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Adsorption of Acid Yellow 99 by polyacrylonitrile/activated carbon composite: Kinetics, thermodynamics and isotherm studies

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ABSTRACT

The adsorption of Acid Yellow 99 (AY99) onto polyacrylonitrile/activated carbon (PAN/AC) composite was investigated in aqueous solution in a batch system with respect to contact time, pH and temperature. Experimental data indicated that the adsorption capacity of (PAN/AC) composite for AY99 was higher in acidic rather than in basic solutions. Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms and the isotherm constants were determined. The activation energy of adsorption was also evaluated for the adsorption of AY99 onto (PAN/AC) composite. The pseudo-first-order and pseudo-second-order model equations were used to analyze the kinetics of the adsorption process. The dynamic data fitted the pseudo-second-order kinetic model well. The activation energy, change of free energy, enthalpy and entropy of adsorption were also evaluated for the adsorption of AY99 onto (PAN/AC) composite. The thermodynamics of the adsorption indicated spontaneous and exothermic nature of the process. The (PAN/AC) composite was characterized using Fourier transform infrared spectroscopy (FTIR) and its morphology was determined by scanning electron microscopy (SEM). The results indicate that (PAN/AC) composite could be employed as low-cost material for the removal of acid dyes from textile effluents.

1. Introduction

The industrial wastewater usually contains a variety of organic compounds and toxic pulp mills and dyestuff manufacturing discharge highly colored wastewater which have provoked serious environmental concerns all over the world [1–3]. Dyes can be classified as anionic (direct, acid and reactive dyes), cationic (basic dyes) and non-ionic (disperse dyes) [4]. The removal of color from waste textile effluents has become environmentally important [5]. The most widely used methods for removing color effluents from water include coagulation [6], electro-chemical [7], oxidation [8], ozonation [9], solvent extraction [10], adsorption [5,11], photocatalytic degradation [12], etc. but only that of adsorption is considered to be superior to other techniques. This is attributed to its low cost, easy availability of adsorbents, simplicity of design, high efficiency, ease of operation and biodegradability [13]. Consequently, kinetic studies, which provide information for the rate of removal of pollutants from solution and the adsorption equilibrium data are essential for the design of water treatment units involving an adsorption process.

The basic feature of an adsorption process is surface accumulation from intermolecular penetration of material. It is now customary to differentiate between two types of adsorptions. If the attraction between the solid surface and the adsorbed molecules is physical in nature, the adsorption is referred to as physical adsorption (physisorption). Generally, in physical adsorption the attractive forces between adsorbed molecules and the solid surface are van der Waals forces and they being weak in nature result in reversible adsorption. On the other hand if the attraction forces are due to chemical bonding, the adsorption process is called chemisorption. In view of the higher strength of the bonding in chemisorption, it is difficult to remove chemisorbed species from the solid surface.

Activated carbon is perhaps the most widely used adsorbent in the adsorption processes due to its high specific surface area and high adsorption capacity [14–16]. In order to decrease the cost of wastewater treatment, attempts have been made in finding inexpensive adsorbents. So, the research of the recent years mainly focused on utilizing economic materials as alternatives to activated carbon; amongst them, the composite materials. A composite is a material that consists of two or more constituent materials or phases. Polymers with activated carbon are being considered as alternative low-cost adsorbents due to their specific surface area and high chemical and mechanical stability [17–20].

The aim of this study is to investigate the adsorption of Acid Yellow 99 onto polyacrylonitrile/activated carbon (PAN/AC) composite as a low cost adsorbent. Effects of different parameters such as contact time, pH, dye concentration, temperature, adsorbent concentration on both equilibrium and the rate of adsorption were studied. The kinetics, isotherms

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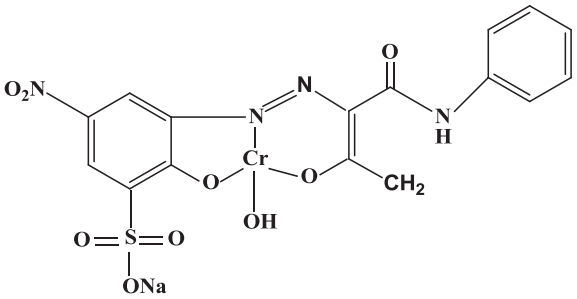


Fig. 1. Structure of AY99 dye.

and thermodynamic parameters were also calculated to determine the rate constants and adsorption mechanism.

2. Materials and methods

2.1. Materials

A commercial textile dye Acid Yellow 99 (Fig. 1) was obtained from Cromatos SRL, a dye company located in Italy and was used as received without further purification. Activated carbon (particle diameter 300–500 μm) was purchased from Calgon Company, USA. Activated carbon was washed several times with bidistilled water and then dried at 120 °C for 24 h. Samples were then preserved in the desiccator over anhydrous $CaCl_2$ for further use.

2.2. Material characterization

The SEM results of the PAN/AC composite sample before and after the adsorption processes were obtained using (JEOL 5600LV) scanning microscope to observe surface modification. FTIR spectrum of PAN/AC composite sample was recorded (KBr) on a Perkin-Elmer BX Model Fourier transform infrared spectrometer. UV–visible spectrophotometer (Perkin-Elmer AA800 Model AAS) was employed for absorbance measurements of samples. An Orion 900S2 model digital pH meter and a Gallenkamp Orbital Incubator were used for pH adjustment and shaking, respectively.

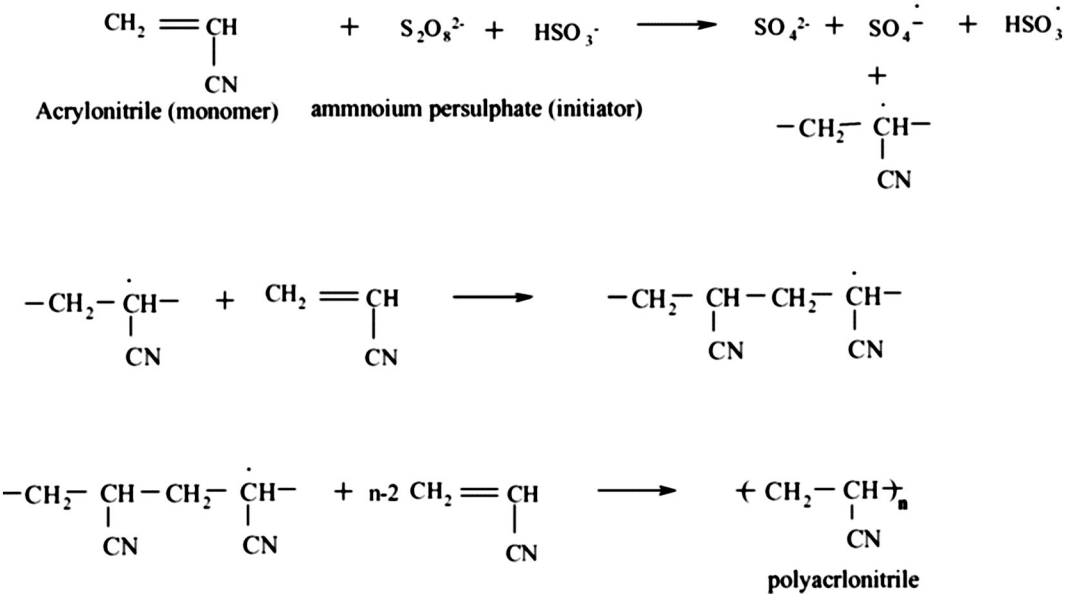
2.3. Preparation of polyacrylonitrile/activated carbon (PAN/AC) composite

Polyacrylonitrile/activated carbon (PAN/AC) composite was prepared [21] by adding 30 g of acrylonitrile (monomer) to 20 mL of bidistilled water in a 250 mL three neck round bottom flask, then adding 0.1 g of potassium persulfate and 10 g of activated carbon to the mixture. The mixture was stirred by a magnetic stirrer and the reaction was allowed to proceed at 60–70 °C for about 24 h until gel formation. The precipitate was filtered and washed with water, ethanol, 0.1 mol L^{-1} HCl solution and water, respectively. The final product (composite) was left to be dried under vacuum at 50 °C for 24 h and stored on desiccator prior to use in the sorption study. The polymerization reaction is given in Scheme 1.

FTIR spectrum of (PAN/AC) composite was recorded in the region 400–4000 cm^{-1} (Fig. 2). The band at 2921 cm^{-1} corresponds to the asymmetric stretching vibration of methylene group (νCH_2) and its bending vibration at 1454 cm^{-1}. The band at 2244 cm^{-1} corresponds to the CN group.

2.4. Adsorption experiments

The adsorption experiments of anionic dye AY99 were carried out in batch equilibrium mode. A 0.2–0.6 g sample of (PAN/AC) composite with 50 mL aqueous solution of a 40–150 mg/L AY99 solution at various pHs (1–9) reached for 90 min was adjusted by adding a small amount of HCl or NaOH solution (1 M) using a pH meter. The optimum pH was determined and used through all adsorption processes. Experiments were conducted for various time intervals to determine whether adsorption equilibrium was reached and the maximum removal of AR57 was attained. The solution was then filtered through a Whatman (number 40) filter paper to remove any organic or inorganic precipitates formed under acidic or basic conditions and the filtrates were subjected to quantitative analyses. The equilibrium concentration of each solution was determined at the wavelength of UV-maximum (λ_{max}) at 418 nm. Dye adsorption experiments were also accomplished to obtain isotherms at various temperatures (25–50 °C) and at a range of 40–150 mg/L dye concentrations for 90 min by using a water bath with shaker. Calibration curves were constructed to correlate concentrations to different absorbance values. Construction of this calibration curves was verified and the maximum wavelengths that corresponded to maximum absorbance for the dye were determined.



Scheme 1. Schematic representation of the polymerization of acrylonitrile.