



Nature-like solution for removal of direct brown 1 azo dye from aqueous phase using humics-modified silica gel



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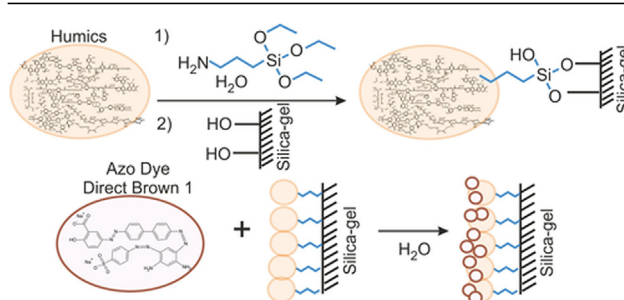
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HIGHLIGHTS

- Silanol humic derivatives are obtained by reaction with amino-organosilane in water.
- Silanol humic derivatives are immobilized onto silica gels using aqueous sorption.
- Humics-modified silica gels efficiently remove trisazo dye from aqueous phase.
- Similar approach can be used for removal of azo dyes released to aquatic environments.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 16 March 2015

Received in revised form

4 September 2015

Accepted 19 November 2015

Available online xxx

Handling Editor: Min Jang

Keywords:

Azo dye

Direct brown 1

Removal

Silica gel

Humic substances

Organosilanes

Immobilization

ABSTRACT

The objective was to estimate suitability of humics-modified silica gels for adsorptive removal of the Direct Brown 1 trisazo dye from aqueous phase. The major advantage of the proposed adsorbents is that of an ecologically sound procedure of immobilizing silanized humic derivatives onto silica gel in aquatic solutions. The silanized humic derivatives, in turn, are obtained without a use of organic solvent by reacting natural humic materials from peat and coal with 3-aminopropyltriethoxyorganosilane in water. These silanized derivatives are surface active and are capable of self assembling into humic adlayers at the water solid interface. A use of this approach allows for immobilization of up to 220 mg of humic materials per 1 g of SiO₂. The adsorption capacity of humics-modified silica gels with respect to the Direct Brown 1 trisazo dye varied from 3.5 up to 8.8 mg per 1 g of SiO₂. The maximum sorption obtained for the silanized derivative with 50% modification degree was comparable to adsorption capacity of activated coal to this dye (7.5 mg g⁻¹). The results of this adsorption study, warrant further studies of azo dye removal from aqueous environments.

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1. Introduction

Azo dyes account for more than 50% of all the produced dyes (Chequer et al., 2011). As a result, they are the most common group of synthetic colorants released into the environment (Chung and

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Stevens, 1993; Maguire and Tkacz, 1991; Saratale et al., 2011; Solis et al., 2012). Many azo dyes and products of their degradation (e.g., aromatic amines) are toxic and expose mutagenic and carcinogenic effects on living organisms that raises serious environmental concerns (Mathieu-Denoncourt et al., 2014; Pereira and Alvis, 2012). Adsorption is one of the most effective processes of dye removal from contaminated water widely employed by industries (Allen and Koumanova, 2005; Babel and Kurniawan, 2003; McKay et al., 1980). Recent research has focused on developing cost-effective alternatives to activated carbon (Mohan et al., 2002; Yagub et al., 2014). Many have reported the feasibility of using various low cost adsorbents such as peat, lignite, clay, zeolites, coal fines, fly ash, different agricultural by-products and biosorbents (Crini, 2006; Gupta and Suhas, 2009; Mittal et al., 2013; Ong et al., 2007; Srinivasan and Viraraghavan, 2010).

In this context, the adsorption of pollutants by humic substances (HS) deserves specific attention (Perminova and Hatfield, 2005). HS are natural hyperbranched polyelectrolytes, which possess aromatic backbone highly substituted with functional groups. In nature, humic coatings attached to the surface of mineral particles engender higher sorption capacities for soils and sediments with respect to organic chemicals including azo dyes (Mathieu-Denoncourt et al., 2014; Olcay et al., 2009). This suggests that the immobilization of humic coatings onto surface of solid sorbents might increase substantially their sorption affinity for azo dyes. Indeed, in the prior work of Prado et al. (2003), it was reported that modification of silica gel with humic acid yielded sorbent with enhanced sorption capacity for removal of indigo carmine dye from aqueous phase. However, the process of sorbent preparation included treatment of silica gel with aminoorganosilane in toluene at 140 °C during 72 h, which makes the proposed procedure prohibitively expensive and ecologically not safe, while the prepared sorbent might contain traces of organic solvent.

The objective of this study was to propose a protocol of preparation of humics-modified silica gel suitable for azo dye removal from aqueous phase, which would be free of the above disadvantages. For this purpose, humic material is first reacted with aminoorganosilane in the aqueous phase; after which, the resultant silanized derivative is immobilized onto silica gel surface. Both reactions are carried out in aqueous phase that exclude residual contamination of the sorbent with organic solvent. Schematically the proposed approach is presented in Fig. 1.

Sorption properties of the prepared humics modified silica gel were demonstrated on azo dye Direct Brown 1. This dye was chosen as a representative of the sulfonated azo dyes which are highly water soluble and most refractory to biodegradation (Olcay et al.,

2009).

2. Material and methods

2.1. Materials

Direct Brown 1 (C.I. 30045) azo dye belonging to direct application class and trisazo chemical class was employed as the test dye. Its molecular formula is $C_{31}H_{22}N_8Na_2O_6S$, and molecular weight is 680.615. Structural formula is shown in Supplementary Materials.

Direct Brown 1 was purchased from Sigma–Aldrich. Stock solution of the dye was prepared in MilliQ water at concentration of 200 mg/L. All other reagents used were of analytical reagent grade.

Two types of humic materials were used in this study. The first one was commercially available potassium humate (Sakhalin Humate) isolated from leonardite and designated as CHS. Peat sodium humate (PHS) was obtained from low moor peat by single extraction with 1 M NaOH. 3-aminopropyltriethoxysilane (APTES) was purchased from Penta Ltd. (Russia, Moscow). It was of technical-grade and used without further purification. Silica gel 60 was purchased from Merck and had specific surface area of $540 \text{ m}^2 \text{ g}^{-1}$.

2.2. Functionalization of humic materials using APTES

A wide range of reagent ratios were used for modification of humic materials with APTES. The reaction stoichiometries were calculated on the basis of carboxyl group available in CHS and PHS. The content of carboxyl groups was determined using Ca-acetate method (Swift, 1996) and accounted for 2.7 and 2.9 mmol g^{-1} for CHS and PHS, respectively. Given that 1 g APTES contains 4.5 mmol of amine-groups, a 1:1 M ratio of COOH and NH_2 groups was reached by treating 1 g of CHS with 1.67 g (1.75 mL) of APTES. The reaction was run at three different APTES-to-humics molar ratios, nominally: 0.2, 0.5, and 1.0. These ratios corresponded to 20, 50, and 100% modification degree of carboxyl groups available within the humic backbone.

Prior to synthesis, a weight of potassium or sodium humate (CHS or PHS, respectively) was dissolved in distilled water in a beaker while stirring with a magnetic stirrer. A required aliquote of APTES was added dropwise to the obtained humate solution under continued stirring, and pH of the reaction mixture was adjusted to 4 with 5 M HCl. Then, the solution was transferred to a round bottom flask, and rotor-evaporated to dryness. The resulting products were stored in sealed vials. They looked like dark brown amorphous powders. The names of the samples obtained were constructed as CHS-APTES-X or PHS-APTES-X, where X is modification degree. In

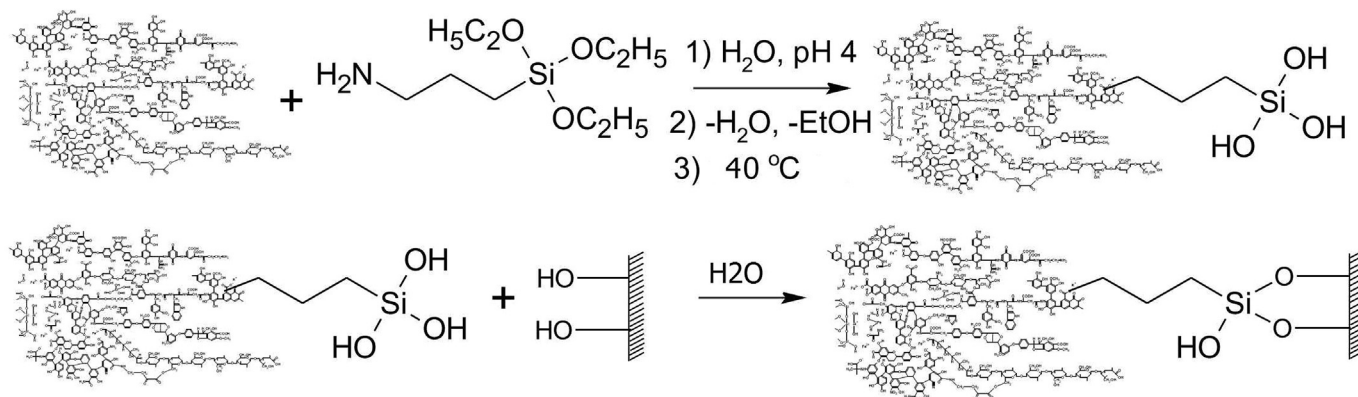


Fig. 1. Schematic reaction pathways for synthesis of silanized humic materials using 3-aminopropyltriethoxysilane (APTES) in aquatic medium and of their immobilization onto the silica gel surface in aqueous phase.

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