



EMISSION REDUCTION OF COLORED WASTE WATER AFTER CONTACT WITH A NATURAL SORBENT WITH A SPECIAL FOCUS ON THE THERMODYNAMICS OF ADSORPTION

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Abstract: The possibilities of using an inexpensive sorbent for dyes removal from waste waters after textile dyeing were investigated in this work. Ashes from city heating plant that arise as a by-product in the burning process during the city central heating operated were sorbent. After chemical modification of the ashes it were transformed to the efficient sorbent. Based on the results from this paper, it can be said that the sorbent produced from ashes has potential for the textile dyes removal from aqueous solutions and emission reduction of toxic dyes. A metal complex textile dye was used and the adsorption thermodynamics were studied. On the basis of obtained results, it can be concluded that the natural sorbent is an efficient sorbent for metal complex removal dye from aqueous solution and has a potential for use on an industrial scale. Characterization of other similar, solid waste materials can help explain adsorbate-sorbent interactions in order to optimize and increase efficiency of adsorption process as an environmentally acceptable process. Negative values of free energy change indicate a spontaneous nature of adsorption, negative values of free enthalpy change indicate an exothermic adsorption process and negative values of free entropy change indicate a decrease of disordered system at solid – liquid interface during adsorption. Based on adsorption, kinetic and thermodynamic parameters it can be concluded that chemisorption of the dye on the sorbent is also present together with physical adsorption.

Keywords: ashes, dyeing, metal complex dye, enthalpy, entropy, free energy.

1. INTRODUCTION

Last few decades several decolorization methods were reported, some of them adopted in textile industry. Among many dye removal techniques, adsorption procedures give the best results because they can be used to remove various coloration materials. The most of commercial systems use activated carbon as a sorbent for dye removal from waste water due to its excellent adsorption abilities. Although activated carbon has advantages as a sorbent, its widespread use is limited due to high costs. To reduce treatment costs attempts are made to find cheap alternative sorbent [1].



Dye removal with various sorbents is subject of some recent research works. Waste agriculture materials, sugar cane pith, wood sawdust, pine bark, corncob, rice bran, rice husk, coconut shell fibers, walnut shell, and soy and cotton seed hull were investigated for their adsorption properties and it was reported that these materials can adsorb various pollutants including dyes. Waste sawdust and sugar cane pith are also able to adsorb significant quantities of wastewater dyes while palm tree particles were used in basic dyes adsorption [2, 3].

This paper attempts to explain the absorption of metal complex dye on sorbent from ashes obtained after burning of brown coal in the city heating plant using thermodynamic principles. This can impact on a better understanding of the adsorption of waste dye to a waste solid sorbents to reach a wider and more practical application on a larger scale.

2. EXPERIMENTAL PROCEDURE

2.1 Materials and methods

The sample, city heating plant ashes, used in the experiments, was obtained after burning of brown coal. One of the reasons for the use of ash as adsorbent, lies in the fact that it is a waste material that is easy to find and practically it is very inexpensive means. After collecting and drying the ash was sieved to 0.7 mm particle size. After combustion the ash contains many metal salts, especially oxides making basic pH of ash solution in distilled water. In this form the ash has not a satisfactory adsorption power (tested practically), and its modification is necessary by treatment with 8 % sulfuric acid for 40 min. The treatment is repeated until ash water extracts become neutral or slightly acidic with pH 6-7. The treatment is followed by distilled water rinse and air drying. The constant amount of ashes of 1-4 g was used, and 100 cm³ of solution contained dye concentrations of 10-100 mg/dm³, while the equilibrium time was 30 min. The procedure is based on similar research [3].

Models of waste water after dyeing were prepared with metal complex dye C.I. Acid Blue 193. Preliminary results showed the most efficient adsorption occurred at pH 10.

Thermodynamic parameters for adsorption systems were calculated using following equations [4]:

$$\ln\left(\frac{k_2}{T}\right) = \ln\left(\frac{k_b}{h}\right) + \frac{\Delta S}{R} - \frac{\Delta H}{R \cdot T} \quad (1)$$

$$\Delta G = \Delta H - T \cdot \Delta S \quad (2)$$

where: k_2 (g/mg min) is second order adsorption rate constant; T (K) is temperature; k_b ($1.38065 \cdot 10^{-23}$ J/K) is Boltzmann's constant; h ($6.626 \cdot 10^{-34}$ J·s) is Planck's constant; ΔS (J/K·mol) is entropy change; R (8.314 J/Kmol) is universal gas constant; ΔH (J/mol) is enthalpy change; ΔG (J/mol) is Gibbs free energy change.

Plot $\ln(k_2/T)$ vs. $1/T$ gives a straight line from where enthalpy and entropy changes can be calculated.

Thermodynamic parameter values are actual indicators for practical application of the process. In some adsorption processes entropy and enthalpy are considered in evaluation of spontaneous process.

Rate constant is also expressed as a temperature function with Arrhenius type equation [5]:

$$k_2 = A \cdot \exp\left(\frac{-E_a}{R \cdot T}\right) \quad \ln k_2 = \ln A - \frac{E_a}{R \cdot T} \quad (3)$$

where: k_2 is second order adsorption rate equilibrium constant, g/mg min; A is sorption frequency factor; E_A is Arrhenius activation energy, J/mol; R is gas constant equal 8.314 J/mol K; T is process temperature, K.

The plot $\ln k_2$ vs. $1/T$ is a straight line with slope $-E_a/R$. Activation energy gives an idea on adsorption type which is mostly physical or chemical.

3. RESULTS AND DISCUSSIONS

The H_2SO_4 treatment of ashes increases the surface area and pore volume, while decreases its average pore diameter. The adsorption capacity of the ash enhances with increasing pH value in basic solution, which may be explained by surface condition of the ashes and by the changes of the dye in the basic solution [3].

SEM tests of sorbent samples has shown finely scattered material consisting of heterogeneous particles with irregular shape originating from agglomerates, probably from particular minerals, mostly below 5 μm in size. Micrograph in Fig. 1a shows magnification of 1000 $\times$ and in Fig. 1b it is 5000 $\times$ (Fig. 1).

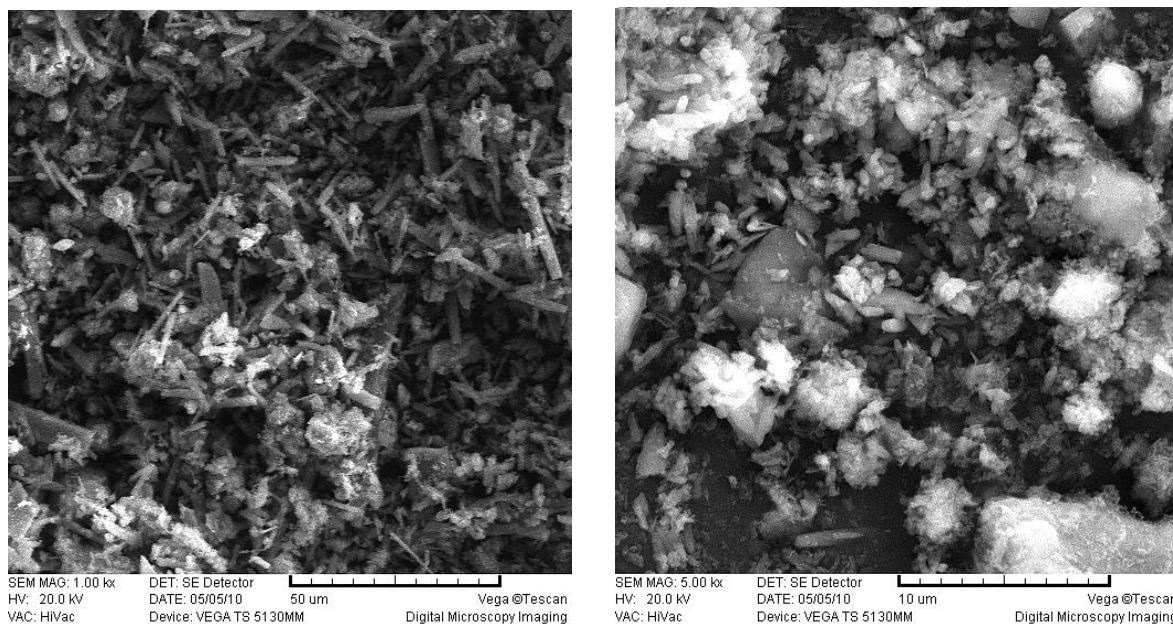


Fig. 1: Micrographs of studied sorbent, 1000 $\times$ to the left, b) 5000 $\times$ to the right

Temperature has two main effects on adsorption process. It is known that higher temperature increases diffusion rate of bound molecules over outer boundary layers into pores of sorbent particle. Moreover, adsorption equilibrium capacity of particular sorbent-adsorbate system is changed [3, 4].

Fig. 2 shows adsorption plots of used dye and all sorbent doses and on the bases of them (slope and intercept), major thermodynamic parameters, as adsorption process enthalpy and entropy were determined and on their basis the change of *Gibbs* free energy is calculated.

Graphs in Fig. 3 represents *Arrhenius* adsorption graphs for dye and serve for determination of process activation energy of all sorbent doses.

From these diagrams (figs. 2 and 3) it calculated values of thermodynamic parameters, entropy, enthalpy, Gibbs free energy and activation energy for studied dye, all sorbent doses, all initial concentrations and all studied temperatures of adsorption.

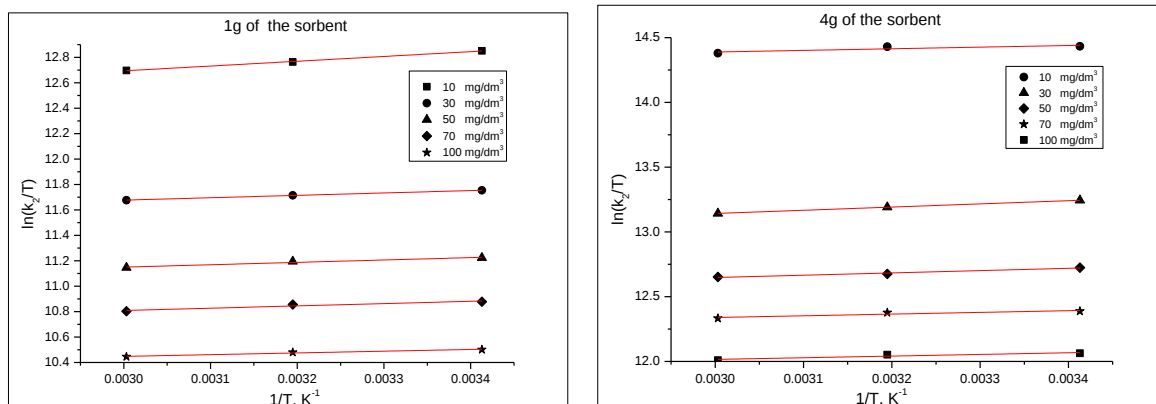


Fig. 2: Plots $\ln(k_2/T)$ vs. $1/T$ for adsorption of the dye on sorbent

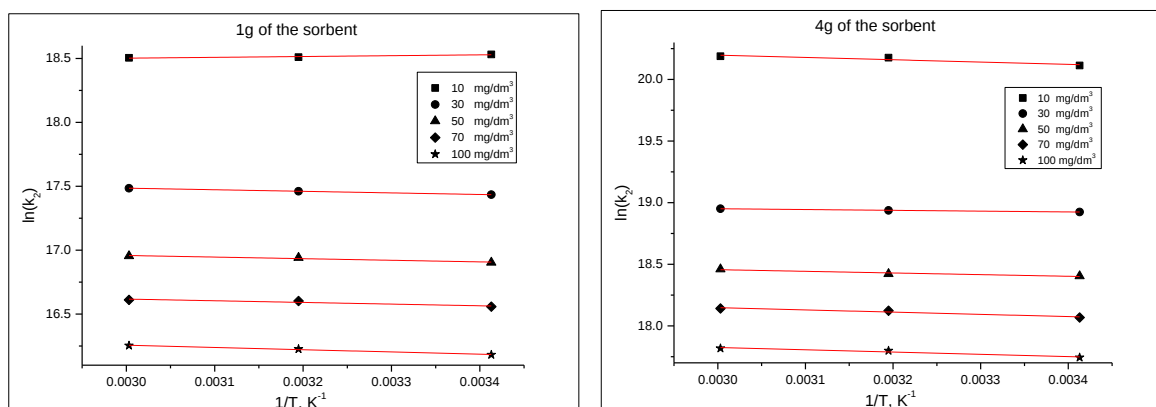


Fig. 3: Arrhenius graphs of the dye adsorption on sorbent

The results confirm the fact that activation energy of surface reaction has positive values. In our case, E_a has small values indicating fast reactions which can be affected also by the fact that some structurally different parts of sorbent may take a role of a catalyst decreasing activation energy. It is also known that, when reaction occurs in more steps, molecularity is decreased reducing activation energy. On the other hand, when association mechanism is considered, reaction rate is increased because of facilitated electron transfer, rearrangement of some reactant atoms into more favorable positions, better orientation etc. When considering these mechanisms, superposition of adsorption and desorption processes should also be taken into account [6].

Entropy is decreased when initial adsorbate concentration is increased, but increased when sorbent quantity is increased. Energy released during adsorption process compensates entropy loss of adsorbed molecules, i.e. stronger forces release more energy [7].

As entropy is a state function that can be considered as a measure of “bound” energy of an isolated system, i.e. energy that, contrary to “free” energy, cannot be converted to work, negative changes of entropy (-1.17 to -1.65 J/K·mol) correspond to reduced degree of freedom of adsorbed dye; that indicates decreasing of disordered system at solid-liquid interface during dye adsorption on sorbent. Moreover, reaction rate depends also on the probability of forming of activated complex having adequate configuration. If the structure of activated complex is more ordered then entropy reduction is higher and reaction rate is also lowered due to the effect of entropy factor. Adsorption entropy can be changed in two directions during forming of monolayer. First, entropy is decreased



due to increasing of adsorbed molecules order; when some surface covering is reached, increased movements of loosely bound particles may bring about the entropy increase. Entropy is an extensive state property of a system and its value depends on the substance quantity in the system [5].

Gibbs free energy is increased discontinuously with adsorbate quantity but continuously with temperature increase. By increasing sorbent mass the free energy is changed discontinuously showing similar and highest values with 1 and 3 g of sorbent. Since adsorption reaction can occur only if the change of total Gibbs free energy is negative, then negative values of free energy indicate spontaneity of adsorption process, i.e. favoring dye adsorption at 20, 40 and 60°C. Thereby, feasibility and spontaneous nature of adsorption process is confirmed at applied temperatures with good affinity of dye molecules to sorbent surface [8].

Negative values of enthalpy change (between -0.3 and -3.13 kJ/mol) indicate exothermic nature of adsorption interactions of studied dye and sorbent and the process is therefore energetically stable. It could be also concluded that breaking of bonds between adsorbate molecules and sorbent surface occurred because adsorbed molecules were not bound strongly on sorbent surface. They are in dynamic equilibrium with other molecules in bulk phase and can move only two dimensionally on the surface itself. When it is compared to three dimensional movements in bulk phase, this means enthalpy loss, indicating an exothermal process of adsorption [9].

Similar investigation reveal different results. The negative values of ΔG and positive ΔH obtained indicate that the black dye adsorption by sorbent is a spontaneous and endothermic process. The positive value of ΔS suggests that increased randomness at the solid/solution interface occurs in the internal structure of the adsorption of black dye onto sorbent [10].

Next, the negative ΔG suggests that the sorption of metal complex textile dye onto agro-residue is feasible and spontaneous thermodynamically. The positive ΔH suggests that this process is endothermic in nature while the positive ΔS indicates the increased randomness at the solid/liquid interface during the sorption process. The activation energy for the metal complex textile dye sorption by agro-residue was 45.84 kJ/mol indicating the physisorption process is predominant [11].

Also, molecules of the metal complex textile dye can remove by fungi, so the negative values of ΔG confirm the feasibility and spontaneous nature of the fungal biosorption processes at 25°C with a high degree of affinity of the dye ions for each biosorbent surface. The positive value of ΔH for *A. niger* biosorption (50.96 kJ/mol) suggests the endothermic nature of adsorption process favourable at higher temperatures and possible strong bonding between dye and the sorbent while the negative value of ΔS (-0.17 kJ/mol·K) revealed the decreased randomness at the solid/solution interface and no structural modification in *A. niger* during the adsorption of dye. The negative ΔH values of (-39.70) and (-14.48 kJ/mol) confirmed the exothermic nature of dye biosorptions on *R. arrhizus* and *T. versicolor* while positive ΔS values of 0.12 and 0.04 kJ/mol·K reflected the affinity of these biosorbents to dye in solution and some structural changes in sorbate and biosorbents, respectively. Generally, the change in adsorption enthalpy for physisorption is between 20 and 40 kJ/mol, but chemisorption is in the range of 80 - 400 kJ/mol. The values of the change in enthalpy indicated that each adsorption process is physical in nature [12].

4. CONCLUSIONS

On the basis of obtained results, it can be concluded that the natural sorbent is an efficient sorbent for removal of metal complex dye from aqueous solution and has a potential for use on an industrial scale. Characterization of other similar, solid waste materials can help explain adsorbate-sorbent interactions in order to optimize and increase efficiency of adsorption process as an environmentally acceptable process.



On the basis of experimental results the following conclusions are made:

- Negative values of free energy change indicate a spontaneous nature of adsorption.
- Negative values of free enthalpy change indicate an exothermic adsorption process.
- Negative values of free entropy change indicate a decrease of disordered system at solid – liquid interface during adsorption.
- Values of activation energy explain the type of adsorption.
- Based on adsorption, kinetic and thermodynamic parameters it can be concluded that chemisorption of the dye on sorbent is also present together with physical adsorption.

REFERENCES

- [1] A. A. Pelaez-Cid, A. M. Herrera-Gonzalez, M. Salazar-Villanueva and A. Bautista-Hernández, "Elimination of textile dyes using activated carbons prepared from vegetable residues and their characterization", *J. Environ. Manage.*, vol. 181, pp. 269-278, 2016.
- [2] A. A. El-Zahhar, N. S. Awwad and E. E. El-Katori, "Removal of bromophenol blue dye from industrial waste water by synthesizing polymer-clay composite", *J. Mol. Liq.*, vol. 199, pp. 454-461, 2014.
- [3] S. Banerjee, G. C. Sharma, M. C. Chattopadhyaya and Y. C. Sharma, "Kinetic and equilibrium modeling for the adsorptive removal of methylene blue from aqueous solutions on of activated fly ash", *J. Environ. Chem. Eng.*, vol. 2, pp. 1870–1880, 2014.
- [4] M. Dogan, Y. Zdemir and M. Alkan, "Adsorption kinetics and mechanism of cationic methyl violet and methylene blue dyes onto sepiolite", *Dyes Pigments*, vol. 75, pp. 701-713, 2007.
- [5] M. Dogan, M. H. Karaoglu and M. Alkan, "Adsorption kinetics of maxilon yellow 4GL and maxilon red GRL dyes on kaolinite", *J. Hazard. Mater.*, vol. 165, pp. 1142–1151, 2009.
- [6] M. Ugurlu, "Adsorption of a textile dye onto activated sepiolite", *Micropor. Mesopor. Mat.*, vol. 119, pp. 276-283, 2009.
- [7] A. Ozcan, E. M. Oncu and A. S. Ozcan, "Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto natural sepiolite", *Colloid. Surface. A.*, vol. 277, pp. 90-97, 2006.
- [8] S. Karaca, A. Gurses, M. Acikyildiz and M. Ejder, "Adsorption of cationic dye from aqueous solutions by activated carbon", *Micropor. Mesopor. Mat.*, vol. 115, pp. 376-382, 2008.
- [9] F. Renault, N. Morin-Crini, F. Gimbert, P. Badot and G. Crini, "Cationized starch-based material as a new ion-exchanger adsorbent for the removal of C.I. Acid Blue 25 from aqueous solutions", *Bioresource Technol.*, vol. 99, pp. 7573-7586, 2008.
- [10] M. Saakshy, S. K. Singh, A. B. Gupta and A. K. Sharma, "Fly ash as low cost adsorbent for treatment of effluent of handmade paper industry-Kinetic and modelling studies for direct black dye", *J. Clean. Prod.*, vol. 112, pp. 1227-1240, 2016.
- [11] F. Deniz and S. Karaman, "Removal of an azo-metal complex textile dye from colored aqueous solutions using an agro-residue", *Microchem. J.*, vol. 99, pp. 296–302, 2011.
- [12] Z. Aksu and G. Karabayır, "Comparison of biosorption properties of different kinds of fungi for the removal of Gryfalan Black RL metal-complex dye", *Bioresour. Technol.*, vol. 99, pp. 7730–7741, 2008.