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Thermodynamics of reactive dye adsorption on the bottom ashes

This paper describes the adsorption thermodynamics of textile reactive dye from aqueous solution on the bottom waste ashes formed by burning brown coal at the local city heating station. Reactive dyes are identified as problematic agents in the waste waters because they are water-soluble. In the waste-water, they are found in larger quantities than the other kinds of dyes and mainly in the hydrolyzed form, so they cannot be so easily removed by the systems of the conventional treatments. The values of thermodynamic parameters are the actual indicators for practical application in the adsorption process. Based on characteristic diagrams are determined the thermodynamic parameters, enthalpy and entropy of adsorption, and based on those determined the Gibbs's free energy changes. In all cases, there is a negative sign of the thermodynamic parameters. Based on the results, it can be concluded that absolutely dominates the physical dye adsorption. Certain anomalies (several cases) in some indicators may indicate an error and the existence of, for example, chemical interactions in the system.

Key words: adsorption, ash, reactive dye, entropy, enthalpy, free energy

1. INTRODUCTION

The first major challenge in the selection of favorable adsorption sorbents that are the most promising, mainly due to higher capacity and adsorption rate, high selectivity and low prices. The next genuine challenge is to clearly identify the mechanism of adsorption, especially the interactions involved in the interconnections of adsorbent/adsorbate. Adsorption processes, where the waste products are used as the adsorption devices - ashes, can be very useful and effective, but above all make simple and inexpensive materials as opposed to the conventional processes of the waste waters refinements.

Properties of the adsorption and equilibrium data, known as adsorption isotherms, describe how contaminants react with adsorbents, and thus are critical to the choice and wider application [1-4]. A precise mathematical description of equilibrium adsorption capacity is indispensable for the accurate prediction of adsorption parameters and quantitative comparison of adsorption behavior for different adsorbent systems (or for different experimental conditions) [5, 6].

Mathematical modeling is undoubtedly a valuable tool for analysis and the concept of adsorption systems and for theoretical evaluation and interpretation of thermodynamic parameters as well. However, the

isotherm can match the experimental data under one set of conditions but can be prone to total failure under another. In addition, none of the existing model is not fully applicable. This is understandable taking into account the hypotheses associated with their deviation.

Reactive dyes are typically based on the nitrogen chromophors combined with the various types of the reactive groups, for example vinyl sulphone, chlorotriazine, tri-chloro-pyrimidine, di-fluoro-chloro-pyrimidine. Azo-reactive dyes are characterized by the presence of one or more azo bonds. Almost 45% annually produced textile dyes, belong to the reactive class because of the intensive usage this kind of dyes for dyeing of cellulose, wool and viscous-rayon fibers.

Reactive dyes are identified as problematic agents in the waste waters because they are water-soluble. In the waste-water, they are found in larger quantities than the other kinds of dyes and mainly in the hydrolyzed form, so they cannot be so easily removed by the systems of the conventional treatments [7]. These dyes are more problematic than any other dyes and must be removed from the waste waters completely [8]. The removal of these dyes from the waste waters is a main challenge of the natural environment protection and there is a constant need of the efficient process, which can solve the problem of the dyed waste water.

Reactive dye applied in this paper belongs to the group of anionic dye due to the sulfo groups in its structure. It is a dye for cellulosic fibers dyeing by continuous processes. Dye is especially known for its

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high reliability, simple dyeing and great patience color.

2. EXPERIMENTAL PART

2.1. Materials

As and adsorbent bottom ash, from local city heating station was used. After collecting and drying, sieving to the particle size of 0.5 mm is carried out. Crude ash was abundantly rinsed with distilled water, dried in the air, again sifted and used in the experiment. In the process of adsorption, the reactive dye, C.I. Reactive Blue 49 from the textile factory was used.

2.2. The adsorption procedure

Adsorption test was performed in a glass Erlenmeyer flask in which the adsorbent is suspended in the solution dye - adsorbate. Erlenmeyer flasks are placed on the shaker - shaker at 150 rpm at a certain temperature and kept in a specified time. The amount of ash was varied in the amount of 1 to 4 g, while the solution in a constant volume of 100 cm³, contained concentrations of dye, 10, 30, 50, 70 and 100 mg/dm³. Processing time, with constant stirring, was 5, 10, 20, 30, 45 and 60 min, while pH varied from 2 to 12, was regulated by adding 1M solution of sulfuric acid or sodium hydroxide.

The mentioned dye concentrations were taken from the reason that they generally correspond to residual amounts of dyes in the solution after the wool textiles dyeing. Practically, in the experiment, commensurable concentration of pure dye with no add-ons that typically go with dyeing. It was found that equilibrium adsorption time of the dye on the ashes is achieved in 60 min, with the extension of time of treatment the adsorption did not significantly alter.

Upon completion of the adsorption, the solutions of dye and ash are passed through a filter paper. What follows is the determination of the absorption solution on the spectrophotometer UV-VIS spectrophotometer (*Cary 100 Conc UV-VIS, Varian*) at 575 nm.

SEM measurements were conducted on the device *VEGA TS 5130mm (TESCAN)* using a detector for secondary electrons. Ash used is a relatively fine-bulk material with heterogeneous particles of wide-spread shapes and forms that come from agglomerates of individual minerals, in general, less than 5 µm in size. Micrograph in Figure 1 emits a view with 5000x magnification.

Diffraction measurements were performed on the *Bruker D8 Advance diffractometer* in θ/θ "scan-step" mode in the range of angles 2θ diffraction of 10° to 90° in steps of 0.05° and a total exposure of 5 s per step. On the diffractogram obtained using, the *EVA*

software package v.9.0 into which is incorporated crystallographic database PDF-2, phase identification of an adsorbent was carried out, semi-quantitative phase analysis was done and the results of this analysis are shown in Table 1.

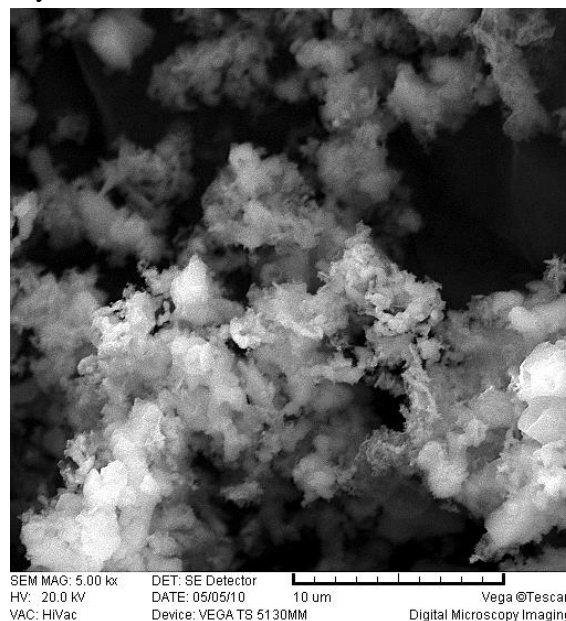


Figure 1 - Micrograph of the applied adsorbent

X-ray spectrum strips of the adsorbent, Table 2, reveal the presence of minerals, mainly dominated by gypsum and quartz, followed by calcite and aluminum hydrogen sulfate, and finally with a share below 10 % coming ferchilidit, melanterit, oldhamit and iron sulfate.

As the calcium and silicon compounds (sulfate and oxide) are present for the most part (including 50 % shift) and how it is known that these elements are more stable than in silicate compounds than as the oxides, it leads to the conclusion that there was no combustion at high temperatures [9].

Table 1 - The chemical composition of the ash according to diffraction measurements

| Ingredients | Mass content, % |
|---|-----------------|
| Ca(SO ₄)·2H ₂ O | 28.5 |
| SiO ₂ | 26.5 |
| CaCO ₃ | 13.2 |
| Al ₃ (HSO ₄)(SO ₄) ₄ ·9H ₂ O | 13.0 |
| K ₂ Ca(CO ₃) ₂ | 6.6 |
| FeSO ₄ ·7H ₂ O | 6.4 |
| CaS | 4.5 |
| FeSO ₃ | 1.3 |

3. RESULTS AND DISCUSSION

The values of thermodynamic parameters of the actual indicators for practical application process. In some adsorption processes, and entropy and energy are considered and must be taken into account in defining the process that occurs spontaneously.

3.1. Temperature effect on the adsorption

Temperature effect on the quantity of the adsorbed dye by the unit of ash mass was inquired in the temperature scale from 20 - 60°C at the changing starting concentrations of dye, figure 3. The diagrams on this picture bring the result for the maximal starting concentration of dye and the smallest quantity of ash, 1 g. The results for the other applied dye concentrations and adsorbent quantity were not shown because there were not bigger visual variations.

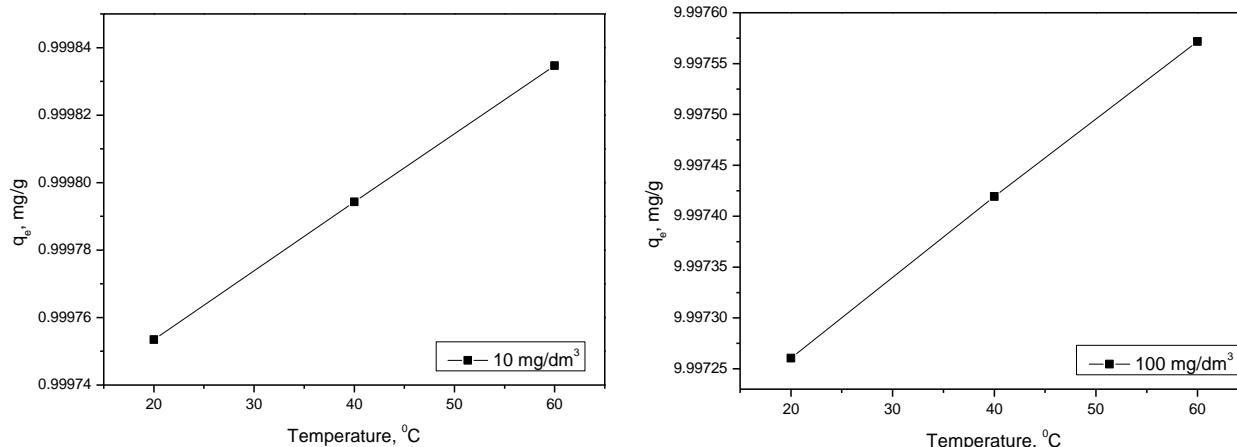


Figure 3 - Temperature effect on the amount of the adsorbed reactive dye by the unit of the mass of ash (q_e) for the lowest (left) and highest (right) starting concentration (ashes 1 g, processing 60 min)

3.2. The thermodynamic of adsorption

Thermodynamic parameters for adsorption systems were calculated using the following equation [11, 12]:

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

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

Where: k_2 (g/mg·min) - the rate constant of adsorption of the second order, T (K) - temperature, k_b ($1,38065 \cdot 10^{-23}$ J/K) - Boltzmann's constant, h ($6,626 \cdot 10^{-34}$ J·s) - Planck's constant, ΔS (J/K·mol) - change in entropy, R (8,314 J/K·mol) - universal gas constant, ΔH (J/mol) - change of enthalpy, ΔG (J/mol) - change of Gibbs free energy.

It was deduced that higher temperature simplifies dye removal with adsorption on an adsorbent. The data also shows that the temperature effect is not so significant because the changes were inconsiderable, in comparison to the adsorption at 20 and 60°C.

The amplification of the adsorption with temperature can be assigned to the increased number of active surface locations that are available for adsorption on every adsorbent, porosity and the overall cubage of the pores of the adsorbent. The intensity of the adsorption can also derive from the decreased thickness of the limitary layer, which surrounds the adsorbent with the temperature when the resistance, against transmission of adsorbent mass in the limitary layer, is reduced. This can also be the result of an increase in dye-molecule mobility with an increase of their kinetic energy and increased diffusion speed inside of the particles of adsorbents due to the temperature increase [10].

Graph of $\ln(k_2/T)$ versus $1/T$ gives a straight line with a slope $-\Delta H/R$ and intercept $[\ln(k_b/h) + \Delta S/R]$, where the change in enthalpy and entropy is calculated.

Figures 4 and 5 are diagrams for reactive dye and all amounts of adsorbent based on which (slope and intercept) are determined the basic thermodynamic parameters, enthalpy and entropy of adsorption, and based on those determined the change of Gibbs's free energies.

Table 2 - 4 brings specific values of the determined thermodynamic parameters, entropy, enthalpy and free energy for applied dye, any quantity of adsorbents, initial concentrations and applied temperatures.

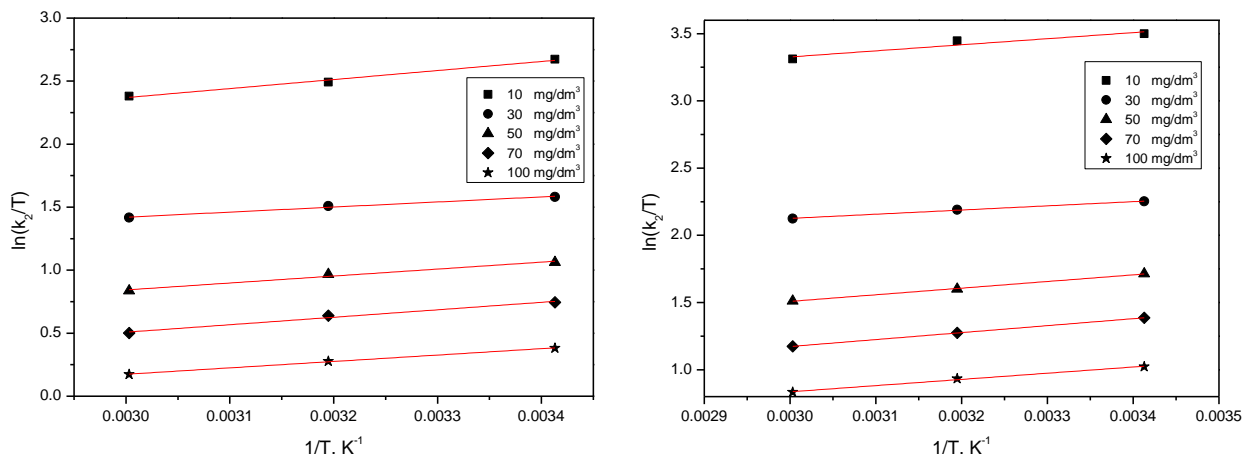


Figure 4 - Ln (k₂/T) vs 1/T for adsorption of reactive dye on ashes (1 g left, 2 g right)

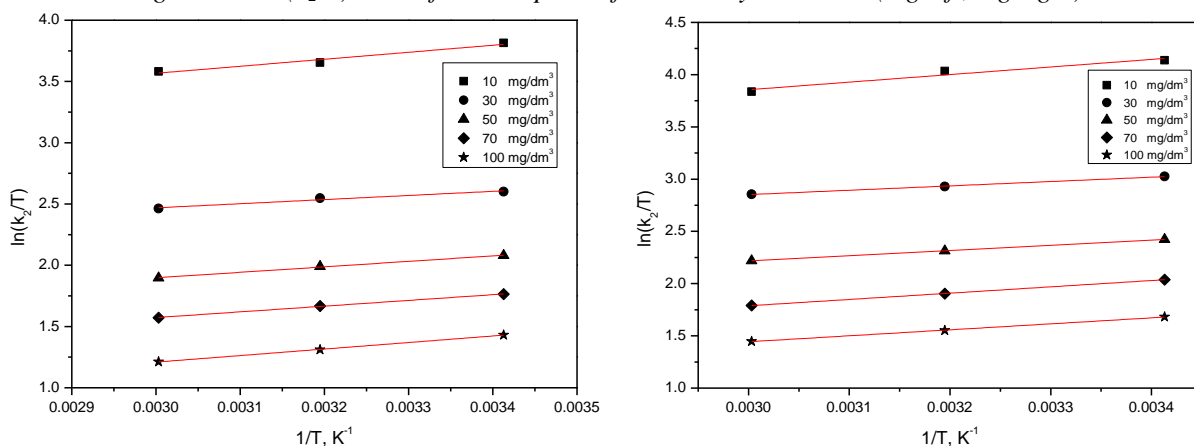


Figure 5 - Ln (k₂/T) vs 1/T for adsorption of reactive dye on ashes (3 g left, 4 g right)

Table 2 - Thermodynamic parameters of adsorption of reactive dye on ashes (1 g/100 cm³)

| Dye conc., mg/dm ³ | ΔS , J/mol·K | ΔH , kJ/mol | ΔG , kJ/mol | | |
|----------------------------------|-------------------------|------------------------|---------------------|-------|-------|
| | | | 20°C | 40°C | 60°C |
| 10 | -2.93 | -5.82 | -5.25 | -5.13 | -5.02 |
| 30 | -2.92 | -3.30 | -2.63 | -2.55 | -2.45 |
| 50 | -2.95 | -4.60 | -3.78 | -3.59 | -3.55 |
| 70 | -3.02 | -4.78 | -4.11 | -3.91 | -3.81 |
| 100 | -3.03 | -4.35 | -3.39 | -3.31 | -3.24 |

Table 3 - Thermodynamic parameters of adsorption of reactive dye on ashes (2 g/100 cm³)

| Dye conc., mg/dm ³ | ΔS , J/mol·K | ΔH , kJ/mol | ΔG , kJ/mol | | |
|----------------------------------|-------------------------|------------------------|---------------------|-------|-------|
| | | | 20°C | 40°C | 60°C |
| 10 | -2.69 | -3.65 | -2.97 | -2.89 | -2.81 |
| 30 | -2.73 | -2.88 | -1.89 | -1.87 | -1.71 |
| 50 | -2.80 | -4.02 | -3.39 | -3.35 | -3.25 |
| 70 | -2.89 | -4.27 | -3.58 | -3.55 | -3.44 |
| 100 | -2.96 | -3.69 | -2.99 | -2.90 | -2.86 |

Table 4 - Thermodynamic parameters of adsorption of reactive dye on ashes (3 g/100 cm³)

| Dye conc., mg/dm ³ | ΔS , J/mol·K | ΔH , kJ/mol | ΔG , kJ/mol | | |
|----------------------------------|-------------------------|------------------------|---------------------|-------|-------|
| | | | 20°C | 40°C | 60°C |
| 10 | -2.68 | -4.18 | -3.12 | -3.08 | -3.01 |
| 30 | -2.72 | -2.84 | -2.11 | -1.95 | -1.90 |
| 50 | -2.79 | -3.69 | -2.85 | -2.75 | -2.71 |
| 70 | -2.88 | -3.80 | -3.09 | -2.96 | -2.89 |
| 100 | -2.95 | -4.27 | -3.46 | -3.35 | -3.29 |

Table 5 - Thermodynamic parameters of adsorption of reactive dye on ashes (4 g/100 cm³)

| Dye conc., mg/dm ³ | ΔS , J/mol·K | ΔH , kJ/mol | ΔG , kJ/mol | | |
|----------------------------------|-------------------------|------------------------|---------------------|-------|-------|
| | | | 20°C | 40°C | 60°C |
| 10 | -2.52 | -6.05 | -5.14 | -5.03 | -4.86 |
| 30 | -2.63 | -3.55 | -2.75 | -2.68 | -2.61 |
| 50 | -2.78 | -4.17 | -3.43 | -3.21 | -3.08 |
| 70 | -2.85 | -5.04 | -4.22 | -4.10 | -4.02 |
| 100 | -2.92 | -4.61 | -3.98 | -3.81 | -3.72 |

According to the Tables 2 - 5, entropy increases with increasing initial concentration of adsorbate and is generally decreased with increasing amount of adsorbent. Reorientation or restructuring of water around the molecules of a dye is very unhelpful as far as the entropy is concerned, since it disturbs the existing water structure and imposes a new and ordered structure at the nearby water molecules. Energy released during the adsorption process compensates for the loss of entropy of adsorbed molecules, the stronger the forces, the more energy is released [11, 13].

As it can be stated that entropy can be thought of as a measure of "linked" energy of a closed material system, i.e. Energy which is in contrast to "free", it can not be converted into work, the change of the negative entropy (approximately - 3 J/K·mol) correspond to the reduction of degrees of freedom of the adsorbed dyes, i.e. suggests that disordered system is decreased at the interface solidly - solution during the adsorption of a dye on the ashes [13].

Free energy decreases continuously with an increasing temperature. By increasing the mass of ash free energy changes discontinuously, showing a close and the highest values for 1 and 4g of an adsorbent. Since the adsorption reaction is feasible only if the overall Gibbs free enthalpy change is negative, then (-) values of free energy indicate the feasibility and spontaneous nature of the process, i.e. favours the adsorption of the applied paint at 20, 40 and 60 °C. This is to confirm the feasibility of the process and spontaneous nature of adsorption at the applied temperatures with high affinity of the molecules for the surface of the adsorbents.

Small negative values of enthalpy change (between -2.9 to - 6.0 kJ/mol) indicate that the process is one of the physical adsorption, including weak exothermic attractive force, and that the process is energy-stable. Increasing the concentration of adsorbate as increasing concentration of adsorbent enthalpy change occurs mostly discontinuous. These phenomena can be explained with the fact that in the adsorption process the break of the link between adsorbate molecules and adsorbent surface occurred [14].

Energy released during adsorption is manifold during the measuring in the range of energies that originate from adsorption by different forces, for example. Van der Waals 4-10 kJ/mol, hydrophobic connection 5 kJ/mol, hydrogen bond 2-40 kJ/mol, coordinating ties about 40 kJ/mol, dipole connection 2-29 kJ/mol, chemical bond about 60 kJ/mol . In our case the change of enthalpy during adsorption on the ashes of dye, suggests that the adsorption reaction system of the dye largely excludes the Van der Waals connections, hydrophobic interactions and, to a lesser extent,

dipolar forces, since these interactions carry smaller amounts of energy [15].

4. CONCLUSION

Adsorption has certain advantages over conventional treatment processes because it eliminates the complete molecule, not leaving the parts in water. This is especially important for dyes containing metals, where the linked metals (e.g. Cr, Co, Cu) remained in the waste water and perhaps even more harmful non-complex form.

Removal of reactive dyes with ash was investigated under various conditions. Based on these results, we can say that the ashes of local city heating station are efficient adsorbent for removing reactive dye from aqueous solutions with a reasonable tendency of use in industrial environments. The characterization of other, similar in nature, solid waste materials, can help in clarifying the interaction adsorbate - adsorbent, which leads to greater efficiency and optimization of the adsorption, as an environmentally very acceptable procedure.

Based on experimental results can be drawn the following conclusions:

- **Negative values of free energy changes** indicate the spontaneous nature of adsorption: $\Delta G = - 2.45$ to -5.25 kJ/mol for 1 g of ash and all the applied temperatures; $- 1.71$ to -3.58 kJ/mol for 2 g ash and all used temperatures; $- 1.95$ to -3.46 kJ/mol for 3 g ashes and all the applied temperatures; $- 2.61$ to -5.14 kJ/mol for 4 g ashes and all the applied temperatures;
- **Negative values of free enthalpy changes** show that the adsorption process is taken to include the weak attractive forces that are exothermic: $\Delta H = - 3.30$ to -5.82 kJ/mol for 1 g of ash, -2.88 to -4.27 kJ/mol for 2 g ash; -2.84 to -4.27 kJ/mol for 3g ash, -3.55 to -6.05 kJ/mol for 4 g of ash;
- **Negative values of free entropy changes** indicate a reduction of unstable systems at the interface solidly - solution during the adsorption; $\Delta S = - 2.92$ to -3.03 J/mol·K for 1 g of ash, -2.69 to -2.96 J/mol·K to 2 g of ash, -2.68 to -2.95 J/mol·K for 3g ash, -2.52 to -2.92 J/mol·K for 4g ash.
- **Based on the thermodynamic data**, it can be concluded that absolutely dominates the physical dye adsorption. Certain anomalies (several cases) in some indicators may indicate an error and the existence of, for example, chemical interactions in the system.

Undoubtedly, many offer cheap adsorbents used for commercial purposes for the future. Based on this study, adsorbent based on ash shows good ability to

remove certain types of reactive dyes. Naturally, there are some limitations and problems. Despite numerous publications on low-cost adsorbents, for now there is little information contained in the full study of the individual adsorbents. Variable chemical nature of wastewater in a different period may reinforce the problem of the dye of specific adsorbents more. For the design of adsorption system, it is necessary to understand the mechanism of adsorption process in order to achieve optimization. It is also important to understand the adsorption mechanism for the efficient activation and regeneration of adsorbents. Although much has been achieved in the field of low-cost sorbents, it is still much work necessary to predict the effect of adsorption process for removing dye from actual industrial wastewater under operating conditions, (ii) to better understand the adsorption mechanism and (iii) use of low-cost adsorbents in industrial scale.

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IZVOD

TERMODINAMIKA ADSORPCIJE REAKTIVNE BOJE NA KOTLOVSKI PEPEO

Ovaj rad opisuje termodinamiku adsorpcije tekstilne reaktivne boje iz vodenog rastvora na kotlovski otpadni pepeo nastao posle sagorevanja mrkog uglja u gradskoj toplani. Reaktivne boje su identifikovani kao problematični agensi u otpadnim vodama, jer su rastvorljive u vodi. U otpadnoj vodi se nalaze u većim količinama nego druge vrste boja i uglavnom u hidrolizovanom obliku, tako da se ne mogu tako lako ukloniti sistemima konvencionalnih tretmana prečišćavanja. Vrednosti termodinamičkih parametara u adsorpcionim procesima su stvarni pokazatelji za praktičnu primenu. Na osnovu karakterističnih dijagrama se određuju termodinamički parametri, entalpija i entropija adsorpcije, a na osnovu njih promena Gibbs-ove slobodne energije. U svim slučajevima, postoji negativan predznak termodinamičkih parametara. Na osnovu rezultata, može se zaključiti da dominira fizička adsorpcije boje. Određene anomalije (nekoliko slučajeva) kod nekih pokazatelja mogu ukazivati na greške i postojanje, na primer, izvesne hemijske interakcije u sistemu.

Ključne reči: adsorpcija, pepeo, reaktivna boja, entropija, entalpija, slobodna energija

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