



# Comparison between the removal of Reactive Black 5 from aqueous solutions by 3-amino-1,2,4 triazole,5-thiol and melamine grafted chitosan prepared through four different routes



Khalid Z. Elwakeel<sup>a,\*</sup>, S. El-Kousy<sup>b</sup>, Hadeel G. El-Shorbagy<sup>c</sup>, M.A. Abd El-Ghaffar<sup>d</sup>

<sup>a</sup> Environmental Science Department, Faculty of Science, Port-Said University, Port-Said, Egypt

<sup>b</sup> Chemistry Department, Faculty of Science, Menofia University, Shebin El-Kom, Menofia, Egypt

<sup>c</sup> Water Quality Audit Department, Al-Menofia Water and Wastewater Company, Menofia, Egypt

<sup>d</sup> Department of Polymers and Pigments, National Research Centre, Dokki, Cairo, Egypt

## ARTICLE INFO

### Article history:

Received 18 August 2015

Received in revised form 2 December 2015

Accepted 10 December 2015

Available online 18 December 2015

### Keywords:

Chitosan

3-Amino-1,2,4 triazole,5-thiol

Melamine

Removal

Reactive Black 5

## ABSTRACT

Chitosan was modified through four different modification routes. First, epichlorohydrine cross-linked Chitosan was grafted with 3-Amino-1,2,4 triazole,5-thiol and melamine to produce RI and RII, respectively. Second, glutaraldehyde cross-linked chitosan was chemically modified using ammonium hydroxide then grafted with 3-Amino-1,2,4 triazole,5-thiol and melamine to produce RIII and RIV, respectively. The prepared polymers were characterized via FTIR, TGA, elemental analysis, water regain and surface area. RIII and RIV shows higher thermal stability, bigger surface area, and lower water regain, than RI and RII. Removal of Reactive Black 5 (RB5) anions from their aqueous solutions were studied using the modified chitosan adsorbents under various parameters such as pH, agitation time, and temperature. The maximum adsorption capacities are 0.492, 0.330, 0.622 and 0.698 mmol g<sup>-1</sup> for RI, RII, RIII, and RIV, respectively, at pH 3 and 25 °C. The nature of interaction of RB5 with the adsorbents was identified. Uptake kinetics and adsorption isotherms were modeled using conventional and simple equations: best results were respectively obtained with the pseudo-second order rate equation and the Langmuir equation. The thermodynamic parameters have been calculated: the adsorption is endothermic, spontaneous and contributes to increase the entropy (randomness) of the system. RI and RII gives higher desorption yield than RIII and RIV, this probably due to the presence of the quaternary ammonium moiety in the last two sorbents.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

Common contaminants found in wastewater include 6 biodegradable, volatile and recalcitrant organic compounds, toxic metals, suspended solids, dyes, microbial pathogens and parasites. In recent years, disposal of toxic industrial effluents into water bodies without proper treatment is the major source of water pollution. Due to the various applications of basic and reactive dyes, about 2–50% of the dyestuff is industrial wastewater and released into the environment. Billions of cubic meters of wastewaters polluted by synthetic organic dyes are daily produced worldwide due to their extensive use in the industry [1]. In general, the concentration of dyes present in textile wastewater in the

range of 10–1000 mg L<sup>-1</sup> [2], and above the concentration of 1 mg L<sup>-1</sup>, Dyeing effluent has serious destructive impact on the environment and affects adversely on the biological activity of flora and fauna [3]. Therefore, the major problem concerning environmental pollutants is removing dyes from wastewater produced in industrial activities. Reactive Black five (RB5) dye is diazo acidic reactive dye, has two sulfonate groups and two sulfato-ethylsulfon groups in its molecular structure and negative charges in aqueous solution [4]. This dye uses widely in the textile industries for the dyeing of cotton, woolen and nylon fabrics, and also uses in pharmaceutical industry. Numerous techniques, such as physical, chemical and biological decolorization methods, have been carried out to treat wastewater containing dyes these technologies are varying in its economic value, efficiency and ability of using. The applicability of any wastewater technology should be related not only to its degradation or detoxification efficiency, but also to its environmental impacts. In this regard, adsorption is one of the most promising techniques used in dye removal [5,6]. An

\* Corresponding author.

E-mail addresses: [Khalid\\_Elwakeel@yahoo.com](mailto:Khalid_Elwakeel@yahoo.com), [khalid\\_elwakeel@sci.psu.edu.eg](mailto:khalid_elwakeel@sci.psu.edu.eg) (K.Z. Elwakeel).

important adsorbent is chitosan and its derivatives. Chitosan holds a special place among natural organic matrices for synthesis of adsorption materials. Reactive amino and hydroxyl groups on chitosan can be modified by chemical and physical methods easily [7,8]. Chitosan has been widely investigated as an adsorbent to capture dyes from aqueous solutions because of its low cost, easy availability, environmental friendly behavior [9–11], ready chemical modifications and remarkable adsorption capacities. However, one shortcoming for chitosan to be used as adsorbent is that chitosan readily dissolves in acidic conditions which pH is below 6 [12]. In an acidic solution, the amine groups on chitosan can be protonated by hydrogen ions ( $H^+$ ), which causes the chitosan to dissolve. This is considered to be one of the weaknesses of chitosan that could limit its successful use as an adsorbent in an acidic environment [13]. To improve the stability of the adsorbent as well as the biodegradability, mechanical strength and solutes diffusion in it, polymer networks are cross-linked [14,15]. The modification of chitosan-based adsorbents by grafting synthetic or natural materials is a promising method for the preparation of novel adsorbents and enables one to introduce special properties and expand the applications of chitosan derivatives in the environmental field [16,17]. The reactivity of chitosan can be improved by grafting new functional groups such as amine and thio compounds [16]. 3-Amino-1,2,4 triazole,5-thiol (AZ) has triazole moiety, amino and thiol group, these functional groups are amenable to interact with RB5 molecules. In addition, AZ is nontoxic and inexpensive compound compared with many other organic compounds. It is known that most of triazole compounds are reported as green materials due to environmentally friendly effect [18]. Melamine (MA) is a cheap chemical raw material. There are three free amino groups and three aromatic nitrogen atoms in MA molecule, which is capable of interacting with dye molecule. However, as far as we know, chitosan-based adsorbents using MA as modifier has rarely been reported in the literature. So, it is expected to obtain inexpensive and high efficient adsorbent by grafting MA onto chitosan [19]. The objective may consist in increasing the density of adsorption sites, in improving the adsorption capacity and comparing the adsorption behavior of four chitosan derivatives that is grafted with 3-Amino-1,2,4 triazole,5-thiol and melamine through four different modification routes. These materials are being tested for RB5 removal through the study of pH effect, the investigation of competition effects, the determination of adsorption isotherms and thermodynamic characteristics and the identification of controlling steps in uptake kinetics. Finally desorption of RB5 is studied with the objective of verifying the possibility to recycle the adsorbent.

## 2. Chemicals

Chitosan ( $M_{wt} = 10253$ ) with degree of deacetylation of 82%, glutaraldehyde 25%, ammonium hydroxide solution 33%, epichlorohydrine, 3-Amino-1,2,4 triazole,5-thiol (AZ), melamine (MA) and Reactive Black 5 (RB5) were Aldrich products. All other chemicals were Prolabo products and were used as received.

### 2.1. Grafting of 3-Amino-1,2,4 triazole,5-thiol (AZ) or melamine (MA) on chitosan

3-Amino-1,2,4 triazole,5-thiol and melamine were grafted on both epichlorohydrine treated chitosan and ammonia treated chitosan/glutaraldehyde.

#### 2.1.1. Grafting on epichlorohydrine treated chitosan resin—first method

Six grams of chitosan was dissolved in 20% aqueous solution of acetic acid, then precipitated using 2.5 M NaOH solution. The gel

obtained was washed with distilled water several times and kept for us. The obtained chitosan gel was suspended in 50 mL of DMF and 25 mL epichlorohydrine. The above mixture was stirred for 24 h at 80 °C. The solid product obtained was filtered off and washed several times with water followed by ethanol and referred by (R01).

**2.1.1.1. Grafting of AZ (preparation of RI).** R01 was treated with of 3-Amino-1,2,4 triazole,5-thiol solution (3 g of AZ was dissolved in 200 mL hot distilled water). The reaction mixture was stirred at 100 °C for 12 h. The product was filtered off and washed with distilled water, methanol, and acetone then dried in air and referred by (RI).

**2.1.1.2. Grafting of MA (preparation of RII).** R01 was treated with melamine suspension (4 g of MA was dissolved in 150 mL hot distilled water). The reaction mixture was stirred at 100 °C for 24 h. The product was filtered off and washed with distilled water, methanol, and then dried in air and referred by (RII).

#### 2.1.2. Grafting on ammonia treated chitosan/glutaraldehyde resin—second method

**2.1.2.1. Chitosan/glutaraldehyde synthesis.** Seven grams of chitosan were dissolved in 20% aqueous solution of acetic acid, till complete dissolution. The obtained chitosan solution was reacted with (15) mL of glutaraldehyde solution (25%), and then heated for 24 h at 80 °C. The gelatinous product obtained was filtered off and washed several times with diluted acetic acid solution to remove any unreacted chitosan solution and distilled water, respectively, and referred by (R02).

**2.1.2.2. Reaction with ammonium solution.** The product obtained in the previous step (R02) was treated with 100 mL of ammonium hydroxide solution. The reaction mixture was stirred at 100 °C for 12 h. The product obtained was filtered off, washed with methanol and then dried in air and referred by (R03).

**2.1.2.3. Reaction with epichlorohydrine.** The product obtained in the previous step (R03) was treated with 25 mL of epichlorohydrine dissolved in 75 mL of DMF solution. The reaction mixture was stirred at 100 °C for 12 h. The product was filtered off and washed with distilled water and methanol, respectively, and referred by (R04).

**2.1.2.4. Grafting of AZ (preparation of RIII).** Two grams of the product obtained in the previous step (R04) was added to one gram of 3-amino-1,2,4 triazole,5-thiol (AZ) dissolved in 150 mL boiled distilled water. The reaction mixture was stirred at 100–120 °C for 24 h. The product obtained was filtered off and washed with distilled water, methanol, and then dried in air and referred by (RIII).

**2.1.2.5. Grafting of MA (preparation of RIV).** Two grams of the previously obtained epichlorohydrine modified resin (R04) was added to one gram of melamine suspended in 150 mL hot distilled water. The reaction mixture was stirred at 100–120 °C for 24 h. The product was filtered off and washed with distilled water, methanol, and then dried in air and referred by (RIV).

## 2.3. Characterization of the resins

### 2.3.1. FT-IR analysis

FT-IR spectra of prepared adsorbents were recorded using Nicolet IR200 FT-IR Spectrometer with the standard KBr-pellet technique, in the region 4000–400  $cm^{-1}$ .

Download English Version:

<https://daneshyari.com/en/article/221929>

Download Persian Version:

<https://daneshyari.com/article/221929>

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