

Reuse of dye-colored water post-treated with industrial waste: Its adsorption kinetics and evaluation of method efficiency in cotton fabric dyeing



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ARTICLE INFO

Keywords:

Wastewater
Adsorption kinetics
Dyeing
Water reuse
C.I. Direct Black 22

ABSTRACT

In this study, the potential for the use of an industrial waste (IW) as an adsorbent for the treatment of aqueous solutions containing C.I. Direct Black 22 was investigated. A kinetic study was performed to investigate the best conditions for adsorption, evaluating the effect of temperature and the adsorbent mass on the thermodynamics of the adsorption processes. Under the best conditions, 95.7% efficiency was achieved within 24 h. Pseudo-second-order kinetics models were applied to the experimental data and the correlation coefficients (r^2) were higher than 0.98. The treated water was successfully reused in a cotton dyeing process. The best results were obtained with thermally-treated industrial waste, where lower color difference (ΔE) values were observed (0.32–0.70) for dye concentrations of 0.5, 1.0 and 1.5% (w/w). In the case of the raw industrial waste, ΔE values of 0.54 (1.5%, w/w, dye) and 1.36 (2.0%, w/w, dye) were obtained.

1. Introduction

The various types of water pollution have increasingly drawn the attention of researchers. This is because many pollutants, such as heavy metals [1], dyes [2], drugs [3,4] and wastewater from agriculture [5], which have appeared as part of the modernization process [6], are dangerous even at low concentrations. Effluents originating from the textile industry represent the most polluting of all industrial wastes [7], due to the high concentrations of dyes and some auxiliary compounds. The presence of these recalcitrant substances in the water is harmful to aquatic life, since the light penetration is reduced [7], and to humans.

Many processes have been reported in the literature for the treatment of aqueous solutions containing dyes, such as photo-oxidation [8,9], chemical oxidation [10–12] and biological treatments involving enzymes [13,14]. In these methods the dye molecule is degraded and an incomplete degradation route can lead to the presence of compounds which are even more toxic than the original molecule [10]. Adsorption methods, on the other hand, remove the dye molecule entirely without generating any fragments and for this reason they have become an attractive alternative for wastewater treatment [15,16]. In order to find new utilities for the exhausted adsorbent, our research group has recently started to study the application of these as fillers for the production of blends and composites with a great variety of polymers.

The application of adsorption methods has enhanced the treatment of wastewater originating from the textile industry. These physico-

chemical processes are usually highly efficient in binding a wide range of dye molecules onto the solid surface of an adsorbent, promoting the removal of color from these effluents [14,17,18].

Alternative adsorbents such as humin [19], *Phragmites australis* (a reed species) [20], residues of *Salvia miltiorrhiza* Bge [21], rice husk [22], swede rape straw [23], quince seed mucilage [24], coffee residues [25], corn fibers and luffa peels [26] have been used in attempts to remove color from water. Some adsorbents offer a high adsorption capacity, for instance, Agarwal et al. [27] obtained 99.71% of color removal from aqueous solutions of methylene blue (30 mg L^{-1}) using *Ephedra strobilacea* sawdust modified with phosphoric acid.

The high consumption of water in the textile industry for processes such as printing, washing, dyeing, bleaching, soaking and finishing makes the reuse of wastewater a necessity [28]. The reuse of water obtained through the treatment of textile effluents using adsorbents in new dyeing processes is increasing because of the high percentage of water that can be reused for fabric dyeing [12]. In the literature, the most commonly reported cases of water treatment have been aimed at the final disposal of the effluent, without verifying the possibility for the reuse of the matrix at the same production plant [29]. Hu et al. [30] used ozone (O_3) systems combined with mesoporous carbon aerogel and cobalt oxide nanoparticles ($\text{O}_3/\text{O}_3\text{-MCA}/\text{O}_3\text{-MCA-Co}_3\text{O}_4$) to remove color from dyeing baths containing C.I. Reactive Blue 19. The treated water was reused in new cotton (CO) fabric dyeing processes and on comparing the samples with those dyed using distilled water a color difference (ΔE) of 1.54 was obtained, using only O_3 to degrade the

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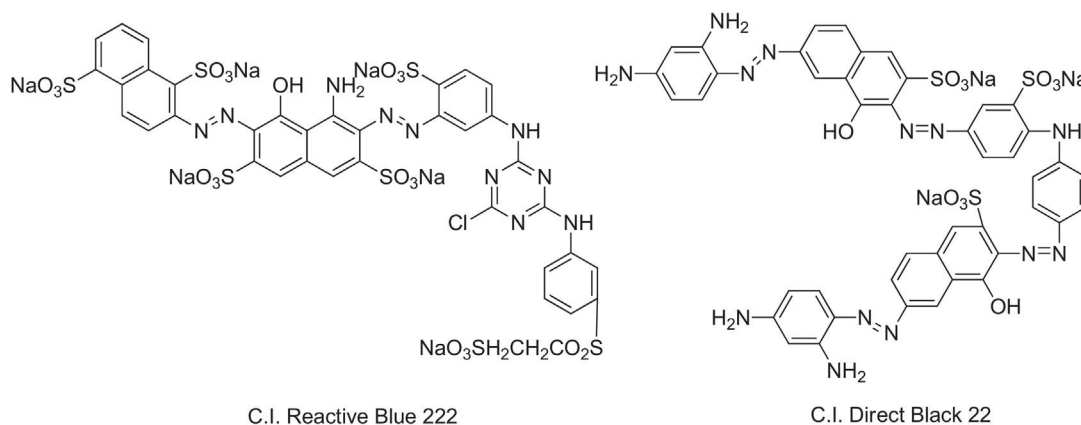


Fig. 1. Chemical structure of the dyes C.I. Reactive Blue 222 [30] and C.I. Direct Black 22 [31].

dyeing bath. In the case of O_3/MCA and $O_3-MCA-Co_3O_4$ systems, values of 0.68 and 0.19, respectively, were obtained.

In this context, in this study the removal of C.I. Direct Black 22 textile dye from aqueous solutions using an industrial waste originating from the clarification of soy oil as a dye adsorbent, with no prior chemical treatment, was investigated. The C.I. Direct Black 22 adsorption kinetics and the thermodynamics of the process were investigated at different temperatures and the treated water was used in cotton dyeing with C.I. Reactive Blue 222, a dye widely used at textile plants in the vicinity.

2. Experimental

2.1. Materials

The dyes C.I. Direct Black 22 and C.I. Reactive Blue 222 (Fig. 1) were donated by Dystar. The industrial waste (IW) was provided by the company Bunge and was comprised of ‘filtration earth’ (composed of bentonite) used to clarify vegetable oils before use. Na_2SO_4 and Na_2CO_3 were obtained from Vetec.

2.2. Preparation of the adsorbent and adsorbate

The IW used in this study received no chemical treatment and it was dried for 24 h at 60 °C, herein referred to as raw IW (IWR). A sample of the IWR was then thermally treated at 180 °C (IWT). The two adsorbent samples were then sieved through different granulometric sieves (63 μm for IWR and 44–63 μm for IWT) and the initial pH of the aqueous extract was 3.9. For the kinetics experiments, an aqueous solution of 0.1 g L⁻¹ C.I. dye was prepared. Direct Black 22 was used as the adsorbate. A stock solution of the dye was prepared in a concentration of 1.0 g L⁻¹ and then diluted to appropriate concentrations to obtain a calibration curve.

2.3. Procedure for kinetics studies on color removal

In the first section of this study, the kinetics experiments were carried out by placing an aqueous solution of C.I. Direct Black 22 (0.1 g L⁻¹; 50 mL) in an Erlenmeyer flask. Different amounts of adsorbent (IWR) (0.5 and 1 g) were then added and different temperatures (20, 30, 40 and 50 °C) were applied. The experiments were conducted in a Dubnoff bath with shaking (130 rpm) for 120 h. The system was maintained at a controlled temperature until reaching equilibrium. Aliquots were analyzed by UV–visible spectrophotometry at pre-determined time intervals, using a Shimadzu 1800 spectrophotometer to acquire data at λ_{max} 540 nm. All experiments were carried out in triplicate. The absorbance values were converted to concentration based on the calibration curve ($y = 0.051x + 0.002236$,

$r^2 = 0.9980$).

After the kinetics experiments, the data were mathematically treated using kinetics models to establish the equations which describe the behavior of the absorbance from the solution as a function of contact time with the adsorbent. Eq. (1) [31] was used to obtain these results, in which: t = time; k (k_{obs}) = pseudo-second-order rate constant in g mg⁻¹ min⁻¹; q_t (g L⁻¹) and q_e (mg g⁻¹) are the amount of dye adsorbed at time t and at equilibrium, respectively.

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} \quad (1)$$

After obtaining the rate constant, the linearized Arrhenius equation (Eq. (2)) [10] was used to calculate the activation energy:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (2)$$

in which: k (k_{obs}) = rate constant; A = frequency factor; E_a = activation energy; R = gas constant; T (K) = absolute temperature.

Entropy and enthalpy were calculated using the Eyring equation (Eq. (3)) [10], where k_b and h are the Boltzmann's and Planck's constants, respectively.

$$\ln\left(\frac{k_{obs}}{T}\right) = \ln\left(\frac{k_b}{h}\right) + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad (3)$$

Finally, the free energy was determined using Eq. (4) [10,31]

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (4)$$

2.4. Dyeing procedure using the treated water

In the second part of the study, the cotton fabrics were dyed with 0.5, 1.0, 1.5 or 2.0% (w/w) of C.I. Reactive Blue 222, based on the weight of the fabric. In this experimental section, 10 g of the fabric cut into 10 cm × 10 cm samples was used. Dyeing was performed in a high-temperature Kimak Tubotest AT 7RP dyeing machine with a liquor ratio of 1:10 and pH of 11–13 using Na_2CO_3 (12 g L⁻¹). In all cases, the wetting agent Biorol (1 g L⁻¹) and Na_2SO_4 were used (60 g L⁻¹). The dyeing bath temperature was fixed at 62 °C (45 min). The dyed samples were soaped, washed with running water and left to dry at ambient temperature. The experiments were conducted using distilled water (standard) and water treated with IWR and IWT. All experiments were carried out in triplicate. In order to analyze the results, the percentage exhaustion, which is a measure of how much of the dye migrated from the dyeing bath onto the fiber, was calculated. Absorption values for aliquots collected before and after the dyeing process were obtained on a 1800 Shimadzu UV-visible spectrophotometer and % exhaustion was calculated according to Eq. (5)

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