS-*g*-PANIs, 0.1 g) dispersed in 100 mL of AR4 and DR23 dyes solutions (10 ppm). Afterwards, solutions pHs were adjusted at 2, 3, 4, 6, and 9 with 0.1 mol L^{-1} of HCl or NaOH solutions, and pH was optimized in 2. Beside of pH, the adsorbent amount (0.01, 0.05 and 0.1 g), contact time (0–100 min), and initial dyes concentrations (10, 30, 60, and 90 ppm) were also optimized. The dye concentrations for each