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Use of solid wastes of the soda ash plant as an adsorbent for the removal of anionic dyes: Equilibrium and kinetic studies

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Abstract

Solid wastes (SW) from the distiller waste (DW), which is the by-product of the ammonia-soda process (the Solvay method) for the production of soda ash, has been used as an alternative adsorbent for removing the anionic dyes from aqueous medium. The effects of pH, initial dye concentration and temperature were investigated on kinetics and equilibrium of the adsorption. The results indicated that adsorption was strongly pH dependent. The typical dependence of dye uptake on temperature and the kinetics of adsorption indicated the process to be chemisorption. The results showed that as the pH increased, extent of dye uptake increased and $Ca(OH)_2$ particles precipitated at higher pHs were mainly responsible for the removal of anionic Procion Crimson H-EXL (Reactive Red 231) dye. The necessary time to reach the equilibrium was found to be less than 2 min. Dye uptake process followed the pseudo-second-order rate expression. The Freundlich isotherm best fitted for the adsorption of the dye on SW. Various thermodynamic parameters, such as ΔG°, ΔH° and ΔS° were calculated. The thermodynamics of PC/SW system indicated spontaneous and exothermic nature of the process.

Keywords: Soda ash waste; Wastewater; Dye removal; Adsorption; Isotherm; Kinetics

1. Introduction

The remaining dye molecules, even at very low concentrations in the wastewater of textile industries, are common water pollutants. Their presence in water is highly visible and undesirable and may significantly affect photo-synthetic activity in aquatic life due to reduced light penetration.

Adsorption is an effective process for the removal of dyes from waste effluents [1]. Currently, activated carbons are the most common adsorbents because of their higher adsorption capacities. However, because of its relatively high cost, in relatively recent years, there has been an increasing interest in utilizing low cost adsorbents to remove dyes from wastewater. This has led to a search for industrial wastes, agricultural by-products and natural materials as alternative adsorbents.

Furthermore, anionic dyes are, in general, more problematic than cationic dyes. Mostly, surface charge of these adsorbents is reversed into positive by pre-adsorption of some multivalent cations prior to the adsorption attempt [2].

The utilization of waste materials is increasingly becoming of vital concern because these wastes represent unused resources and, in many cases, present serious disposal problems. During the past decade, a great deal of attention has been given to methods of converting these materials into useful products [3].

Distiller waste (DW) is the main waste material, which is the by-product of the ammonia-soda process (the Solvay method) for the production of soda ash. Nowadays DW, containing $CaCl_2$, unprocessed NaCl, $CaCO_3$, $CaSO_4$, $Ca(OH)_2$ and other substances, creates a huge problem for the ammonia-soda plants [4,5]. The considerable amount of chloride left in the solid wastes restricted to use of them in agriculture and in cement industry.

In this study, the solid waste (SW) from the distiller waste (DW) has been used as an alternative adsorbent for removing the anionic dyes from aqueous medium. The effects of pH, initial dye concentration and temperature were investigated on kinetics and equilibrium of the adsorption. The pseudo-first and pseudo-second-order, and intraparticle diffusion kinetic models were applied. The amount of dye molecules adsorbed at equilibrium was measured. The Langmuir and Freundlich isotherm models were tested for their applicability. The thermodynamic

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Nomenclature

b	Langmuir constant (L/mg)
C_e	equilibrium concentration (mg/L)
C_0	initial dye concentration in solution (mg/L)
ΔG°	Gibbs free energy of adsorption (kJ/mol)
ΔH°	enthalpy change of adsorption (kJ/mol)
k_i	rate parameter of intraparticle diffusion model (mg dye/g adsorbent $\text{min}^{-0.5}$)
k_1	rate constant of pseudo-first-order model (min^{-1})
k_2	rate constant of pseudo-second-order model (min g adsorbent/mg dye)
K_F	Freundlich constant ((mg/g)$(\text{L/mg})^{1/n}$)
K_o	sorption equilibrium constant
n	Freundlich constant
q_e	adsorption capacity in equilibrium (mg/g)
q_t	amount of adsorption at time t (mg/g)
Q^0	maximum adsorption capacity (mg/g)
r^2	linear correlation coefficient
R	universal gas constant (=8.314 J/mol K)
ΔS°	entropy change of adsorption (J/mol K)
t	time (min)
T	absolute temperature (K)

parameters were evaluated to define mechanisms of the process.

2. Materials and methods

2.1. Materials

The solid waste (SW) was obtained from the distiller wastewater (DW) provided by Sisecam Mersin Soda Ash Plant, Turkey. The waste sample was analyzed for its chemical composition by using the XRF method and found to contain 112.49 g/L $CaC1_2$, 50.16 g/L NaCl, 3.09 g/L $CaSO_4$, 5.59 g/L $CaCO_3$, 6.43 g/L $Ca(OH)_2$, 1.33 g/L MgO, 1.03 g/L Al_2O_3, 0.43 g/L SiO_2 and 0.13 g/L Fe_2O_3.

Prior to use as an adsorbent, the interference of chloride, which results from NaCl and $CaCl_2$ in the supernatant of the distiller wastewater, was eliminated by elutriation using deionized water. As procedure, the solid was allowed to settle and then the supernatant was decanted (fivefold dilution for each wash). The procedure was repeated five times until it is chloride free. This was checked by the addition of $AgNO_3$ after washing with distilled water to make sure that no precipitate is formed, which is the evidence of chloride existence [4]. The inherent pH of the suspension of the waste without dye was measured as 12.03. A WTW 340i model pH meter was used for measurement of pH of solutions.

The resulted solid sample, which consists mainly of CaO (as $Ca(OH)_2$ in wastewater), $CaCO_3$ and $CaSO_4$ as principle minerals, was dried at 105 °C for 3 h and used as the adsorbent for adsorption studies.

The sample of adsorbent exhibited a uniform particle size distribution. The d_{80} value was determined as about 70 μm by the sub-sieve technique. Bulk and the true density of the sample was measured as 1.42 and 2.47 g/L (by calculation), respectively. The specific surface area of the adsorbent was determined as 10.63 m^2/g by a FlowSorb II-2300 BET apparatus using nitrogen gas as the adsorbate.

An azo reactive Procion Crimson H-EXL (CI Reactive Red 231) having in common the group aminochlorotriazine, a commercially available dye (the purity is above 95% according to the manufacturer) produced by Dystar Textilfarben GmbH & Co., was used as model dye for anionic character without purification. It is solid-dark brown granular powder and soluble in water (140 g/L at 20 °C). The natural pH of the dye solution (500 mg/L) without adsorbent was measured as 7.52. The concentration of the dye in the solution after equilibrium adsorption was determined with Shimadzu brand UV-160 UV visible spectrophotometer by measuring absorbance at λ_{max} of 546 nm for PC.

2.2. Experimental procedure

The adsorption of PC from aqueous solution onto solid waste (SW) was performed using batch equilibrium technique. Adsorption tests were done as a single stage batch test by using Velp DLH model mechanic stirrer. A suspension containing 1 g of adsorbent sample was mixed by stirring the mixture at 200 rpm with a 1 L aqueous solution of dye at a known initial concentration in a flask that immersed in a bath in thermostatted water keeping constant working temperature. An aliquot of the solution was withdrawn at the pre-determined time intervals, and was centrifuged at 5600 rpm for 10 min in order to remove any adsorbent particles. The residual dye concentration in the filtrate was subsequently determined using the spectrophotometer at the wavelength corresponding to the maximum absorbance. The adsorption tests were continued until the equilibrium concentration was reached. The effect of contact time on the amount of dye adsorbed was investigated as a function of initial concentration of dye, pH and temperature. The obtained data from the adsorption tests were then used to calculate the adsorption capacity, q_e (mg/g), of the adsorbent by a mass–balance relationship, which represents the amount of adsorbed dye per the amount of dry adsorbent. All of the experiments were duplicated to check the reproducibility of data and the average value was taken. Replicate experiments showed a maximum deviation of 2.01% in dye uptake measurements.

3. Results and discussion

3.1. Effect of pH on adsorption of PC onto SW

To determine the pH effect on adsorption capacity of SW for PC, dye solutions were prepared at different pH levels within 6–12 after introducing adsorbent at 25 °C and initial dye concentration of 500 mg/L.