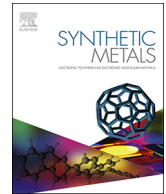




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Enhanced adsorption of cationic and anionic dyes from aqueous solutions by polyacid doped polyaniline



Junjie Shen^{a,b,*}, Salman Shahid^{a,b}, Ida Amura^{a,b}, Adem Sarihan^{a,b,c}, Mi Tian^{a,b}, Emma AC Emanuelsson^{b,*}

^a Centre for Advanced Separations Engineering, University of Bath, Bath, BA2 7AY, United Kingdom

^b Department of Chemical Engineering, University of Bath, Bath, BA2 7AY, United Kingdom

^c Higher Vocational School, Bilecik Seyh Edebali University, Bilecik, 11210, Turkey

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ABSTRACT

A new high surface area polyaniline (PANI) adsorbent was synthesized by matrix polymerization of aniline in the presence of a polyacid, poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA). Morphological and physicochemical properties of PANI-PAMPSA were characterized by field emission scanning electron microscope (FESEM), Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), nitrogen adsorption/desorption and zeta potential measurement. Adsorption properties were evaluated using methylene blue (MB) and rose bengal (RB) as model dyes.

The results showed that PANI-PAMPSA obtained a well-defined porous structure with a specific surface area ($126 \text{ m}^2 \text{ g}^{-1}$) over 10 times larger than that of the emeraldine base PANI (PANI-EB) ($12 \text{ m}^2 \text{ g}^{-1}$). The maximum adsorption capacities were 466.5 mg g^{-1} for MB and 440.0 mg g^{-1} for RB, higher than any other PANI-based materials reported in the literature. The FTIR analysis and zeta potential measurement revealed that the adsorption mechanisms involved π - π interaction and electrostatic interaction. The adsorption kinetics were best described by a pseudo-second-order model, and the adsorption isotherms followed the Langmuir model. The thermodynamic study indicated that the adsorption was a spontaneous endothermic process. Overall, the convenient synthesis and the high adsorption capacity make PANI-PAMPSA a promising adsorbent material for dye removal.

1. Introduction

Synthetic organic dyes from wastewater of textile, paper, plastic, cosmetics, pharmaceutical and food industries are a major source of environmental contamination [1,2]. It is estimated that 5000 tons of dyes are discharged into the environment every year [3]. These dyes impart color to water which not only damages the aesthetic nature of water, but also interferes with the transmission of sunlight and thus disturbs the biological metabolism processes of aquatic communities [4,5]. More importantly, most of the dyes have serious harmful effects on human beings, which span from skin and eye irritation to dysfunction of brain, liver, kidney and reproductive system [1]. Due to the low biodegradability of dyes, the conventional biological methods are not effective in treating dye effluents [1]. A wide range of physicochemical

techniques has been employed to remove dyes, such as adsorption [2], coagulation [6], membrane filtration [7], oxidation [8], electrochemical destruction [9] and photochemical degradation [10]. Among these techniques, adsorption has attracted great attention because of its easy operation, low cost, and high efficiency [1]. Numerous types of adsorbents, such as activated carbon, zeolite, alumina, silica, biomaterials, and polymers have been extensively used for dye removal [2,11].

Polyaniline (PANI) is one of the most studied conducting polymers due to its ease of synthesis, low cost, environmental stability and the unique doping/dedoping property [12]. The emeraldine base PANI (PANI-EB) and the emeraldine salt PANI (PANI-ES) can be efficiently switched to each other by doping (protonation) and dedoping (deprotonation), respectively [13,14]. The utilization of PANI as a potential

Abbreviations: PANI, polyaniline; PAMPSA, poly(2-acrylamido-2-methyl-1-propanesulfonic acid); MB, methylene blue; RB, rose bengal; CV, crystal violet; MO, methyl orange; PR, procion red; OG, orange G; CBB, coomassie brilliant blue; RBBR, remazol brilliant blue R; AG, alizarine cyanine green; MG, malachite green; CR, Congo red; TMP, tin (II) molybdophosphate; ZSP, zirconium (IV) silicophosphate; PTSA, *p*-toluenesulfonic acid; CSA, camphorsulfonic acid

* Corresponding authors at: Department of Chemical Engineering, University of Bath, Bath, BA2 7AY, United Kingdom.

E-mail addresses: J.Shen@bath.ac.uk (J. Shen), E.A.Emanuelsson-Patterson@bath.ac.uk (E.A. Emanuelsson).

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Table 1
A selective summary of adsorption capacities of PANI-based materials for dye removal.

Material	Dye	Maximum adsorption capacity (mg g ⁻¹)	Reference
<i>PANI-EB</i>			
PANI nanoparticle	MB	6.1	[19]
PANI nanotube	MB	9.2	[20]
PANI nanotube/silica composite	MB	10.3	[21]
Nanostructured crosslinked PANI	MB	13.8	[22]
Nanoporous hypercrosslinked PANI	CV, MO	245, 220	[23]
<i>PANI-ES</i>			
PANI-HCl	PR	18.4	[15]
PANI-HCl	MO	154.6	[24]
PANI-HCl	MB	192.3	[25]
PANI-HCl	OG, CBB, RBBR, AG	175, 129, 100, 56	[26]
PANI-HCl/chitosan composite	OG, CBB, RBBR	322, 357, 303	[27]
PANI-HCl/TMP nanocomposite	MG	78.9	[28]
PANI-HCl/ZSP nanocomposite	MB	12	[29]
PANI-H ₂ SO ₄	MO	75.9	[30]
PANI-phytic acid hydrogel	MB	71.2	[31]
PANI-PTSA	OG, CBB, RBBR, AG	342, 207, 171, 95	[32]
PANI-CSA	OG, CBB, RBBR, AG	400, 231, 254, 151	[32]
PANI-CSA/polyamide 6 composite	MO	81.9	[33]
PANI-PAMPSA	MB, RB	466.5, 440.0	This study

adsorbent for dye removal is due to two reasons: (1) its large amount of amine and imine functional groups are expected to interact with organic compounds [12]; (2) the charge transfer induced by doping enables PANI to interact with ionic species via electrostatic interaction [15]. There are several excellent reviews in the literature discussing the applications of PANI-based materials for the removal of dyes from wastewater/aqueous solutions, and the reader is referred in particular to those by Zare and coworkers [16], and Huang and coworkers [12]. A selective summary of adsorption capacities of PANI-based materials is provided in Table 1. Although PANI is widely used for dye removal, there are two main challenges restricting its actual performance. Firstly, the bare PANI-EB particles can easily aggregate because of the inter- and intramolecular interactions, which significantly reduces the surface area and hence results in lower adsorption capacities [12]. Secondly, PANI doped by small molecule acid is prone to dedoping because the small molecule acid evaporates easily at room temperature [17,18], which will reduce the surface charge of PANI and therefore affect the electrostatic interaction between PANI and dye.

The present work aims to overcome these challenges by doping PANI with a polyacid, namely poly(2-acrylamido-2-methyl-1-propane-sulfonic acid) (PAMPSA). PAMPSA is a strong polyacid distinguished by flexible polymer backbone and short distances between sulfonic groups of neighbouring repeat units [34]. PAMPSA offers many advantages compared to small molecule acids: (1) PAMPSA can easily adapt its conformation to match the spatial distribution of nitrogen sites in PANI and form a double-strand structure [34,35]. The double-strand structure confers a higher stability than the single-strand structure formed between small molecule acid and PANI [36]; (2) PAMPSA is not volatile and will not cause dedoping; (3) PAMPSA brings large amount of sulfonic, carbonyl and amide functional groups into PANI, which may improve the processability and create more adsorption sites. Our previous research found that PAMPSA as a dopant can improve the porosity and chemical stability of PANI membranes for organic solvent nanofiltration [37]. However, to the best of our knowledge, there has been no study about PAMPSA doped PANI (PANI-PAMPSA), or any polyacid doped PANI, as adsorbents for dye removal.

Hence, the objective of the present work was to investigate the adsorption properties of PANI-PAMPSA towards a cationic dye (methylene blue, MB) and an anionic dye (rose bengal, RB). The experimental variables affecting optimal adsorption were evaluated. The kinetics, isotherms, thermodynamics, and mechanisms of adsorption were elucidated in detail.

2. Materials and methods

2.1. Chemicals

Analytical grade MB, RB, aniline, ammonium persulfate (APS), hydrochloric acid (HCl), N-methyl-2-pyrrolidone (NMP), 4-methyl piperidine (4MP) were obtained from Sigma-Aldrich, UK. The structure and chemical properties of MB and RB are summarized in Table S1. PAMPSA (MW 800,000 g mol⁻¹) was supplied by Fisher Scientific, UK. Deionized (DI) water was produced by an ELGA deionizer from PURELAB Option, USA.

2.2. Synthesis

PANI-PAMPSA was synthesized by matrix (template) polymerization. This approach uses polyacid as a template to promote the ‘head-to-tail’ coupling of aniline along the chain of the polyacid macromolecule, leading to the formation of a well-defined molecular structure of PANI [38–40]. Specifically, 18.23 mL (0.2 mol) of aniline, at 4:1 monomer to acid repeat unit molar ratio, was dissolved in 200 mL of 0.1 M PAMPSA solution. The polymerization of aniline was initiated by the slow addition of 128 mL of 1.56 M APS solution using a peristaltic pump at a speed of 20 mL h⁻¹ at 15 °C. The mixture was left for 24 h under stirring for full polymerization. The final solution was filtered and the obtained PANI-PAMPSA was rinsed with DI water to remove unreacted chemicals, and then washed with acetone to remove oligomers. To prepare PANI-EB, 18.23 mL (0.2 mol) of aniline was dissolved in 200 mL of 1 M HCl solution. The polymerization process was similar to PANI-PAMPSA, but the powder obtained was stirred in 33.3% (w/v) ammonia solution for 4 h to deprotonate the emeraldine salt. The obtained PANI-EB was then rinsed with DI water to remove excess ammonia and then washed with acetone to remove oligomers. Both PANI-PAMPSA and PANI-EB were dried in a vacuum oven at 60 °C for 24 h, and then ground using mortar and pestle. The final color of PANI-PAMPSA was dark green, and the final color of PANI-EB was purple bronze.

2.3. Characterization

The morphological and physicochemical properties of PANI-PAMPSA were characterized in comparison to PANI-EB. Morphology of the samples was studied by a JEOL 6301 F field emission scanning electron microscope (FESEM). Fourier transform infrared (FTIR) spectra were obtained by a PerkinElmer Spectrum 100 ATR-FTIR spectrometer. Each

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