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Synthesis and characterization of iodo polyurethane foam and its application in removing of aniline blue and crystal violet from laundry wastewater

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Abstract

A new sorbent was prepared by treating polyurethane foam with HCl and replacing the amino functional groups with iodine atoms. The properties of iodo-polyurethane were studied with infrared, ultraviolet and visible spectroscopy, bulk density, pH_{ZPC} and elemental and thermal analysis. Removal of aniline blue and crystal violet dyes from water with iodo-polyurethane were investigated with the batch technique. Maximum removal was achieved at pH 7–12. The effect of the initial dye concentration on the equilibrium adsorption from aqueous solutions with iodo-polyurethane was found to have a good correlation, with $r^2 = 0.995$ and an intercept of 0.039 when analyzed in the Langmuir and Freundlich isotherm models. The capacity of iodo-polyurethane for aniline blue and crystal violet were 0.24 and 0.45 mmol g^{-1}, respectively (188.9 and 183.6 mg g^{-1}). The values of ΔG and ΔH were −7.7 kJ mol^{-1} and −26.1 kJ mol^{-1}, respectively, indicating that sorption is spontaneous and exothermic. The sorption rate of the dyes onto iodo-polyurethane was rapid, with 50% removal within 50 s. The pseudo-second order equation best described the kinetics of absorbed aniline blue and crystal violet ($r^2 = 0.994$). A modified equation ($y = ax^{0.n}$) was used to treat deviation from the Morris–Weber model for the sorption diffusion mechanism of crystal violet onto iodo-polyurethane. Use of iodo-polyurethane for removing aniline blue and crystal violet contamination from laundry wastewater is thus possible.

Keywords: Aniline blue; Crystal violet; Iodo-polyurethane; Wastewater

1. Introduction

Laundry involves washing, usually with water containing detergents or other chemicals, agitation, rinsing, drying and ironing. Washing is often done above room temperature to increase the activity of any chemicals used, to increase the solubility of stains and to kill any microorganisms that may be present on the fabric. Various chemicals can be used to increase the solvent power of water, such as the compounds in soap root or ash lye.

Textile laundry wastewater is among the major sources of hazardous dyes in the environment [1]. Some

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dyes are carcinogenic and hazardous for aquatic organisms [2] and can cause health disorders, such as severe damage to the kidneys and the central nervous system [3]. Aniline blue and crystal violet dyes are extensively used in the textile industry [4]; these dyes are toxic to mammalian cells and are mitotic poisons and proven potent carcinogens [5]. Removal of dyes from wastewater before its discharge into the environmental is important to avoid polluting underground water.

Many methods are used to treat wastewater before discharge into natural water, including adsorption [6], oxidation [7], microfiltration [8], coagulation [9] and degradation [10]. Adsorption is the most effective technique because it is easy, inexpensive, can treat concentrated dyes, and the spent sorbent can be regenerated for further use [11]. The sorbents used to remove dyes from wastewater include polyurethane [12–16] organo-bentonite [17], carbon [18], Zn_2Al–NO_3 [19] and miswak [20].

Polyurethane foam is a good sorbent for some organic and inorganic pollutants in wastewater [21,22]. As its high basicity decreases its sorption capacity, low basicity polyurethane must be prepared. In previous studies, we developed polyurethane containing a polyhydroxyl functional group, which has high sorption capacity [23,24]. Polyhydroxy polyurethane foam was prepared from commercial polyurethane by replacing the primary amine with a hydroxyl group. In the work reported here, we prepared iodo-polyurethane foam by treating the matrix of polyurethane with HCl, diazotizing the amino functional groups with $NaNO_2$ and then replacing the azo groups with iodine atoms. Iodo-polyurethane is inexpensive, stable and has high sorption capacity for removing aniline blue and crystal violet dyes from wastewater. The compound can also be recycled many times with no significant decrease in sorption capacity.

2. Experimental

2.1. Materials

Aniline blue ($C_{37}H_{32}N_5O_9S_3$, 786.9 g/mol) and crystal violet ($C_{25}H_{30}N_3Cl$, 407.98) were purchased from BDH (Poole, England), and stock solutions (1 mg mL^{-1}) were prepared by dissolving 0.1 g of dye in 100 mL of H_2O. A series of 25 mL of dye standard solutions (0.4–8.0 μg mL^{-1} dye) were used to determine the calibration curve.

Iodo-polyurethane was prepared as follows: 5.0 g of commercial polyurethane foam were soaked in 0.5 L of HCl (2 mol L^{-1}) for 24 h and then washed with distilled H_2O. The preparation was diazotized with $NaNO_2$ (50 mL of 2 mol L^{-1}) in an ice bath, and the diazonium salts were washed with ice-cold water and coupled with 2 mol L^{-1} KI. The orange iodo-polyurethane was washed with H_2O and then dried in air.

2.2. Apparatus

All spectrophotometric measurements were performed with a Shimadzu Model UV-1800 (Shimadzu Corporation, Japan). pH was measured with a pH meter from Microprocessor pH Meter (HANNA Instruments).

2.3. Recommended procedure

An aliquot of 0.1 g of iodo-polyurethane was mixed with 25 mL of dye solution (1 μg mL^{-1}) then shaken for 30 min, and the aniline blue and crystal violet concentrations remaining in solution were measured at $\lambda = 599$ and 592 nm, respectively. The percentage of removed dye and the capacity of iodo-polyurethane (Q, mmol g^{-1}) were calculated from $\%E = ((C_o - C)/C_o) \times 100$ and $Q = (C_o - C)V/m$.

To determine the iodo-polyurethane surface acid sites, 25 mL of 0.05 mol L^{-1} NaOH solution were added to 0.1 g of iodo-polyurethane, and the solution was shaken for 24 h. Then, 10.0 mL of the residual solution were titrated with HCl (0.05 mol L^{-1}) in the presence of methyl orange as the indicator, and the basic sites were back-titrated with 0.05 mol L^{-1} NaOH and HCl solutions.

To determine the pH_{ZPC} of iodo-polyurethane, a series of flasks containing 25 mL of solution at pH 1–13, adjusted with HCl and NaOH, were prepared, and the solution was added to 0.1 g of iodo-polyurethane. After 24 h, the final pH (pH_f) of the solutions was measured, and the difference between the initial and final pH values ($\Delta pH = pH_f - pH_i$) was plotted against the pH_i. The pH_{ZPC} was noted as the pH at which the initial pH equalled the final pH.

3. Results and discussion

3.1. Characterization of iodo-polyurethane

The pH_{ZPC} of polyurethane and iodo-polyurethane (Fig. 1) were 8.9 and 6.9, respectively, showing that iodo-polyurethane is less basic than polyurethane. The surfaces sites of iodo-polyurethane are positively charged at pH lower than 6.9 and become negatively charge at pH greater than pH 6.9. The negatively charged iodo-polyurethane surface is due to free unshared electron pairs of iodine and ether oxygen. Iodo-polyurethane is therefore suitable for extracting basic species at