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The adsorption–desorption mechanisms on the powdered activated carbon (PAC) of an anionic textile dye (RBY 3GL)

Ahmet Gürses[a,*], Duygu Yalvaç[a], Kübra Güneş[a], Elif Şahin[a], Metin Açıkyıldız[b]

[a]*Department of Chemistry, K. K. Education Faculty, Ataturk University, 25240 Erzurum, Turkey, emails: ahmetgu@yahoo.com, agurses@atauni.edu.tr (A. Gürses)*
[b]*Department of Chemistry, Faculty of Science and Art, Kilis 7 Aralık University, 79000 Kilis, Turkey*

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ABSTRACT

Adsorption has many superior properties compared with other techniques for wastewater treatment. Activated carbon has been widely used as a versatile adsorbent with optimal sorption properties for the adsorption of chemical species from their aqueous solutions. One of the main drawbacks of the adsorption process in terms of sustainability is the difficulty of regeneration of treated activated carbon or the production of relatively unstable secondary wastes with waste disposal processes based on adsorption. Moreover, the elucidation of the mechanism of adsorption–desorption is extremely important in terms of regeneration or reuse of adsorbents and designing a sustainable adsorption systems. In this study, it has been aimed the examination of adsorption–desorption behavior of an anionic textile dye (Remazol Brilliant Yellow 3GL) from the aqueous solution on powdered activated carbon using of the corresponding experimental isotherm data together with their mathematical modeling. Experimental isotherms indicate that the adsorption and desorption of the anionic dye on activated carbon took place through the different pathways and exhibited the hysteresis lobes, which are similar to that of gas–solid systems. Also, it was determined that at low equilibrium dye concentrations, the adsorption and desorption pathways overlapped, and the shape of lobes changed with increasing temperature.

Keywords: Adsorption; Desorption; Anionic dye; Activated carbon

1. Introduction

An increasing water demand combined with the lack of natural water resources has made mandatory the extensive use of many technologies for the treatment and reuse of brackish water and secondary effluents from wastewater plants [1]. In desert regions like the Middle East, where freshwater is scarce and costly, it may be economically viable to reuse the wastewater for both agricultural and domestic purposes. However, wastewater contains pollutants such as organics, total dissolved solids, ammonia, boron, dyes and heavy metals and hence must be treated before use [2].

A number of removal technologies have been developed, which include dyestuff adsorption [3,4], electrochemical oxidation or reduction methods [5,6], electrochemical treatment combined with ultrasound technique [7], electrochemical coagulation [8], advanced oxidation [9] and membrane separation processes [10,11]. Each of these techniques offers advantages but also has limitations, such as significant amounts of chemicals, high operating and maintenance costs, and large amounts of excessive sludge [12]. However, adsorption is the most popular physicochemical treatment for the removal of dyes and other many dissolved organics from wastewaters [13]. In addition, activated carbon (AC) has been the water industry's standard adsorbent for the reclamation of municipal and industrial wastewater for potable use for almost 3 decades [14]. About 8.10^5 tons

* Corresponding author.

of 10,000 different synthetic dyes are used globally in textile industries. Textile wastewater is a complex and highly variable mixture of many polluting substances, including dyes [15]. Because Remazol Brilliant Yellow 3GL (RBY 3GL) is a common and typical anionic textile dye, it has been chosen as a representative example in this study. Anionic textile dyes have negative charge due to the excessive presence of the OH^- ions in aqueous solution. The adsorption of anionic dyes by hydrophobic and porous adsorbents from their aqueous solutions occurs predominantly through non-specific physical interactions such as van der Waals interactions, hydrophobic bonding, hydrogen bonding, dipole–dipole interaction, π–π electron interactions etc. [16]. It is therefore expected that the adsorption–desorption behavior of different types of dyes, especially on microporous hydrophobic materials, is similar. ACs are porous carbonaceous hydrophobic materials, which can be produced from both vegetable and animal sources, and they are frequently used as adsorbent for air pollution control as well as for wastewater treatment [17,18].

AC is commonly used as an adsorbent for decolorization but due to its high cost, it is not used in industrial scale [19]. The sustainability of the adsorption process greatly depends on regeneration of saturated AC. In order to reuse AC, chemical regeneration can be carried out by desorption of adsorbates using suitable solvents or by decomposition of adsorbed species using oxidizing chemical agents [20].

Although adsorption process has been widely studied by many researchers, the researches on the clarification of adsorption–desorption mechanisms are basic requirements for the design of adsorption systems and sustainability of process. This study aims the investigation of adsorption–desorption behavior of an anionic textile dye from the aqueous solution on powdered activated carbon (PAC) as well as mathematical modeling of the experimental adsorption–desorption data.

2. Material and methods

2.1. Materials

In this study, the obtained commercial PAC from Merck KGaA, Darmstadt, Germany (Catalog No. 2184) was used as adsorbent. The Brunauer-Emmet-Teller surface area, mean particle size, the micropore volume and mesopore volume of PAC were 900 m^2/g, 150 μm (<80%), 0.294 cm^3/g and 0.058 cm^3/g, respectively [21]. To remove moisture and other impurities, the AC sample was dried at 120°C for 3 h under vacuum and then transferred to stoppered bottles flushed with nitrogen before the adsorption experiments. A reactive textile dye (RBY 3GL, $C_{26}H_{24}ClN_9Na_2O_{12}S_3$), which is a representative example of anionic textile dyes, was chosen as adsorbate (Fig. 1).

2.2. Methods

Adsorption experiments were carried out using a thermostatic shaker at a shaking speed of 150 min^{-1} in 100 mL glass flasks containing 100 mL distilled water containing 0.1 g of AC and various initial concentrations (50, 75, 100, 125, 150 and 200 mg/L) of RBY 3GL. The flasks with their contents were shaken for the equilibrium adsorption time of 4 h [22] at the 298 K and natural pH. At the end of adsorption period, the dye solutions were separated from the adsorbent with centrifugation for 5 min at 3,750 min^{-1}. The RBY 3GL concentration in the supernatant solution was analyzed with UV spectrophotometer (Shimadzu 1201 UV-Vis) at 427 nm, which is the maximum wavelength of the dye solution. To calculate the dye concentrations from the absorbance values of solutions, the calibration curve, which is very reproducible and linear over the concentration range, was used. The amount of RBY 3GL adsorbed per gram of adsorbent (mg/g) was calculated from the difference between the concentrations in the solution before and after adsorption.

The desorption experiments were performed using a thermostatic shaker at a shaking speed of 150 min^{-1} in 100 mL glass flasks containing 100 mL distilled water with 0.1 g of the dye-loaded AC for the different equilibrium concentrations of the dye. The flasks with their contents were shaken for two h at the 298 and 323 K. The separation of supernatant and the analyzing of dye concentration were carried out like that of the adsorption experiments. In these experiments, the solution pH was unchanged, and only the effect of temperature was investigated, as it was intended to investigate the desorption behavior, not the regeneration of active carbon.

3. Results and discussion

3.1. Adsorption–desorption isotherms

Fig. 2 represents desorption isotherms of dye at 298 and 323 K together with its adsorption isotherm at 298 K. As seen from this figure, the adsorption–desorption isotherms on the AC (PAC) of dye exhibit different pathways, and thus, a hysteresis lobe appears. The adsorption and desorption behaviors of dye at low equilibrium dye concentrations are significantly similar to each other, whereas its adsorption state begins to be more favorable with increased equilibrium dye concentrations. At the same equilibrium dye concentration, the adsorbed dye amount is much higher in

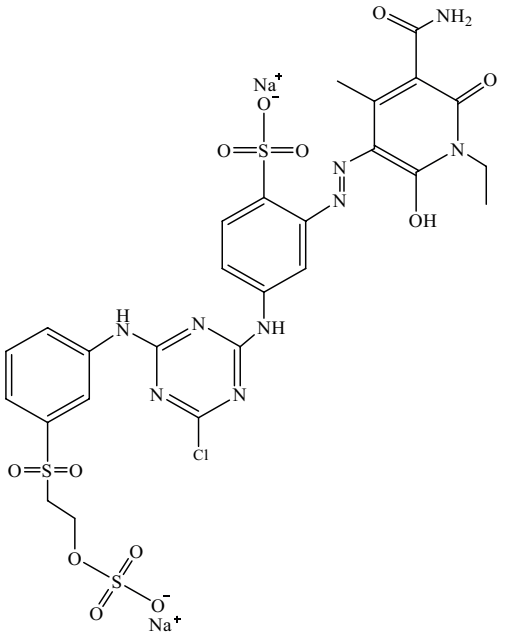

Fig. 1. Molecular structure of RBY 3GL.

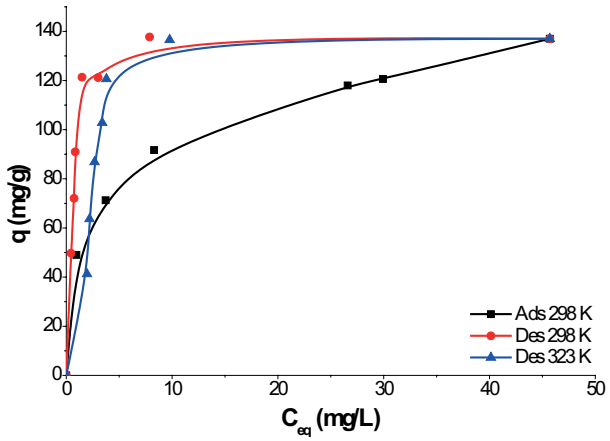

Fig. 2. The adsorption–desorption isotherms of RBY 3GL at 298 and 313 K.

the case of desorption. However, at the highest equilibrium dye concentrations, adsorption and desorption tendencies are quite similar. From these results, it can be said that the dye adsorption increases with increasing equilibrium dye concentrations, while its desorption has a tendency to remain constant. The adsorption on the hydrophobic AC (PAC) of negatively charged dye ions in the solution is predominantly due to the concentration difference. The adsorption of dye may increase also due to the hydrophobic interactions between dye molecules and AC surface and also dipole–dipole interactions among the dye molecules. For this reason, the tendency of the dye molecules to desorb is higher in the higher dye equilibrium concentration. This can also explain why hysteresis lobe has appeared. Therefore, desorption, which can take place in the form of ion diffusion toward the solution from micropores, requires a very high amount of adsorbed dye. In other words, a significantly higher dye ion desorption can occur only when the ion concentration in the micropores is sufficiently high.

There are a lot of studies that investigate the adsorption by the many commercial and/or synthesized ACs of the anionic dyes such as Brilliant Red HE-3B [23], Procion Red MX-5B [24], Reactive Red 120 [24], Methyl Orange [25], Reactive Blue, Reactive Red, Reactive Yellow [26], Remazol Brilliant Blue R [27], Rhodamine B [28] and Congo Red [29]. Whereas, the desorption studies related to the anionic dyes are extremely limited, and they were usually focused on the regeneration of adsorbents [28]. The maximum adsorption capacities determined for above anionic dyes are in the range of 93.1–162.0 mg/g and 10.5–35.4 mg/g. The adsorption capacity obtained in this study is also very close to the higher values. This may also indicate that the adsorption of anionic dyes on AC takes place predominantly via non-specific physical interactions.

On the other hand the high adsorption yield appeared in the beginning of the adsorption of dye can be attributed to the increased adsorption tendency due to the lower desorption tendency.

As a result, it can be said that the adsorption–desorption behavior described by dye concentration in the solution and surface depend not only on the nature of diffusion but also on the effectiveness of the interparticle interactions occurred in the pores.

The same adsorbed amount need to be higher equilibrium dye concentrations when desorption temperature increases. This indicates that the adsorption state is more favorable, and desorption tendency increases with increasing temperature. The hysteresis lobe appearing due to the difference between the adsorption–desorption behaviors also supports this interpretation. Especially, in the case of higher quantities of adsorbed dye, the increase in desorption temperature caused a marked difference in adsorption–desorption behavior.

The isosteric desorption enthalpy $(\Delta H_{des})_q$ and entropy $(\Delta S_{des})_q$ have been calculated by considering the certain amounts of the adsorbed dye. These quantities were calculated using Eqs. (1) and (2) [30]. The calculations were based on the same amount of adsorbed dye at different temperatures that corresponded to different equilibrium dye concentrations where the adsorption efficiencies were the highest.

$$\frac{d(\ln C)}{d(\frac{1}{T})} = -\frac{(\Delta H_{des})}{R} \tag{1}$$

$$\frac{d(\ln C)}{d(\ln T)} = \frac{(\Delta S_{des})}{R} \tag{2}$$

where C, T and R represent the equilibrium dye concentration, absolute temperature and gas constant, respectively. The calculated isosteric desorption enthalpy (–31.5 kJ/mol) indicates that desorption process is exothermic, and it can be explained with the increasing of effective interactions in the adsorption and/or the presence of the extra interactions based on the adsorption density in the pores. The calculated entropy value (101.6 J mol^{-1} K^{-1}) was quite high and positive, which points to an increased disorder of the system.

3.2. Mathematical modeling

In this study, some empirical mathematical models were developed to predict adsorbed amount of dye (q) based on equilibrium dye concentrations (C_e). First, the fitting of experimental data to various models such as linear, logarithmic, inverse, power, cubic, compound, growth and exponential was investigated for selecting the best equation. Then the final version of the chosen model with further changes, which will increase the R^2 values, was determined by non-linear regression using the SPSS 17.0 package program [31]. The coefficient of determination R^2 was one of the main criteria for selecting the best equation [32].

Obtained final empirical models after some modifications in the equations with determination coefficients (R^2) were expressed by the following equations (Eqs. (3)–(5)) for each experimental condition:

298 K adsorption:

$$q = 2.93.10^{-3}x^2 + 0.681x + \frac{97.45}{x^2} - \frac{153.98}{x} + 103.04 \quad \left(R^2 = 1.000\right) \tag{3}$$

298 K desorption:

$$q = 0.019x^2 - 1.163x + \frac{6.98}{x^2} - \frac{61.87}{x} + 151.89 \quad \left(R^2 = 0.967\right) \tag{4}$$

323 K desorption:

$$q = 0.091x^2 - 5.616x - \frac{116.89}{x^2} - \frac{246.13}{x} + 209.27 \quad \left(R^2 = 0.993\right) \tag{5}$$

where x (mg/L) is the equilibrium dye concentration.

When the regression coefficients are examined, it can be concluded that the derived second-order equations can very well express the effect of the equilibrium dye concentration on the amount adsorbed of dye.

4. Conclusion

In this study, the experimental data obtained from the adsorption of an anionic dye onto a commercial AC from the aqueous solutions were evaluated. The highlighted results are outlined as follows:

- The adsorption and desorption of dye took place through the different pathways and exhibited the hysteresis lobes, which are similar to that of gas-solid systems.
- At low equilibrium dye concentrations, the adsorption and desorption pathways overlapped, and the shape of lobes changed with increasing temperature.
- The isosteric enthalpy change (–69.05 kJ mol^{-1}) indicates that the desorption process is endothermic. The positive isosteric entropy change (227.45 J mol^{-1} K^{-1}) was calculated.
- The adsorption–desorption system very well defined by the second-order equations emphasizing the effect of equilibrium dye concentrations onto adsorbed amount of dye.

As a result, it can be said that the results obtained from this study provide a different perspective on the mechanisms of adsorption-desorption processes at the solid -liquid interface. These results are also of practical importance in assessing the sustainability of a prevalent wastewater treatment process, such as adsorption.

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