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Full Length Article

Highly crystalline polyaniline nanofibers coating with low-cost biomass for easy separation and high efficient removal of anionic dye ARG from aqueous solution

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ABSTRACT

The separation of nanostructured absorbents from the aqueous solution has been the challenge for their practical application due to their small colloidal size. Here, highly polyaniline nanofibers, prepared *via* a simple polymerization method at room temperature using ferric chloride ($FeCl_3$) as an oxidant, were coated on the alkali-pretreated cost-efficient and reusable biomass, i.e, sawdust (PANI-NFs/SD). The obatined PANI-NFs/SD was demonstrated to exhibit easy separation characteristic from SD and highly effective adsorption performance from PANI-NFs. It was characterized *via* FT-IR spectroscopy, scanning electron microscopy, thermogravimetric analysis, X-ray diffraction and Zeta potential measurements. The adsorption of anionic azo dye Acid Red G (ARG) onto PANI-NFs/SD from aqueous solution was carried out at different solution pH, initial dye concentration, adsorbent dosage and temperature. The calculated thermodynamic parameters suggested the feasible, spontaneous and endothermic nature of ARG adsorption onto PANI-NFs/SD. The fitted data showed that the adsorption process followed pseudo-second-order kinetics model and Freundlich isotherm model. The maximum experimental adsorption capacity for ARG at pH 2.0 was found to be 212.97 mg g^{-1} at 308 K. Moreover, the regeneration experiment revealed that PANI-NFs/SD was an effective reusable adsorbent without obvious loss of its original capacity after 29 sequential adsorption-desorption cycles. Mechanism studies indicated that the excellent effective adsorption performance of PANI-NFs/SD was associated with highly doping chemistry of PANI-NFs with high crystallinity.

1. Introduction

In recent decades, tremendous increases of textile industrial activities worldwide have led to the release of various synthetic dyes into aquatic environment. The removal of these dyes has been the focus of extensive research due to their visibility, toxicity, and persistent nature [1]. Among the existing technologies, adsorption has attracted particular attentions due to its simplicity in design and operation, low energy intensiveness, no-toxicity and superior removal performance at low concentrations [2,3].

Polyaniline (PANI), as a significant conducting polymer material, has been extensively applied in dyes' removal due to its ease of preparation, unique reversible acid/base doping/dedoping chemistry property, and good environmental stability [4]. As of late, PANI nanofibers (PANI-NFs) have been demonstrated to have increased processability, improved stability, and higher surface area compared with their conventional bulk counterparts [5] and have been developed for highly effective collection of dyes and metal ions. For example, Madhumita et al. [6] showed that PANI NFs prepared by simple rapidly mixed polymerization exhibited an enhanced adsorption capacity of 312.5 mg g^{-1} for azo dye RB5, while Kim et al. [7] demonstrated the enhanced Cu^{2+} removal efficiency of PANI NFs by doping with phytic acid.

However, the low mass density and small colloidal size of PANI NFs make them hard to be settled, separated and recovered in the practical application and separation of them from aqueous is a time-consuming procedure. Preparing PANI NFs in magnetite composites form is a strategy to conquer this problem [8]. However, one of the most important issues is the toxicity of the released Fe_3O_4 nanoparticles during the adsorption-desorption process which could pose potential threats to the human beings and environment [9]. Nowadays, utilization of low-cost natural biomass, agro-industrial wastes and by-products in

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environmental protection has been attracted much attention due to their abundant, economic, eco-friendly and easy separation characteristics [10]. Coating PANI NFs onto these renewable biomass [11,12] therefore become an alternative economic strategy to solve the tough separation problem.

Wood sawdust, one of the agricultural by-products which are available in large quantities in lumber mills, have little or no economic value, and some of them often have the disposal problem. However, they are potential candidates for supporting PANI-NFs for the following reasons: (a) wood sawdust exhibit the unique porous and hierarchical structures [13] that provide plenty of surface sites for the growth and immobilization of PANI-NFs; (b) the excellent mechanical performance and large size of sawdust endow the adsorbent with easy separation characteristic [10]; (c) they are sustainable, renewable, biodegradable and the combination of PANI-NFs with sawdust will benefit both the environment and wood agriculture.

Form another perspective, it is well known that the cell wall of raw wood sawdust consists of highly oriented and crystalline cellulose (44–48%), less oriented hemicelluloses (20–30%) and lignin (20–27%), and minor low molecular weight components such as ash and silica [14]. The release of soluble organic compounds such as hemicellulose and lignin from raw sawdust in the adsorption and regeneration process would cause secondary pollution and oxygen reduction in water [15]. Pretreated sawdust with NaOH aqueous is an effective strategy that would not only allow the extraction of soluble organic compounds but also convert the polyol structure into a negatively charged cellulose-based material. Plenty of negatively charged sites on the surface would favor the adsorption of protonated aniline *via* electrostatic attraction and therefore ensure the successful decorating of amounts of PANI-NFs, making the composite an effective adsorbent.

Here, PANI-NFs with highly crystallinity were synthesized *via* a simple common polymerization method without adding specific structure-directing dopants or diluting the solution and successfully coated onto alkali-pretreated sawdust to solve the tough separation problem. The separation performance and adsorption capacity for Acid Red G (ARG), a typical azo anionic dye were systematical investigated, as well as the possible adsorption mechanism.

2. Experimental

2.1. Chemicals

All chemicals were purchased from Sinopharm group chemical reagent Co. Ltd and used as received. The sycamore sawdust was obtained from a local lumber mills. ARG was commercial grade and recrystallized twice before used. Fig. 1 shows the chemical structure of ARG. Other dyes including negatively charged methyl orange (MO, $C_{14}H_{14}N_3NaO_3S$, MW 327, λ_{max} = 465 nm), direct grey D (DGD, $C_{24}H_{22}N_6NaO_5S$, MW 530, λ_{max} = 571 nm), acid fuchsine (AF, $C_{20}H_{17}N_3Na_2OS_3$, MW 586, λ_{max} = 525 nm), positively charged rhodamine B (RhB, $C_{20}H_6Br_4Na_2O_5$, MW 476, λ_{max} = 543 nm) and methylene blue (MB, $C_{18}H_{18}ClN_3S$, MW 320, λ_{max} = 663 nm) were also commercial grade. The main characterizations of raw sawdust including chemical structure, composition and surface characterization parameters were available in Supplementary information.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.apsusc.2018.07.074.

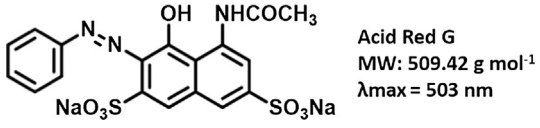

Fig. 1. Molecular structure of Acid Red G.

2.2. Alkaline pretreatment of raw sawdust

The raw sawdust was smashed with a stainless steel grinder and sieved using standard sieves to obtain particles with size of 100–150 μm. Then the alkaline pretreatment process of the sieved sawdust (50 g) was performed in a 1.0 L beaker, with the addition of NaOH (0.1 mol L^{-1}, 500 mL) aqueous. After magnetic stirring for 24 h at room temperature (RT), the sawdust was collected and washed with deionized water several times until neutral pH was obtained. The pretreated sawdust was then dried in the oven at 50 °C for 24 h and the obtained yellow sample was labelled as NaOH/SD.

2.3. Preparation of PANI-NFs modified NaOH/SD

The decorated PANI nanofibers were synthesized *via* polymerization of aniline monomers in the presence of $FeCl_3$ as an oxidant at RT. In a typical process, aniline (2.0 mL) was added into NaOH/SD (1.0 g) suspension (10.0 mL). After stirring for 2 h, ferric chloride hexahydrate (5.4 g) dissolved in HNO_3 solution (0.5 mol L^{-1}, 50 mL) was poured into the above mixture, followed by reacting for 24 h under the mechanical stirring. The product was then filtered and washed with deionized water and acetone until the filtrate became colorless. The modified sawdust was dried at 50 °C for 24 h to afford the dark green adsorbent labelled as PANI-NFs/SD. Control experiment were also conducted *via* the same polymerization process but using ammonium persulfate (APS) instead of $FeCl_3$ as oxidant (PANI/SD) and another two were without the addition of pretreated sawdust using $FeCl_3$ (PANI-$FeCl_3$) and APS (PANI-APS) as oxidants respectively.

2.4. Characterization

Fourier transform infrared spectroscopy (FT-IR) within the spectral range of 400–4000 cm^{-1} were recorded on a Bruker, TENSOR37 infrared spectrometer with KBr pellets. The thermogravimetric analysis (TGA) experiment was performed on the SHIMADZU TA-60WS Thermal Analyzer under N_2 atmosphere at a heating rate of 10 °C/min over a temperature within 30–800 °C. Scanning electron microscopy (SEM) images were obtained using a Gemini SEM 500 Field Emission Scanning Electron Microscope. The point of zero charge (pH_{PZC}) of adsorbent was measured using NanoBrook 90Plus zeta Analyzer. Nitrogen adsorption/desorption isotherm was measured by Builder SSA-4200 instrument using the Barrett-Joymer-Halenda (BJH) method. X-ray diffraction (XRD) patterns of samples were taken on a Rigaku Dmax-RA with a scan rate of 4 deg min^{-1}. X-ray photoelectron spectroscopy (XPS) was performed on the AXIS ULtrabld Spectromrter, Kratos with C 1s signal at 284.8 eV as the reference. Electrical impedance spectra (EIS) were measured using a CHI 660D electrochemical work station with a conventional three electrode cell, with Ag/Ag^+ and Pt foil as the reference electrode and counter electrode, respectively. The adsorbent-modified carbon paste electrode (CPE) was used as working electrode, which was prepared by thoroughly mixing high purity graphite powder, paraffin and adsorbent powder in a ratio of 80:10:10 (w/w) and packing into a glass tube with $\Phi = 3 \times 1$ mm with a fixed copper wire contacting the external circuit. EIS investigations were carried out in 1.0 M H_2SO_4 solution over the frequency range from 1 Hz to 10^5 Hz with ac perturbation of 10 mV at open circuit voltage.

2.5. Adsorption and regeneration experiments

The adsorption experiment was carried out by shaking the mixture of ARG solution with adsorbents at different conditions such as solution pH (2–12), adsorbent dosage (1–5 g L^{-1}), initial concentration of ARG (100–300 mg L^{-1}) and temperature (288–308 K). Then the suspension was left-undisturbed for 3 min and the supernatant was directly collected without centrifugation for SD supported sample, while for pure PANI sample, the supernatant was collected with centrifugation and