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Evaluating the efficacy of alumina/carbon nanotube hybrid adsorbents in removing Azo Reactive Red 198 and Blue 19 dyes from aqueous solutions

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ABSTRACT

Concerning the high volume of wastewater containing dye in Iran and its adverse effects, it is necessary to develop scientific solutions for treating these wastewaters. The aim of this study was to evaluate the efficiency of the alumina-coated multi-walled carbon nanotubes in removing the Reactive Red 198 (RR 198) and Blue 19 (RB 19) dyes. Synthetic samples including dye with different concentrations were prepared. These samples were put in contact with different contents of alumina/multi-walled carbon nanotubes, in different pH values, in different contact times, different temperatures and the presence of sodium sulfate or sodium carbonate. The optimum pH, dye concentration and temperature for removal of the two dyes was 3, 50 mg l^{-1} and 25 °C, respectively. The optimum adsorbent dose for removal the RR 198 dye was 0.5 g l^{-1} and for Blue 19 was 0.4 g l^{-1}. The optimum contact time for RR 198 was 150 min and RB 19 was 180 min. In this condition, maximum removal efficiency for RR 198 and RB 19 was 91.54% and 93.51%, respectively. The adsorption study was analyzed kinetically, and the results revealed that the adsorption fitted a pseudo-second order kinetic model. According to these results alumina/multi-walled carbon nanotubes can effectively remove RR 198 and RB 19 from aqueous solutions.

1. Introduction

Each year more than 10,000 different synthetic dyes are produced all over the world and used extensively in various industries. The amount of dye production in the world is estimated to be about 7×10^5–1×10^6 tons, that one of the big consumers of dyes are textile industries (Ai et al., 2011; Al-Johani and Salam, 2011). The textile industry is known to be one of the major sources of receiving water bodies pollution. The wastewaters generated from the textile industry are

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among the most polluting of all the industrial sectors. Textile industry wastewater is generated by the different production steps like scouring, desizing, bleaching, washing, mercerizing, dyeing, printing and finishing that among the various steps, of dyeing process large volume of water are used. Wastewater resulting from these industrial activities is generally characterized by a high COD, pH, dissolved solids, temperature and dye and surfactant content. It also contains a large variety of pollutants such as organic matter, non-biodegradable matter, toxic substances, detergents and soaps, oil and grease, sulfide, suspended solids, alkalinity and their breakdown products which may have toxic and/or mutagenic effects on life (Radha et al., 2009; Papadia et al., 2011; Cheng et al., 2012).

Dyes based on the chemical structure are classified into groups such as azo, anthraquinone, oxazine, acridine, formazan, phthalocyanine, thiazine, triphenylmethane, triarylmethane, nitroso and nitro, etc. and based on the application are classified into reactive, acidic, direct, vat, disperse, cationic, solvent and sulfur (Amin, 2009; Arasteh et al., 2010). The azo compounds are the largest group of organic-synthetic dyes, and more than 2000 chemicals have been listed in this group. Azo dyes are synthesized by diazotation of aromatic amines and coupled with compounds such as phenols. Therefore due to the presence of a wide range of dyes with different structures, more than 50% of the produced dyes are azo dyes. Among the azo dyes, reactive dyes are the most widely used dyes in the textile industry and are known as the most problematic chemicals in textile industry effluents; due to their high solubility in water and low degradability. These types of dyes are colored compounds that have reactive groups which are able to form covalent bonds between dye and fiber (Celik et al., 2011; Ashrafi et al., 2013). It has been estimated that up to 50% of the reactive dyes used in industry, may be lost to the effluent and their concentration in the wastewater outlet of industries is about 10–200 $mg\,l^{-1}$ (Chen et al., 2007; Aksakal and Ucun, 2010). Reactive dyes are hydrophilic and therefore have little tendency for adsorption on biomass in biological treatment methods. These dyes often have high molecular weight and have aromatic rings and are toxic for microorganisms (Duran et al., 2009; Choi and Al-Abed, 2010). Also they are often stable, resistant to degradation, toxic, carcinogenic and mutagenic; due to their complicated chemical structure and can cause serious health problems like allergy and dermatological diseases (Gao et al., 2013).

Large amounts of these dyes are discharged in the water sources and removing dye from textile wastewater is more important than treating other colorless organics and inorganics because small amounts of dye are clearly visible and detrimental to the water environment. Thus there is an urgent need for textile wastewater to develop effective methods of treatment. In order to remove dyes from textile wastewaters various treatment methods like physical, chemical, biological, membrane separation, radiation, electrochemical, advanced oxidation, photolysis, electrochemical, sonolysis processes, etc. have been investigated (Axelsson et al., 2006; Garcia et al., 2006). However, these methods are relatively ineffective because most dyes as azo reactive dyes are highly water soluble, have complex structures, and are stable to light, chemical and biological degradation, etc. Furthermore, these methods have certain disadvantages such as high capital and operational costs, secondary sludge disposal problems and the release of large volumes of toxic by-products (Gholami-Borujeni et al., 2011, 2013). Among these methods, the adsorption technique is one of the most effective methods and widely used for the removal of the dyes from colored wastewaters due to its simplicity easy availability, ease of operation, biodegradability and cost effectiveness. Adsorption process offers significant advantages over traditional treatment methods especially from the environmental point of view and its ease of operation as well as greater efficiency (Gupta et al., 2011, 2013). Some of the adsorbents, which are used for the removal of these kinds of dyes (RR 198 & RB 19) from aqueous solutions with varying success, include: activated carbon, magnesium oxide, grafted chitosan, modified bentonite, TiO_2 powder, TiO_2 nanotube, etc. (Özcan et al., 2007; Dutta et al., 2009; Natarajan et al., 2014; Srivastava et al., 2014). Among those materials, activated carbon is one of the most frequently adsorbents used for the removal of dyes from colored waters and wastewaters, but due to its high production, regeneration and reactivation procedures cost; research has been concentrated on alternative adsorbents with high adsorptive capacity and low cost (Gholami-Borujeni et al., 2011; Gupta et al., 2013).

Therefore, recently there has been a lot of attention toward using nanotechnology methods. Nowadays using nanomethods, especially carbon nanotubes for removing many pollutants such as heavy metals, sodium hexafluoride, trihalomethanes, volatile fumes, uranium, aromatic ionizable compounds, viruses, folic acid, trichloroethylene and dyes, and also for desalination of saline water and softening water has been under investigation (Kuo et al., 2008; Khataee et al., 2010; Kim et al., 2012; Jung et al., 2013; Kannan et al., 2013). Carbon nanotubes are single layer graphites in the shape of wrapped cylinders. These materials have extraordinary structural, mechanical and electrical characteristics which originate from the special characteristics of carbon bonds, their semi-undimensional structure and cylindrical symmetry. The diameter of carbon nanotubes is about a few nanometers and their length is about a few micrometers and their characteristics are close to ideal graphite fibers. Two important nanotube structures are multi-walled nanotubes (MWCNT) and single walled nanotubes (SWCNT). Carbon nanotubes have a wide surface, small size and multilayer structure which makes them suitable for removing wastewater pollutants (Gong et al., 2009; Gholami-Borujeni et al., 2011, 2013).

In the other words alternatives inorganic solid adsorbents such as alumina, silica and zirconia to carbon have been used for adsorption of various pollutants from aqueous solution (Mahmoud et al., 2010a,b; Afkhami et al., 2011). These adsorbents have high efficiency due to their high surface area, high mechanical properties and good resistivity to thermal degradation, and they exist in several structures and amphoteric properties. The alumina (Al_2O_3) in comparison to other inorganic oxides is the most promising adsorbent as it encompasses excellent physical and textural properties. Alumina has been used for preconcentration and separation of trace amounts of elements like toxic heavy metals of nickel, lead and cadmium (Mahmoud et al., 2010a,b; Gupta et al., 2011). Alumina binder affects the mechanical strength, hydrophilicity, porosity and sorption capacity of the CNTs in the hybrid adsorbent. There is little information available about dye adsorption by alumina coated multi-walled carbon nanotubes. In this study, we have examined the adsorption capacity of Al_2O_3/MWCNTs composite for the removal of RR 198 and RB 19 which have an extensive use in the textile industry. Reactive Red 198 and Blue 19 are two of the most representative and commonly used dyes to dyeing the textile goods. Also