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Synthesis of urethane sodium carboxylate and its dye removal ability from single system



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ABSTRACT

Urethane sodium carboxylate (USC) was synthesized and its dye removal ability was investigated. USC characteristics were studied using FTIR and SEM. Basic Blue 41 (BB41), Basic Red 18 (BR18), and Basic Violet 16 (BV16) were used. The effect of adsorbent dosage, dye concentration and salt on dye removal was evaluated. Adsorption kinetics followed pseudo-second order. The USC adsorption capacity was 474, 538 and 298 mg/g for BB41, BR18 and BV16, respectively. Adsorption isotherm followed with Langmuir isotherm. The results showed that the USC might be a suitable adsorbent to remove dyes from colored wastewater.

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1. Introduction

Dyes can escape from conventional wastewater treatment methods because they are generally designed to withstand physico-chemical and biological degradation. In addition, it is undesirable the presence of dyes in waterways because they deplete the dissolved oxygen and reduces the sunlight penetration [1–11].

The adsorption process is a simple and effective method to remove pollutants from wastewater. Adsorbent materials seem economically attractive for practical application and they are produced on the basis of low-cost materials or even wastes. Different materials have been used as adsorbents [12–16]. They remove pollutants indiscriminately. However, further improvement of their adsorption capacities, mechanical strength, and other properties are needed for a wider application [17].

Polymers are a potential alternative to traditional adsorbents due to their vast surface area, perfect mechanical rigidity, adjustable surface chemistry and feasible regeneration under mild conditions [14,17,18]. Polymeric materials remove different pollutants from aqueous media [19–22] (Table 1). Adsorption capacity of a polymeric adsorbent toward pollutants can be improved using monomers which have functional groups such as

A literature review showed that urethane sodium carboxylate (USC) has not been used to remove dyes from single systems (Fig. 1). In this paper, USC was synthesized and characterized and its dye adsorption ability from single systems was studied. The characteristics of USC were studied using Fourier transform infrared (FTIR) and scanning electron microscopy (SEM). Basic Blue 41 (BB41), Basic Red 18 (BR18), and Basic Violet 16 (BV16) were used as model compounds. The kinetics and isotherm of dye adsorption onto USC was studied in details. The effect of operational parameter such as adsorbent dosage, dye concentration and salt on dye removal was evaluated.

2. Materials and methods

2.1. Materials

Basic Blue 41 (BB41), Basic Red 18 (BR18), and Basic Violet 16 (BV16) were obtained from Ciba and used without further purification. The chemical structure of the dyes is shown in Fig. 2. All other chemicals were of analytical grade and obtained from Merck.

2.2. Synthesis and characterization of USC

Urethane sodium carboxylate (USC) is an anionic polymeric absorbent. The USC was synthesized in three steps. The first, urethane hexacarboxylic acid was synthesized by toluene

amino group, due to the specific interaction of functional groups bound to the polymeric matrixes with the target pollutants.

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 Table 1

 Adsorption capacities of polymeric adsorbents to remove dyes.

Polymeric adsorbent	Adsorbate	$Q_0 (mg/g)$	Ref.
Poly(glycidylmethacrylate) grafted on a cross-linked acrylate based resin	Crystal Violet	77	[19]
ZCH-101	Reactive orange X-GN	233	[20]
Functionalized resin	Reactive brilliant blue KN-R	28	[21]
Amberlite XAD-4	Malachite Green	899	[22]
	Methyl Green	1117	
Amberlite XAD-2	Malachite Green	884	
	Methyl Green	1122	
USC	Basic Blue 41	474	Present
	Basic Red 18	538	study
	Basic Violet 16	298	

diisocyanate (17.42 g, 0.1 mol) and citric acid (38.4 g, 0.2 mol) in the presence of dibutyltin dilaurate (DBTDL, 0.1 g) in 80 mL dry acetone at 45 °C for 3 h. The second step, a sodium hydroxide solution (24 g NaOH in 50 mL water) was slowly added to urethane hexacarboxylic acid at 25 °C. Finally, the USC was filtered and dried at 80 °C vacuum oven for 4 h (Fig. 3).

2.3. Characterization of USC

Fourier transform infrared (FTIR) spectrum (Perkin-Elmer Spectrophotometer Spectrum One) in the range 4000–450 cm⁻¹ was studied. The morphological structure of material was examined by scanning electron microscopy (SEM) using LEO 1455VP scanning microscope.

2.4. Adsorption procedure

The dye adsorption measurements were conducted by mixing of USC in jars containing 250 mL of a dye solution (50 mg/L). The change on the absorbance of all solution samples were monitored and determined at certain time intervals during the adsorption

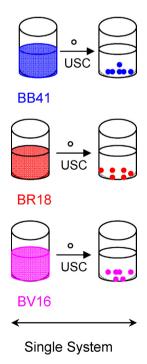


Fig. 1. Dye removal ability of USC from single systems Basic Blue 41 (BB41), Basic Red 18 (BR18), and Basic Violet 16 (BV16).

BB41

$$O_{2}N \xrightarrow{\qquad \qquad N=N \qquad \qquad N} CH_{2}CH_{3}$$

$$CH_{2}CH_{2}N (CH_{3})$$

$$CH_{2}CH_{2}N (CH_{3})$$

$$CH_{2}CH_{2}N (CH_{3})$$

$$CH_{2}CH_{2}N (CH_{3})$$

$$CH_{2}CH_{2}N (CH_{3})$$

$$\begin{array}{c|c}
C(CH_3)_2 \\
C-C=C \\
H \\
Cl^{-1}
\end{array}$$

$$\begin{array}{c|c}
N(C_2H_5)_2 \\
BV16$$

Fig. 2. The chemical structure of dyes.

process. At the end of the adsorption experiments, the solution samples were centrifuged and the dye concentration was determined. The results were verified with the adsorption kinetics and isotherms.

UV–vis spectrophotometer (Perkin-Elmer Lambda 25 spectrophotometer) was employed for absorbance measurements of samples. The maximum wavelength (λ_{max}) of BB41, BR18 and BV16 to determine residual dye concentration in solution was 605 nm, 488 nm and 545 nm, respectively.

The effect of adsorbent dosage on dye removal from single systems was investigated by contacting 250 mL of dye solution with initial dye concentration of 50 mg/L using the jar test at room temperature (25 $^{\circ}$ C) for 60 min at a constant stirring speed of 200 rpm.

The effect of initial dye concentration on dye removal from single systems was investigated by contacting 250 mL of dye solution with USC at room temperature (25 $^{\circ}$ C) at room temperature (25 $^{\circ}$ C) for 60 min at a constant stirring speed of 200 rpm.

The effect of salt (0.02 mol) on dye removal from single systems was investigated by contacting 250 mL of dye solution (50 mg/L) with USC using the jar test at room temperature (25 $^{\circ}$ C) for 60 min at a constant stirring speed of 200 rpm. Different salts (NaHCO₃, NaCl and Na₂SO₄) were used.

3. Results and discussion

3.1. Characterization of USC

In order to investigate the functional groups of USC, Fourier transform infrared in the range 4000–450 cm⁻¹ image was studied (Fig. 4a). It can be seen that NCO stretching vibration of toluene diisocyanate (TDI) in 2250 cm⁻¹ has been disappeared; referring to the fact that TDI has been completely blocked by hydroxyl groups of citric acid. The C–H stretching vibration of ring aromatic was in 3050 cm⁻¹. The C–H stretching vibrations of aliphatic CH₃, CH₂ and

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