



Facile one-pot synthesis of imidazole-functionalized poly-(vinylbenzyl chloride) and its study on the applicability of synthetic dye removal from aqueous system



Brian Hyun Choi ^{a, b}, Kyung-Won Jung ^c, Jae-Woo Choi ^{a, b}, Sang-Hyup Lee ^{a, d},
Young Jae Lee ^c, Kyu-Hong Ahn ^{a, *}

^a Center for Water Resources Cycle Research, Korea Institute of Science and Technology, 5 Hwarang-ro 14-gil, Seongbuk-gu, Seoul, 02792, South Korea

^b Division of Energy and Environmental Engineering, KIST School, Korea University of Science and Technology, 5 Hwarang-ro 14-gil, Seongbuk-gu, Seoul, 02792, South Korea

^c Department of Earth and Environmental Sciences, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul, 02841, South Korea

^d Green School, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul, 02841, South Korea

ARTICLE INFO

Article history:

Received 16 March 2017

Received in revised form

6 September 2017

Accepted 7 September 2017

Available online 8 September 2017

Keywords:

Facile one-pot synthesis

Polymer

Azo dye

Synthetic adsorbent

Adsorption selectivity

ABSTRACT

This study presents a direct and simple one-pot synthesis of 2-methylimidazole grafted poly-vinylbenzyl chloride (^{2-Me}Im-pVBC) using radical polymerization, followed by its studies on the removal of structurally diverse mono and di-azo dyes (Acid Orange 7 (AO7), Acid Yellow 17 (AY17), and Acid Black 1 (AB1)) from aqueous media. Characterization of the material, effect of key factors such as dosage and pH on substrate removal, adsorption kinetics and isotherms, removal selectivity of the examined dyes, and reusability of the adsorbent were assessed. The prepared polymeric material exhibited outstanding removal activity with respect to all three dyes at a wide range of pH, with no significant impact due to the chemical complexity of the substrate. Adsorption kinetics and isotherm studies showcases supreme and rapid affinity towards AO7, with a maximum adsorption capacity of around 2012 mg/g. Lastly, ^{2-Me}Im-pVBC exhibited its sustainability by maintaining 8 cycles of adsorption-desorption process with outstanding substrate removal rate. Therefore, ^{2-Me}Im-pVBC demonstrated promising adsorption performance and exceptional selectivity on all three examined substrates, which can be further developed as an efficient agent for removing synthetic dyes in aqueous system.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Since the initial discovery of synthetic organic dyes (Mauveines) in the 19th century by W.H. Perkin, utilization of organic dyes has been prevalent in multiple industries such as textile, paints, printing, leather, rubber, cosmetics, and so on (Gordon and Gregory, 1983; Pan et al., 2016). The annual production of organic dyes hovers around 750,000 tons and approximately 50% of them are azo dyes (Chudgar and Oakes, 2003; Rafatullah et al., 2010). Azo dyes are organic molecules that possess one or more azo (R–N=N–R') functionality within their chemical structures. Another common chemical feature that azo dyes share is the possession of sulfonic (SO₃) group, which substantially contributes to the water solubility

of the dyes due to its high acid dissociation constant. When azo dyes are decomposed, they release aromatic amine compounds as byproducts, which are toxic, mutagenic, and carcinogenic (Arcos and Argus, 1994; Brown and De Vito, 1993; Chung and Stevens, 1993; Li and Bishop, 2004). Although the exact number is unknown, approximately 10–15% of the manufactured dyes are discharged into the water bodies without proper treatment (Allen et al., 1995; Rafatullah et al., 2010). Thus, it is imperative to discover and optimize novel pathways for proper and efficient treatment of azo dyes from the aquatic ecosystem to preserve and ensure the safety of human health and environment.

Various methodologies to remove azo dyes and mitigate their negative impacts such as biological decomposition (Barragan et al., 2007), coagulation/flocculation (Szygula et al., 2008), electrochemical pathway (Gupta et al., 2007), photocatalysis (Madhusudan et al., 2013; Rajabi et al., 2013; Roushani et al., 2015), oxidation (Bandara et al., 1997), Fenton reactions (Blanco et al., 2014),

* Corresponding author.

E-mail address: khahn@kist.re.kr (K.-H. Ahn).

ozonation (Mezzanotte et al., 2013), and filtration (Zavastin et al., 2012) have been developed and studied extensively. However, no universally applicable method has been identified for the efficient removal of azo dyes. Up to date, adsorption is considered as the most attractive process that many researchers investigate as an alternative due to its high cost efficiency, atom economy, and lack of secondary pollutant generation.

A wide range of materials have been employed as potential candidates for the adsorptive removal of azo dyes. Activated carbon, zeolites, and graphene based materials have showcased high affinities and rapid kinetics for azo dye sequestration (Alpat et al., 2008; Jin et al., 2008; Liu et al., 2012; Meshko et al., 2001; Phan et al., 2006; Saygılı and Güzel, 2016; Saygılı et al., 2015). Despite such positive features exhibited via the composites mentioned above, high cost for synthesizing high-quality products with uniformity and regeneration of the spent sorbents have been some of the major barriers that hinder from those composites from being an attractive alternative to remove azo dyes for large-scale application. To overcome such issues, basic anion exchange resins (i.e. quaternary ammonium grafted polystyrene resins) have been considered as an alternative as it can alleviate the two major problems mentioned above (Greluk and Hubicki, 2009, 2011).

However, quaternary ammonium functionality is known for its toxicity and corrosive nature. To circumvent this issue, polymeric adsorbents and amine or N-heterocycle (i.e. imidazole)- functionalized ionic liquids have received significant attention in dye removal due to their high thermal stabilities, ionic conductivities, and possession of functionalities that are capable of interacting with the target molecules (Gao et al., 2013a; Pei et al., 2007). In particular, an extensive research has been done on the post surface modification of tunable polymers to generate functional group-rich polymeric adsorbents for successfully removing target pollutants with decent removal capacities, allowing such composites to be promising agents for future state of the art technologies in dye sequestration (Gao et al., 2013a,b; Ghorai et al., 2014; Qu et al., 2013). Poly-vinylbenzyl chloride (pVBC) is relatively reactive chloromethyl-rich polymer that can easily undergo functionality modification. Samatya et al. (2012) used N methyl-D-glucamine, a boron selective ligand, as the functional group to generate modified pVBC beads to remove boron. Ajmal et al. (2016) reported the implementation of amidoxime groups via a two-step post surface modification for removing organic dyes, arsenic, and chromium ions. However, such post-surface modification of polymeric materials generally require multi-step syntheses.

Taking the applicability of N-heterocyclic moieties and easily tunable nature of pVBC, we report a facile one-pot synthesis of 2-methylimidazole-functionalized pVBC (denoted as ^{2-Me}Im-pVBC) and its applicability in removing azo dyes. Specifically, the physicochemical properties of the adsorbent, effect of key parameters such as adsorbent dosage and pH on adsorption performance, and selectivity of a particular dye, if existent, were examined to identify some of the key factors on the removal of azo dyes. Adsorption kinetics and isotherm studies were conducted to identify the adsorption behavior and mechanisms of ^{2-Me}Im-pVBC, along with its sustainability via examining its reusability for multiple cycles of adsorption-desorption process.

2. Materials and methods

2.1. Reagents

4-vinylbenzyl chloride (4-VBC, 90%), 2-methylimidazole (2-MeIm), 1,1' azobis (cyclohexanecarbonitrile) (ABCN, 98%), and divinylbenzene (DVB, 80%) were purchased from Sigma Aldrich

Korea. AO7 was purchased from Tokyo Chemical Industry (Japan); AY17 and AB1 were purchased from Samchun Pure Chemical Co., Ltd. (South Korea). All reagents were used without further purification.

2.2. Synthesis of ^{2-Me}Im-pVBC

As presented in Fig. 1, ^{2-Me}Im-pVBC was prepared by the following procedure: 2.4 g of 4-VBC, 0.048 g of DVB, 0.08 g of ABCN, and 1.5 g of 2-MeIm were mixed in a glass vial containing 10 ml of dimethylformamide (DMF, Fischer Sci. UK). The mixture was then heated to 80 °C for 9 h to afford a white solid. The product was then removed from the vial and thoroughly washed with 15 ml of dichloromethane (DCM, Fischer Sci. UK) to remove residual DMF and excess reagents. The synthesized polymer was dried in a vacuum oven at 60 °C for 24 h to remove any residual impurities.

2.3. Characterization of ^{2-Me}Im-pVBC

Scanning electron microscopy (SEM, FEI Inspect F, USA) was conducted to determine the size and morphology of the adsorbent. To identify the elemental composition of the polymer, energy dispersive X-ray spectroscopy (EDS) of the adsorbent was measured as well. Thermogravimetric analysis (TGA, SDT Q600) was performed under N₂ from ambient temperature to 600 °C at a ramp rate of 10 °C/min to identify the thermal stability and melting/decomposition temperature of the adsorbent. The textural properties of the prepared adsorbent such as surface area, pore diameter, and total pore volume were determined by Brunauer-Emmet-Teller (BET) N₂ vapor adsorption/desorption studies at 77K using a nanoporous system post degasification at 150 °C for 6 h (NP-XQ, Mirae Scientific Instruments, South Korea). In addition, the pore size distribution was estimated by the Barrett-Joyner-Halenda (BJH) method from the desorption branch. The Fourier transform infrared (FT-IR) analysis of the naked and exhausted polymeric adsorbent was evaluated to identify/confirm the existence of functional groups and their alterations, if present, after the adsorption of the substrates (NICOLET iS10, Thermo Scientific, USA).

2.4. Batch adsorption experiments

Stock solutions of each substrate dye (AO7, AY17, AB1) were

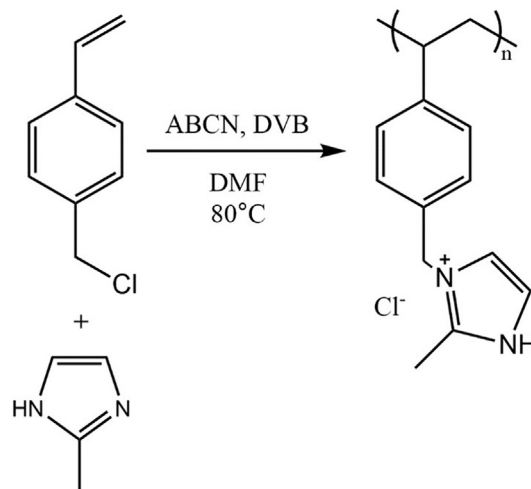


Fig. 1. Synthetic scheme on the one-pot synthesis of ^{2-Me}Im-pVBC.

Download English Version:

<https://daneshyari.com/en/article/5479821>

Download Persian Version:

<https://daneshyari.com/article/5479821>

[Daneshyari.com](https://daneshyari.com)