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Polyaniline nanofibers as highly effective re-usable adsorbent for removal of reactive black 5 from aqueous solutions

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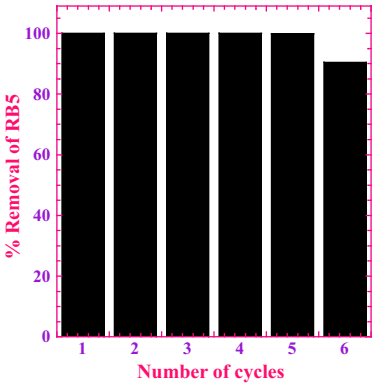
GRAPHICAL ABSTRACT



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ABSTRACT

Polyaniline nanofibers (PANI NFs) with 50–80 nm in diameter were successfully prepared at room temperature (22 °C) using ferric chloride ($FeCl_3$) as an oxidant via a simple rapid mixing polymerization method. The prepared PANI NFs were characterized by FE-SEM, HR-TEM, BET, ATR-FTIR and by Zeta potential measurement method. The adsorption of azo dye Reactive Black 5 (RB5) onto PANI NFs from aqueous solutions was investigated. Adsorption studies were carried out at different initial dye concentrations, initial solution pH and adsorbent doses. The kinetic data fitted well with the pseudo-second-order model while the equilibrium data were satisfactorily described by the Langmuir isotherm model. The Langmuir maximum adsorption capacity of RB5 at pH 6.0 was found to be 312.5, 389.1 and 434.7 mg/g at 25 °C, 35 °C and 45 °C, respectively. Thermodynamic parameters including the Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) changes indicated that the adsorption of RB5 onto PANI NFs was feasible, spontaneous, and endothermic. Moreover, desorption experiments revealed that the PANI NFs can be reused effectively for five consecutive adsorption–desorption cycles without any loss of its original capacity.

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1. Introduction

Synthetic dyes are widely used in textiles, leather, paper, cosmetics, photoelectron chemical cells and other similar industries to color their products. Based on the chemical structures and applied methods, synthetic dyes are classified as basic dyes, acid dyes, reactive dyes, direct dyes, azo dyes, mordant dyes, vat dyes, disperse dyes and sulfur dyes. Azo derivatives are the major class of dyes used in industries [1]. These types of dyes are characterized by the existence of nitrogen–nitrogen double bonds (azo bonds) and the bright colors are due to the azo bonds and the related chromospheres. Even at low concentrations (lower than 1 mg/L), an azo dye in water is clearly visible and therefore undesirable.

Reactive black 5 (RB5) dye is a type of azo dye, and its presence in water is of great concern because its breakdown products have been found to be toxic to aquatic life, carcinogenic and mutagenic [2]. In order to minimize the pollution risks and harmful effects of the dye, effluents should be carefully treated with an appropriate method before discharging the wastewater into the aquatic environment. Several technologies/processes have been employed for the removal of azo dyes from industrial effluents. These include chemical oxidation, electrolysis, biodegradation, ion exchange, advanced oxidation, photocatalysis and adsorption process [3–9]. However, most of these methods have limitations, for example; conventional biological processes are less efficient in removing synthetic azo dyes due to the complex structures, molecular size and nature [10]; while advanced oxidation processes using H_2O_2, UV and O_3 have the potential to eliminate these organic pollutants in wastewater, but these processes of dye removal, is expensive [11,12]. The process is also complex and only effective at lower concentration i.e. less than several hundred up to 1000 mg /L [13].

In addition, some of these techniques yield additional by-products such as organic acids and organic aldehydes [14], which could increase the carcinogenic and toxic properties of RB5 dye.

Among all existing techniques used to remove dye from industrial effluents, adsorption appears to offer the most potential. This is because of its inherent advantages, which include simplicity in operation, low generation of residue and possibility of recycling and reuse of the adsorbent, thus reducing the cost of operation [11,15]. Numerous adsorbents, including activated carbon, fly ash, resin, and chitosan have been used for the removal of RB5 from water [16–19]. However, it is still imperative to explore new adsorbents with high affinity for the dye.

Among various conducting polymers, polyaniline (PANI) has been considered to be one of the most promising materials due to its ease of preparation, well controlled electrochemistry, easy protonation reversibility, excellent redox properties and good environmental stability [20]. In recent years, compared to conventional bulk counterparts, nanostructured PANI (nanofibers, nanotubes, nanorods and nanospheres) have been attracted much scientific interest as they combine the properties of low dimensional organic conductors and high surface area materials. This is due to the enhanced performance related to a large interfacial area that exists between PANI and its environment [21]. Among various nanostructures of PANI, nanofibers (NFs) have high potential in enhancing performance for removal of contaminants from water.

Numerous methods have been used to synthesize PANI NFs, including seeded growth [22], electrochemical synthesis [23] and electrospinning [24]. These methods are complicated and costly to scale-up, and typically require additional steps to yield pure PANI NFs. PANI NFs can also be synthesized using several synthetic methods, without using templates, through the intrinsic growth of NFs during the polymerization of PANI. This can be achieved by either an interfacial or rapid mixing chemical polymerization reaction. In the rapid mixing polymerization technique, the acidic aqueous solutions of aniline and oxidant are mixed rapidly and no aniline monomers are supplied after the formation of PANI nanofibers. Moreover in this method no organic solvent or other assisting techniques are needed [25,26]. Therefore rapid mixing method is ideal for exploring the benefits of the high surface area, and nanostructure for the bulk synthesis of PANI NFs that can be used for numerous applications. Although nanofibrillar products have shown improved performance in PANI NFs gas sensors and rapid bending actuators [27] due to their high surface area, they have not been explored extensively for the removal of toxic pollutants from water.

The present study aims to evaluate the performance of PANI NFs prepared by simple rapidly mixed methodology as an adsorbent for removing RB5 dye from aqueous solutions. The objectives of the present study were to (i) synthesize and characterize PANI NFs, (ii) evaluate the potential of PANI NFs for the removal of RB5 from aqueous solutions, (iii) assess the experimental variables affecting optimal removal of dye, and (iv) explore adsorption isotherms and kinetic models to identify the possible mechanism of dye removal.

2. Experimental

2.1. Materials

Aniline (ANI, 99%,), anhydrous iron(III) chloride ($FeCl_3$), hydrochloric acid, sodium hydroxide and reactive black 5 (RB5) dye powder were purchased from Sigma–Aldrich, USA. All chemicals were of reagent grade. An aqueous RB5 stock solution of 1000 mg/L was used.

2.2. Synthesis of the PANI NFs

PANI nanofibers were synthesized via rapid mixing polymerization of ANI monomers in the presence of $FeCl_3$ as an oxidant at room temperature (22 °C). In a typical polymerization process, 6 g of $FeCl_3$ was dissolved in 80 mL of distilled water in a 250 mL conical flask. Then, 0.8 mL of ANI monomer was syringed all at a time into the oxidant solution under magnetic stirring. The amount of oxidant used was optimized in our earlier studies [28]. The reaction mixture was stirred for 5 min. The polymerization reaction was allowed to proceed without stirring for 24 h. After that, 10 mL of acetone was added to the reaction mixture to stop the reaction. The PANI NFs formed were filtered and washed with deionised water until the filtrate became colorless and thereafter washed with acetone to remove the oligomers. The nanofibers were then dried at 60 °C for 24 h under vacuum, until the total mass became constant.

2.3. Characterization of the PANI NFs

The morphological characterization of the PANI NFs was performed by an Auriga field emission scanning electron microscope (FE-SEM; Carl Zeiss, Germany) and a JEOL JEM-2100 high resolution transmission electron microscope (HR-TEM; JEOL, Japan). A JEOL JEM-2100 HR-TEM instrument with a LaB6 filament operated at 200 kV was used to obtain transmission electron micrographs. Specimens for high resolution transmission electron micrographs were prepared by placing a drop of a dilute suspension of the sample in acetone, on a copper grid. The specific surface area of the PANI NFs was measured by a low temperature N_2 adsorption–desorption technique using a Micromeritics ASAP 2020 gas adsorption apparatus (USA). An attenuated total reflectance Fourier transform infrared (ATR-FTIR) Spectrum 100 spectrometer (Perkin–Elmer, USA), with a germanium crystal was employed to acquire the IR spectrum of the PANI NFs. The point of zero charge