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Equilibrium, kinetic and thermodynamic studies of the removal of triphenyl methane dyes from wastewater using iodopolyurethane powder

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Abstract

The removal and recovery of rosaniline and brilliant green were studied using batch and dynamic processes. The maximum sorption of these dyes (~100%) was obtained in a pH range of 6–10 with a shaking time of 2–5 min. The sorption kinetics were best described by the pseudo-second-order model (R^2 = 0.993). The variation in the sorption of rosaniline and brilliant green with temperature results in average values of ΔH and ΔG (i.e., −65.7 kJ mol^{-1} and −8.1 kJ mol^{-1}, respectively). The sorption capacity of iodo-polyurethane powder (Iodo-PUP) was 106.8 and 154.4 mg g^{-1} for rosaniline and brilliant green, respectively. The dye removal percentage and detection limit were 99.5% and 20 ng mL^{-1}, respectively. The isotherms exhibit good correlation (R^2 = 0.9985) with a zero intercept (0.0045). Successful application was achieved for environmental samples (i.e., industrial, laundry and sewage wastewater). The average recovery and RSD were 85.2% and 4.9%, respectively.

Keywords: Adsorption; Rosaniline; Brilliant green; Polyurethane foam; Kinetics

1. Introduction

Dyes are used extensively in the textile, leather, food processing, cosmetics, paper, and dyeing industries [1]. Dyes become water pollutants due to their presence in the effluents of dye manufacturing industries [2]. Over 10^5 commercially available dyes exist, and more than 7×10^5 tonnes of dye are produced annually [3]. However, approximately 7×10^4 tonnes/year of dyes are discharged into waste streams by the textile industry [4]. Dyes are carcinogenic and possess a serious hazard to aquatic living organisms [5]. In addition, the dyes in water cause human health disorders, such as severe damage to the kidneys and central nervous system [1]. In particular, basic dyes, such as triphenyl methane, are considered to be one of the more problematic classes of dyes [1]. Therefore, the removal of dyes from effluents prior to mixing with natural water is very important. Adsorption is one of the most efficient methods of removing pollutants from wastewater [6–11]. The adsorption processes yield the best results because they can remove different

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types of colouring materials, especially if inexpensive adsorbents are available. Different sorbents have been used to remove dyes from wastewater (e.g., $Ni_{0.6}Fe_{2.4}O_4$ nanoparticles, castor bean, lignocellulose, agricultural waste, cationic polymer, coal, carbonaceous and miswak) [12–22].

The polyurethane sorbent (PUF) is advantageous due to its simple preparation, low cost and high surface area [23–25]. PUF is a good sorbent for the removal of organic pollutants from aqueous solutions, such aromatic acids [26], phenols [27], herbicides [28], β-lactam antibiotics [29], azine and triphenyl methane dye [30]. The Iodo-PUP sorbent was synthesized from PUF, which undergoes hydrolysis and diazotization by sodium nitrite followed by treatment with potassium iodide [1]. The aim of this study is to develop a new, simple, cheap and rapid removal procedure for triphenyl methane basic dyes that have different molecular sizes from wastewater using the modified Iodo-PUP. Iodo-PUP is inexpensive with good stability and a high sorption capacity for the removal of basic dyes from aqueous solutions. In addition, Iodo-PUP can be recycled many times for the removal of dyes from wastewater without significantly decreasing its capacities. The removal behaviour of Iodo-PUP for dyes was studied to optimize the conditions for the optimal removal of dyes. Kinetic, thermodynamic and equilibrium data was obtained.

2. Experimental

2.1. Reagents

The rosaniline and brilliant green dyes were prepared from high purity grade reagents (BDH, Poole, England). A 1 mg mL^{-1} stock solution of the dyes was prepared by dissolving 0.1 g of rosaniline hydrochloride ($C_{20}H_{19}N_3$ HCl, 337.86 g/mol) and brilliant green ($C_{27}H_{34}N_2O_4S$, 482.63 g/mol, λ_{max} = 624.5 nm) in 100 mL of distilled water.

2.2. Apparatus

The rosaniline and brilliant green dyes were determined spectrophotometrically using a Shimadzu UV-1800 spectrophotometer (Shimadzu Corporation, Japan) at λ_{max} 542 and 624.5 nm, respectively. The pH measurements were carried out using a pH metre from Microprocessor pH Meter (HANNA Instruments). The glass column, which contained 1.0 g of Iodo-PUP, was 50.0 cm long, 1.5 cm in diameter with a bed height of approximately 7.0 cm.

2.3. Recommended procedures

The sorption of rosaniline and brilliant green was carried out using a batch technique at 25 °C. A portion of the 0.1 g of Iodo-PUP was mixed with 25 mL of the studied dye solution (1 μg mL^{-1}) in a shaker adjusted to the desired shaking speed. After a certain time period, the dye concentration remaining in the supernatant solution was determined spectrophotometrically.

In the dynamic experiments, 1.0 g of Iodo-PUP was packed into a column (50 cm × 1.5 cm). The bed height (L) of the Iodo-PUP column was approximately 7 cm. 25 mL of the studied dye solutions (1 μg mL^{-1}) were passed through the Iodo-PUP column at a flow rate of 2–5 mL min^{-1}. The stripping of the dye from the Iodo-PUP column was carried out using CH_3OH. The eluates of the dyes were collected and determined spectrophotometrically.

To determine the pHp_{ZC} of Iodo-PUP, a series of flasks containing 25 mL of a solution with a pH in a range 1–13 (solution was adjusted using HCl and NaOH) was added to 0.1 g of Iodo-PUP. After 24 h, the final pH (pH_f) of the solution was measured. The difference between the initial and final pH values ($\Delta pH = pH_f - pH_i$) was plotted as a function of the pH_i. The pHp_{ZC} was the pH at which the initial pH equals the final pH.

A 25 mL portion of each dye solution was shaken with 0.1 g of Iodo-PUP for 30 min. The pH of the dye solution was adjusted prior to equilibration with HCl or NaOH over a range of 1–14. After equilibration, the remaining dyes were determined using the recommended method.

The effect of the shaking time on the extraction efficiency of the dye was studied. 0.1 g of Iodo-PUP was added to a 25 mL of sample at the optimum pH, and automatic shaking was performed for different time intervals (1–60 min).

3. Results and discussion

3.1. Effect of pH on the sorption of dye onto Iodo-PUP

The effect of the pH on the sorption of rosaniline and brilliant green onto Iodo-PUP using the batch technique is shown in Fig. 1. The pH of the aqueous solution was an important parameter that controlled the uptake process. The maximum removal efficiency reached 97–100% for rosaniline and brilliant green in a pH range of 6–12 and 8–12, respectively. At a pH of less than 2.0, the uptake of the studied dyes is too small, and the uptake increased rapidly as the pH value increased. The optimum pH value for the removal of rosaniline and brilliant