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SORPTION OF TEXTILE DYES ON SORBENT MADE FROM COTTON TEXTILE WASTE - EQUILIBRIUM ADSORPTION

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Abstract: *The article analyzes the equilibrium adsorption and thermodynamics of the process of removing a disperse dye from water using a sorbent based on cotton textiles waste. Sorbent is made from cotton knitted fabric waste after cutting, during the procedure of clothes production. The loss after washing of raw cotton waste, before transformation into adsorbent, is about 9%. The yield of sorbent made from washed raw cotton waste is just under 40%. The characterization of the new sorbent showed that there is porosity in the structure of the particles and that the chemical composition is dominated by carbon. Equilibrium adsorption was verified by three models, Freundlich and Temkin. The Freundlich equilibrium isotherm showed the best result, i.e. the fitting curve is closest to the experimental points. Since the staining takes place according to the mechanism predicted by the Freundlich model, a monolayer of adsorbed dye molecules is formed in the initial phase of adsorption. At the same time, more layers of adsorbed dye molecules are formed at non-specific sites on the sorbent through self-association of adsorbed dye molecules. The newly-adsorbed dye molecules can bind to the previously adsorbed molecules within the sorbent. The heat of adsorption, determined from Temkin's model, has values that assume that an exothermic process takes place during the adsorption of the dye on the sorbent.*

Key words: *cotton knitted fabric, cutting, sorbent, disperse dye, equilibrium isotherms, thermodynamics.*

1. INTRODUCTION

Disperse dyes are generally non-ionic materials with limited dissolubility in water that have a substantiality to the hydrophobic fiber, for example, nylon, polyester, etc. [1, 2].

These are mostly substituted compounds of the azo, anthraquinone or diphenylamine compounds, which as being non-ionic, do not contain a solubilizing groups, and therefore, the surface active agents are used which finely distribute dye particles in aqueous dispersion. Since disperse dyes are frequently used in dyeing and since they are insoluble in water, special attention should be paid to the potential environmental problem after dyeing, when wastewater is necessary to be disposed of [3].

One method for removal of organic matters – dyes from aqueous solution is the use of solid sorbents. Properties of such substances, which make them useful, are the following: high porosity and specific surface area, as well as suitable places within for the adsorption of the dye molecules.

The most well-known solid sorbents are activated carbons, which are most frequently used in separation and purification processes. Lately, researches have been reinforced to find alternative inexpensive sorbent to replace expensive activated carbons. Industrial agro-cellulosic materials are potential sources for the preparation of cheap sorbents to remove dyeable and undyeable organic substances of the water [4, 5].

This paper deals with the preparation of the inexpensive sorbent from cotton cellulose waste and model adsorption of textile disperse dye on this sorbent from aqueous solution. Textile waste has emerged from the process of cutting in the process of clothing production. The aim is to use well generated textile material waste, transform it into a cheap sorbent and use it for decolorization of water. With the help of equilibrium models of adsorption as well as thermodynamics of the process, the manuscript shows the method of dye binding, the influence of temperature and the feasibility of the process in general.

2. EXPERIMENTAL PART

2.1 Textile waste processing

Textile waste is derived from cotton knitted fabric for the manufacture of women underwear. It is a by-product of cutting out stacked parts of cotton knitted fabric. Cotton waste, which occurs during this cutting process of one set of cutting layers, in a professional workshop, is about 5 kg.

Sorbent, used for adsorption of disperse dye, is a material obtained by chemical and physical modification of cotton cellulose waste. After collecting, the waste was washed, dried and cut into the finest parts. Then, it was treated with a solution of H_2SO_4 (Tehnohemija, Serbia) (ratio 1:5) for 48h at room temperature. Thereafter, heating at 700°C followed for 1.5 h. Then, cooling and fragmentation were performed, rinsing with distilled water and, finally, the neutralization of aqueous solution of sodium bicarbonate (Tehnohemija, Serbia). Final drying (100°C) and grinding were the last stages in the preparation of the inexpensive sorbent from cotton waste.

2.2 Adsorption process

The test of adsorption model was carried out in glass vessels in which sorbent was suspended in a solution of disperse dye (the adsorbate). Glass vessels were placed on a shaker (120 rpm, circular motion) at a temperature of 20, 40 and 60°C and kept for some time. The amount of sorbent was 1 g, in all cases, while the solution in a constant amount of 0.1 dm^3 contained a disperse dye concentration in the range of 10–100 mg/dm^3. Processing time, with continuous stirring, was 60 min, the pH of the dye solution was 3, in all cases.

Used dispersed dye belongs to the group of monoazo dyes with two nitro and one acetamide group; there are thiophene and diethylaniline in the strucuture, as well. The sign of the dye is C.I. Disperse Green 9 (DG9), it is not dissolved in water and it is used for dyeing polyester textile material at high temperature and pressure.

2.3 Methods

Determining the absorption of dye solution was done is in a spectrophotometer UV-VIS *(Cary 100 UV-VIS Conc, Varian)* at the maximum of the spectrum, i.e. at 680 nm.

SEM and EDS measurements were performed on TESCAN MIRA3 microscope (The Czech Republic).

The *Freundlich* adsorption isotherm is of empirical character and describes the adsorption on energy heterogeneous surface where the adsorbed molecules interact. This model well describes the multilayer adsorption [5].

The *Freundlich* model is shown by the following equation:

$$\ln(q_e) = \ln(K_F) + \frac{1}{n_F} \cdot \ln(C_e) \quad \textbf{(1)}$$

where: K_F - (mg/g)·(dm^3/mg)$^{(1/n)}$ and n_F - constants typical for the proposed system: a sorbent, adsorbate and the solvent; q_e - (mg/g) amount of adsorbed dye (adsorbate) per unit mass of sorbent at equilibrium time; C_e - (mg/dm^3) final (equilibrium) concentration of the dye solution;

The *Temkin* isotherm [6] is represented by the following equation:

$$q_e = B_T \cdot \ln(K_T) + B_T \cdot \ln(C_e) \quad \textbf{(2)}$$

where: K_T - (dm^3/mg) and B_T - *Temkin* constants, the first of which represents the adsorbate - sorbent interactions, and the second is related to the heat of adsorption b_T - (J/mol);

B_T and b_T are connected as follows:

$$B_T = \frac{R \cdot T}{b_T} \quad \textbf{(3)}$$

where: R - (8,314 kJ/mol·K) is a universal gas constant;

3. RESULTS AND DISCUSSION

Since the sorbent is made from cotton textiles waste after cutting out the stacked cutting parts, it is interesting to clarify something about the generated waste. It is calculated the degree of loss from cutting the parts for producing cotton underwear in 3 different widths, whose resulting loss–waste is used to make a sorbent for the adsorption of disperse dye. All cutting images show the expected loss which occurs at fitting of cutting parts. It was found that cutting textile parts with a width of 152 cm causes the least loss of material (14.18%), due to the suitable combination of cut parts compared to other widths (17.57% for 145 cm and 19.54% for 140 cm).

The characterization of the adsorbent was done with the aim of introducing the basic fusion-morphological properties as very important factors for the successful performance of the adsorption process.

The loss after washing of raw cotton waste, before transformation into adsorbent, is about 9% in relation to the pre-washing sample of waste. The yield of the sorption material made from waste cotton textiles is about 40%.

The used powdered sorbent is granular material with a heterogeneous structure of the particles, with indented shape and forms. Inside the particles, there are cracks, cavities and channels, which are the basis of the porosity of the material. Micrograph of Figure 1 shows the appearance of adsorbent particles with a magnification of ×200.

The EDS system enables a quick assessment of the primary composition of the sample. The following chemical elements were detected: C (49.46%), O (48.20%) and Na (2.34%). According to the EDS analysis, carbon is the most abundant, as expected, while the greater presence of oxygen is related to metal oxides (Na), since this metal has been detected, as well as the fact that reaction of adsorbent with the oxygen from the air is possible.

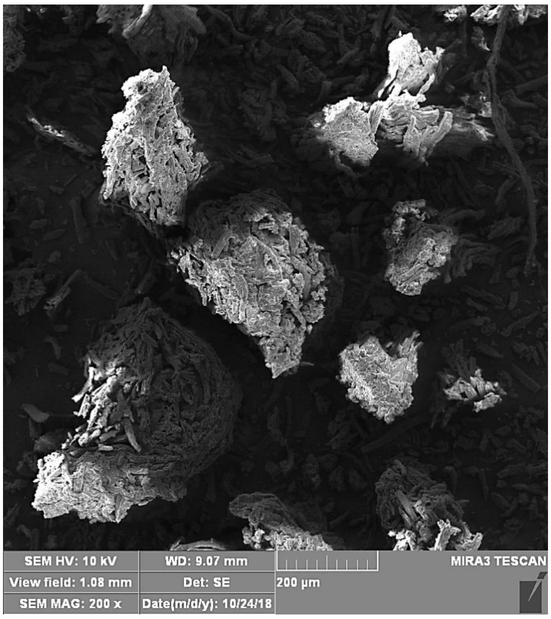

Fig. 1. *SEM micrograph of the applied sorbent*

The diagram of Figure 2 represents a graphical interpretation of the *Freundlich* linear isotherms for the adsorption of the disperse dye on the sorbent, for a constant quantity of a sorbent (1 g) and the temperature range of 20–60°C.

On the basis of this diagram and fitting straight lines according to the *Freundlich* model, the suitability of this model to describe the adsorption of dye applied for the sorbent from textiles waste has been evaluated. Since the fitting lines pass very closely to the experimental points, the validity of the *Freunlich* model is verified.

According to the diagram in Figure 2, the fitting curve at 60°C is located in the top part of the diagram in the topmost position, which shows that the adsorption capacity is the greatest at the highest temperature. Slightly lower position has the fitting curve at 40°C and much lower position was observed at temperatures more than 20°C.

If it is assumed that the dyeing is performed by a mechanism intended by the *Freundlich* model, in the initial phase of adsorption, a monolayer from the adsorbed dye molecule is formed, after which immediately follows the formation of multilayer from adsorbed dye molecules at nonspecific sites in the sorbent via self-association. The newly-adsorbed dye molecules can bind to the previously adsorbed molecules within the sorbent. There are also aggregated dye molecules from the solution, which can also be adsorbed. Dye aggregation within the sorbent and thus the formation of a multilayer of adsorbed dye molecules seems likely given the fact that relatively long and flat disperse dye molecules tend to self-combine in solution via π-π interaction (noncovalent interaction between aromatic rings) between adjacent dye molecules [5].

The coefficients of determination for this isotherm are in the range of 0.970–0.983, which means that *Freundlich* model can be used for a good enough description of DG9 dye adsorption to the sorbent.

K_F, one of the *Freundlich* constants, is used as a relative measure of adsorption capacity. A higher value (K_F = 0.18–0.55, depending on the temperature) indicates a higher adsorption capacity.

Other *Freundlich* constant, n, is an empirical parameter that changes with the degree of heterogeneity, indicating the degree of non-linearity between the receiving capacity of the dye and the concentration of non-adsorbed dye, and relates to the distribution of bound ions on the surface of the sorbent. In general, $1/n<1$ shows that the adsorbate is sufficiently adsorbed on the adsorbent, the adsorption capacity increases, new positions for adsorption appear and the higher the value of n, the stronger the adsorption intensity. The results confirm that $n>1$, i.e. 1.23–1.38>1, or $1/n<1$, i.e. 1/(1.23–1.38)<1.

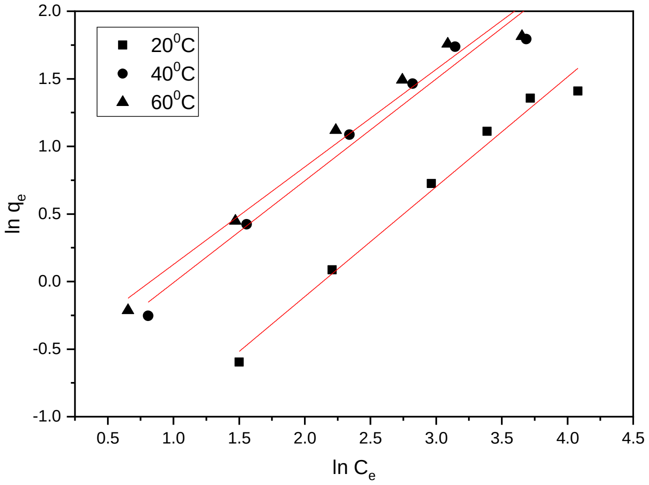

Fig. 2. *Graphic representation of the Freundlich model*

Figure 3 provides a graphical dependence of the variables from the *Temkin* isothermal equations for temperature range 20–60°C. According to the appearance of curves after the fitting, it is noticeable a little weaker coverage of experimental points on the diagram, and, consequently, a somewhat worse result in comparison to the *Freundlich* model.

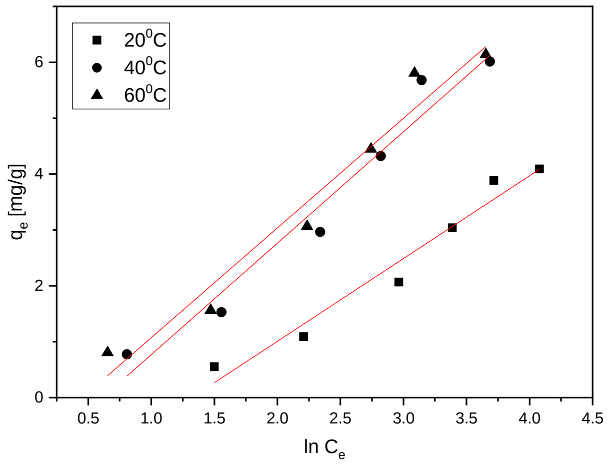

Fig. 3. *Graphic representation of the Temkin model*

The coefficient of determination, R^2, obtained from the *Tempkin* model (0.960–0.964), has smaller values in relation to the previous isotherm which partly diminish the applicability of the *Tempkin* model for the specific case of adsorption.

Values of the *Temkin* constant B_T, associated with the heat of dye adsorption on a sorbent, is in the range 1.48–1.99, while the constant K_T has a values 0,27–0,63 dm^3/mg. Heat of adsorption, b_T, determined from the *Temkin* model, has values from -1.24 ÷ -1.87 kJ/mol, which implies the exothermic process during adsorption of DG9 onto the sorbent.

This adsorption energy will be the sum of all individual adsorptions that occur at different places on the sorbent surface. In addition to the structure of the dye and the substrate, the value of the heat of adsorption is greatly influenced by the presence of an additive or impurity which directly impacts the ability of interaction and binding, both by physical or chemical bonds. Since the heat of adsorption is small and negative, the interaction of dye and sorbent is mainly accompanied by reversible physical adsorption which are supported by weak electrostatic forces (dipolar bonds, *Van der Waals* forces or hydrogen bonds) [7].

4. CONCLUSIONS

By the process of thermochemical conversion, the collected cotton waste from the cutting of cutting deposits was, with the help of sulfuric acid, as an activating agent, converted into a powder adsorbent. The sorbent has a porous structure, and the primary composition is dominated by carbon. Thus produced inexpensive sorbent was used to study the adsorption of disperse dye to the sorbent using several significant models for equilibrium adsorption.

The *Freundlich* equilibrium model best describes the process of adsorption of the disperse dye onto the sorbent from cotton textiles waste after cutting. From the *Temkin* model, the calculated heat of adsorption is small and negative, which means that the interaction of dye and sorbent is mainly accompanied by reversible physical adsorption supported by weak electrostatic forces.

Characterizing other, similar in nature, solid waste materials, can help to elucidate the adsorbate–sorbent interactions, which leads to the optimization and greater efficiency of the adsorption process, as an environmentally friendly procedure.

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