



POTENTIAL USE OF WOOL WASTE AS ADSORBENT FOR THE REMOVAL OF ACID DYES FROM WASTEWATER

BUCIȘCANU Ingrid¹, MAIER Stelian-Sergiu¹, CREȚESCU Igor²

¹“Gheorghe Asachi” Technical University of Iași, Faculty of Textiles, Leather and Industrial Management, Department of Textile and Leather Chemical Technology, 29 Prof. dr. docent Dimitrie Mangeron Blvd, 700050, Iași, Romania, E-Mail: decanat@tex.tuiasi.ro

²“Gheorghe Asachi” Technical University of Iași, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Prof. dr. docent Dimitrie Mangeron Blvd, 700050, Iași Romania, E-Mail: decanat@ch.tuiasi.ro

Corresponding author: Bucișcanu Ingrid, E-mail: iiacomi@ch.tuiasi.ro ibuciscanu@yahoo.com

Abstract: *At present, great amounts of raw wool are treated as waste and raise disposal problems. In the sustainable development context, wool is regarded as a biodegradable renewable resource and due to its complex chemical composition and fiber morphology, can find different useful applications. It is the aim of this paper to investigate the potential use of raw wool waste as a non-conventional adsorbent for Acid Red 337(AcR), currently used for leather and wool dyeing. Two wool-based adsorbents were prepared, namely scoured coarse wool (Wool-S) and wool activated with alcoholic solution of sodium hydroxide (Wool-A). Adsorbent dosage, dye concentration, pH and treatment time were factors taken in consideration for the assessment of the sorbate-adsorbent interaction. The removal efficiency (R %) is mainly dependent on the solution pH and on the activation treatment applied to wool: at pH 3, the removal efficiency reaches the highest values of 42% on Wool-S and 99% on Wool-A. The adsorption rate is slow and needs almost 6 h to reach equilibrium. The experimental data best fitted the Langmuir equilibrium adsorption model, which proves that the adsorbent possess surface active sites to which the dye sorbate binds in monomolecular layer. Raw wool waste is a potential cheap, biodegradable and effective adsorbent for colored wastewater treatment.*

Key words: *renewable resources, wool, keratin, low-cost adsorbent, acid dye, coloured wastewater.*

1. INTRODUCTION

Removal of dyes from wastewater is receiving considerable attention, both from aesthetic reasons and because of their toxicity [1], and mutagenic and carcinogenic potential [2]. Azo dyes, which account for more than 60-70% of the global dyestuffs industry, exhibit these adverse effects on humans and living organisms at particularly high levels [3].

Currently, adsorption is the preferred treatment technology for low-concentration colored wastewater, and activated carbon is considered the most efficient adsorbent [4], but has the disadvantage of being too expensive for many environmental applications. The increased interest in the valorization of renewable resources has driven the development of alternative low-cost adsorbents derived from agricultural and animal wastes, which proved their efficacy in removing different classes of dyes from aqueous solution, both in their native or chemically modified state [5].



During mankind history, wool has been one of the most widely used natural fibers. Keratin, the main constituent of the wool fiber, is responsible for its unique properties. In the last decades, wool has lost ground to the cheaper and performant synthetic fibers, and huge amounts of raw wool are considered a waste that raise serious disposal problems. Valorization of this renewable resource is achieved mainly by keratin solubilization and regeneration into value-added products, such as fertilizers [6] or biomaterials [7]. In the field of pollution treatment, research is focused on the potential use of wool waste as nonconventional adsorbent for heavy metals [8, 9] and dyes [10, 11].

The aim of this paper is to investigate the adsorptive capacity of raw coarse wool and chemically activated wool for one acid dye with mono azo structure, currently used for wool and leather dyeing. Effect of the sorbent dosage, dye concentration, working pH and contact time upon the dye removal efficiency was determined. The adsorbent–adsorbate interaction was investigated by means of kinetic curves and adsorption isotherms.

2. MATERIALS AND METHODS

2.1 Adsorbate and adsorbent materials

The anionic dye chosen as targeted adsorbate was Sellacid Red PF [C.I. Acid Red 337, single azo, molecular formula: $C_{17}H_{11}F_3N_3NaO_4S$, molecular weight: 433.34], supplied by TFL Ledertechnik GmbH, Germany. A dye stock solution was prepared at a concentration of 1000 mg/L, from which the experimental solutions were obtained by dilution to the required concentrations. The pH of the dye solutions was adjusted with NaOH 0.1 N for pH 5 and with H_2SO_4 0.1 N for pH 3 and pH 4 and measured on a WTW InoLab 720 pH meter.

Raw coarse wool from a local farmer, was scoured through a conventional process, with anionic detergent and sodium carbonate. The activation treatment was performed with 1% NaOH and 20% ethanol in aqueous solution at room temperature, under vigorous agitation in a reciprocating shaker, for 2 h. The scoured wool (Wool-S) and the activated wool (Wool-A) were thoroughly washed with distilled water, dried, disentangled, cut into 5 mm pieces and conditioned. A supplementary adsorbent (Wool-H) was obtained by plain hydrolysis with 1% NaOH.

2.2. Equilibrium sorption and kinetics experiments

Batch sorption experiments were carried out in glass vials containing 100 mL dye solution with different initial concentrations (20, 40, 60, 80, 100, 120 mg/L) and wool sorbent amounts accounting for doses of 1, 1.5, 2, or 2.5 g/L. The mixtures were agitated on a magnetic stirrer at 250 rpm and 25°C for 6h, in order to assure the reach of equilibrium. The residual solutions were separated from the wool sorbent by filtration through an inert synthetic polymer mesh.

Dye concentration in residual solutions was photometrically determined on a HACH DR/2010 single-beam spectrophotometer. For the tested acid red dye (AcR), maximum absorbance was recorded at 500 nm. The dye uptake at equilibrium, Q_e (mg/g) was calculated from Eq. 1:

$$Q_e = [(C_0 - C_e) \cdot V] / m_a \quad (1)$$

where C_0 and C_e (mg/L) are the initial and the equilibrium concentration of the tested dye, V (L) is the volume of the solution sample and m_a (g) is the mass of adsorbent. The dye removal efficiency, $R\%$ was calculated with the relationship given in Eq. 2:

$$R\% = [(C_0 - C_e) \times 100] / C_0 \quad (2)$$

The kinetics study was conducted at the same temperature and mixing regime. The initial concentration of all dye solutions was 100 mg/L, the adsorbent dose was 2 g/L, the working pH 3. The supernatant samples were withdrawn at preset time intervals between 15 min and 480 min, and the dye uptake at each time was calculated with a relationship similar to Eq.1.

To estimate the feasibility of the adsorption treatment, several preliminary adsorption tests were conducted with Wool-S, Wool-A, and Wool-H on dye solutions with the initial concentration of 100mg/L and adsorbent dosage of 2 g/L, at pH 5 and pH 3, respectively. The mixtures were contacted for 6h and left overnight before the absorbance of the residual solutions was measured.

3. RESULTS AND DISCUSSION

3.1. Preliminary adsorption tests

Comparative values of the removal efficiency, R of the AcR dye from aqueous solution on the tested sorbents are presented in **Fig. 1**. The scoured wool (S-W) exhibited a modest adsorptive capacity both at pH 5 and pH 3; the increase of R from 29% to 42% show a little influence of pH upon the native wool affinity for the dye. Both activation treatments improved the AcR dye uptake, which proves that the alkaline treatment created new functional groups that act as active sites on the sorbent material. Addition of alcohol to the treatment solution produced a slight but visible improvement of R, by about 8%. At pH 3, the Wool-A product was able to remove the dye almost entirely (R= 99 %), which is more than twice as much as the removal ability of Wool-S (R = 42%). PH lowering had a great influence on the adsorption capacity of the tested wool. The R values show that a simple chemical treatment can significantly improve the affinity of wool fiber for acid dyes

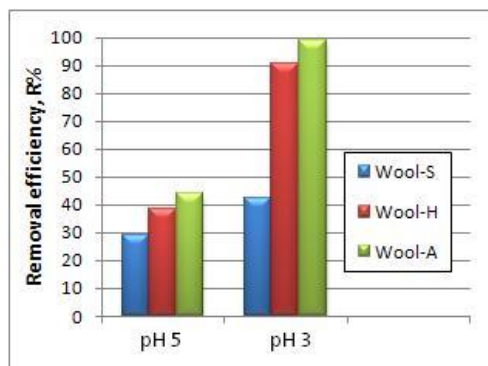


Fig. 1: Estimative values of removal efficiency of Acid Red 337 on the wool adsorbents ($C_0=100$ mg/L; adsorbent dosage: 2g/L)

3.2. The influence of adsorbent dosage and pH on the dye uptake

For a given initial dye concentration of, the removal efficiency increases with the increase of the adsorbent dosage up to a point and then suffers a slight decrease (see **Fig. 2**).

The pH influence is very strong and must be related to the keratin protein properties and to the activation treatment. Keratin macromolecule is an amphoteric polyelectrolyte, whose overall charge depends on the pH of the aqueous media. The pH at which the macromolecule is electrically neutral due to the balance between the positive and the negative charge of the side chains is called the isoelectric point (pH_{iz}). The pH_{iz} of keratins specific to wool is around 5 [12]. At $pH < pH_{iz}$, the protein carries a net positive charge, given by the $-NH_3^+$ protonated groups while at $pH > pH_{iz}$, has a net negative charge given by the $-COO^-$ deprotonated groups; at pH 5, Wool-A is in the isoelectric

domain, and few positively charged groups are available to interact with the dye anion. At pH 3, the number of the positively charged active sites, is significantly increased, and also the retention capacity of the activated wool fibers, which determines a removal efficiency of more than 90%.

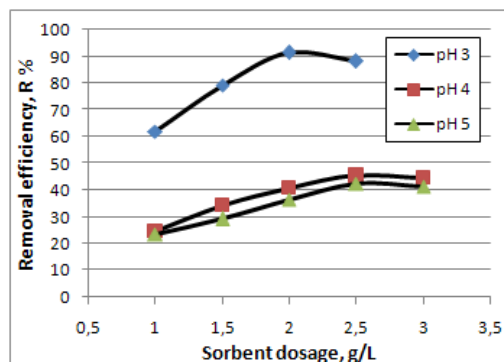


Fig. 2: Influence of sorbent dosage on the removal efficiency of AcR, at different pH values ($C_0 = 100 \text{ mg/L}$)

3.3. The process kinetics

The experimental kinetic curves are presented in **Fig. 3**. The overall sorption process is slow and needs almost 6 h till completion on activated wool, and about 2 h on nonmodified wool. Both on Wool-S and Wool-A, high adsorption rates were observed within the first 60 min but the equilibrium dye uptake was low on Wool-S (about 10 g/mg), and high on Wool-A (about 48 g/mg).

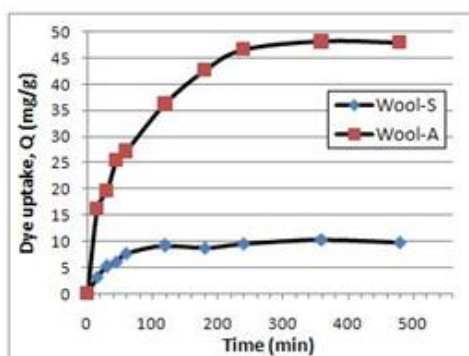


Fig. 3: Experimental kinetic curves of AcR on tested wool adsorbents ($C_0 = 100 \text{ mg/L}$; adsorbent dosage: 2 g/L, mixing rate = 250 rpm, $t^\circ = 25^\circ\text{C}$)

This behavior must be correlated to the changes induced in the wool fiber morphology by the activation treatment. The outer surface of the native wool is hydrophobic and blocks the penetration of more dye molecules inside the wool fiber; the adsorption process will stop in a short time. The activation treatment removes the superficial greasy matter and opens up the fiber structure; the dye uptake is higher but the penetration of dye molecules inside the fibers till the reach of equilibrium will last longer.

3.4. The equilibrium isotherms and sorption process modeling

The experimental sorption isotherms are given in **Fig. 4**. At the working pH, the maximum

adsorption capacity of 58 mg/g was recorded on the Wool-A sorbent, while a minimum dye uptake, of 13 mg/g was recorded for the Wool-S material. The higher equilibrium uptake on Wool-S is due to the increased number of active sites, which are created inside the wool fiber as the result of keratin macromolecule splitting during the alkaline hydrolytic treatment.

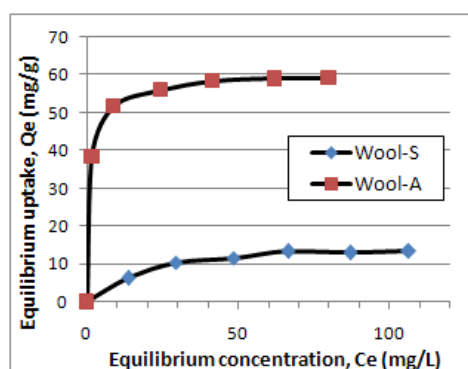


Fig. 4: Adsorption isotherms of Acid Red dye at pH 3 (Wool-A dosage = 1 g/L)

The Langmuir isotherm model assumes that adsorbent surface is homogeneous and possess identical active sites, on which the adsorbate accommodates in a monomolecular layer; the model coefficients are the maximum adsorption capacity, Q_m (mg g^{-1}) and k (L mg^{-1}), a thermodynamic constant related to the free energy of adsorption. A dimensionless constant termed as separation factor, R_L is defined as $R_L = 1 / (1+k \cdot C_{0M})$, where C_{0M} is the highest initial dye concentration; values of $0 < R_L < 1$ indicate favourable conditions for sorbate-adsorbent interaction in accordance with the Langmuir model [13]. The lower R_L , the stronger the interaction between the sorbate and the substrate and irreversible attachment of the sorbate molecules.

Table 1: Calculated parameters of the Langmuir isotherm model

Adsorbent material	Wool-S				Wool-A			
	Q_m (mg g^{-1})	k (L mol^{-1})	R_L	R^2	Q_m (mg g^{-1})	k (L mol^{-1})	R_L	R^2
Model coefficient	15.67	0.0591	0.123	0.9915	60.24	0.712	0.00996	0.999

The values of the calculated parameters of the Langmuir isotherm model, as given in **Table 1**, show that the equilibrium experimental data are best fitted by the Langmuir model. The predicted maximum monolayer adsorption capacities, Q_m are close to the experimental equilibrium uptake and correlation coefficients, R^2 are close to unity. The decrease of the R_L value with one order of magnitude proves that the alkaline treatment created new active sites with high binding capacity.

5. CONCLUSIONS

Coarse raw wool activated through a simple chemical treatment can be used for efficient removal of acid dyes from aqueous solution.

The alkaline activation treatment determines chemical alteration of the keratin macromolecules and changes of the wool fiber morphology, with a positive influence on the adsorption capacity of the tested wool.



The removal efficiency is significantly influenced by the solution pH and the adsorbent dosage. Best results were obtained at solution pH 3 and sorbent dose of 2 g/L, on solutions with dye concentration lower than 100 mg/L.

Raw wool waste is a renewable resource that can find valuable application as a cheap, biodegradable adsorbent for colored wastewater treatment. Further research is needed to analyze the influence of chemical auxiliaries on the dye uptake in real wastewater-sorbent systems.

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