Removal of Direct Dyes from Aqueous Solution Using Various Adsorbents

Ö. Yavuz*, A. H. Aydin

Dicle University, Faculty of Science and Art, Deparment of Chemistry, TR 21280, Diyarbakir, Turkey

Abstract

Dyestuff production units and dyeing units have always had a pressing need for techniques that allow economical pre-treatment for colour in the effluent. The effectiveness of adsorption for dye removal from wastewaters has made it an ideal alternative to other expensive treatment options. Removal of direct dyes [direct yellow 50 (DY50), direct red 80 (DR80) and direct blue 71(DB71)] from an aqueous solution by different adsorbents such as activated carbon, raw kaolinite and montmorillonite was investigated. The adsorption isotherm data were fitted to the Langmuir isotherm. Parameters of the Langmuir isotherm have been determined using the adsorption data. Adsorption capacity of RAC (commercial activated carbon), HAC (activated carbon obtained from shell of hazelnut), KC (raw kaolinite) and MC (montmorillonite) increased in the following order: DY50 > DR80 > DB71, DB71>DR80>DY50, DR80>DB71>DY50 and DB71>DR80 (DY50 showed no absorption) for the direct dyes, respectively.

Introduction

Textile industries have shown a significant increase in the use of synthetic complex organic dyes as colouring materials[1]. Different processes for colour removal typically include physical, chemical and biological schemes. Some processes, such as electrochemical techniques and ion pair extraction, are relatively new for textile waste treatment, while others have been used in the industry for a long time.

Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, simplicity of design, use of operation and insensitivity to toxic substances [2]. Adsorption has been used extensively in industrial process for separation and purification. The removal of coloured and colourless organic pollutants from industrial wastewater is considered as an important application of adsorption processes [3].

At the present, there is a growing interest in using low-cost, commercially available materials for the adsorption of dyes. A wide variety of materials such as peat [4], various silicas [5], activated clay [6], banana pith [7], natural manganese mineral [8], shale oil ash [3], goat hair [9], alum sludge [10], natural zeolite [2], and mixtures of fly ash and soil [11] have been investigated as low-cost alternatives to activated carbon [12].

Many studies have been conducted to evaluate adsorption of dyes onto a wide range of natural and synthetic, organic and inorganic sorbents. Highest adsorption capacities have been reported for: 940 mg Reactive Black 5, 1190 mg Reactive Orange 96 and 1750 mg Reactive Red 120/g cucurbituril [13]; 104.2 mg Acid Green 27, 53,5 mg Acid Violet 27 and 51.0 mg Indigo Carmin/g living mycelium of Trametes versicolor [14]; 242 mg Basic Red 18/g palm-fruit [15]; 13.95 and 15.17 mg Acid Blue 29/g peat and fly ash, respectively [16]; and 1119, 873, 875, 190 and 120 mg Safranin and

*Corresponding author; e-mail: omer@dicle.edu.tr

914, 312, 277, 158 and 250 mg Methylene Blue/g as-dorbent for bark, rice hisk, cotton waste, hair and coal, respectively [17]; 5.92 mg direct red and 4.42 mg acid brilliant blue/ g banana pith, respectively [7]; 159.0 mg Maxilon Goldgelb GL EC 400 and 309.0 mg Maxilon Schwarz FBL-01 300/g granular activated carbon, and 14.9 mg Maxilon Goldgelb GL EC 400 and 55.86 mg Maxilon Schwarz FBL-01 300/g natural zeolite, respectively. [2]; 160 mg Drim yellow-K4G, 140 mg Drim blue-KBL and 100 mg Drim red K4BL/ g shale oil ash [3]. Approximately 88% of Dianix Blue [125 mg/dm³] could be removed from wastewater with 75 mg/dm³ recycled alum sludge at pH 9.13 [10]; 97.9% of Levafix Brill Blue EBRA[1.0 g/dm³] could be removed with a solution containing minimum 3 g/dm³ by chemical precipitation at pH 10.5-11.0 [18].

This study was calculated to investigate the adsorption capacities of locally available low-cost adsorbents kaolinite from Izmir, and shell of hazelnut from the Black Sea region of Turkey, for direct dye removal from wastewaters. The adsorbents used were kaolinite, montmorolinite and activated carbon obtained from shell of hazelnut, and their performance was evaluated against a commercial granular activated carbon.

Material and Methods

Adsorbate

Commercial quality direct dyes were obtained from Aldrich and used without any further purification. The results of the characterization and structure of direct dyes are given in Table 1 and Figure1, respectively. A stock solution of direct dyes was prepared in distilled water.

Adsorbents

Commercial activated carbon and Montmoronolite K 10 were supplied by Reidel de Häen (18003, powder, RAC) and Fluka (69866, MC), respectively. The adsorbent, raw kaolinite was collected from Usak-Turkey. It was sieved with 200 mesh (75μm) size and dried at 110°C and kept in bottles for use.

Preparation of Activated Carbon

Activated carbon (HAC) was prepared as follows: shell of hazelnut was ground and sieved (1.5 mm). This shell of hazelnut was used in a calcination process and the experiment was carried out as follows: a mixture of 250 g of shell of hazelnut, 110 g of ZnCl$_2$ and 110 g of water was kept overnight, then the mixture was calcinated at 350°C. Then, chemically prepared activated carbon was washed with water and dried [19]. The activated carbon was then used in adsorption experiments.

Procedure

Adsorption experiments were conducted in which aliquots of dye solution with known concentrations were introduced into glass bottles (100 cm³) containing accurately weighed amounts (1.0 g) of the absorbent. The bottles were shaken at 25°C using immersed water bath for a prescribed length of time to obtain equilibrium. The adsorbent was then removed by centrifuge at 4000 rpm or filtered by polypropylene syringe filters (0.45 μm).

The equilibrium concentrations of dyes were determined by a UV-visible spectrometer (Shimadzu UV 160).

Results and Discussion

The maximum wavelengths (λ_{max}) and extinction coefficients (ε) of prepared dye solutions were determined and are given in Table 1.

Effect of Shaking Time

The time-dependent behaviour of dye adsorption was examined by varying the contact time between adsorbate and adsorbent in the range of 10-60 min. The concentrations of dyes were kept as $5 \cdot 10^{-4}$ mol/dm³ while the amount of adsorbents added was 0.100 g. The dyes remaining plotted at a function of contact time (Figure 2) showed that the equilibrium between dyes and the ad-
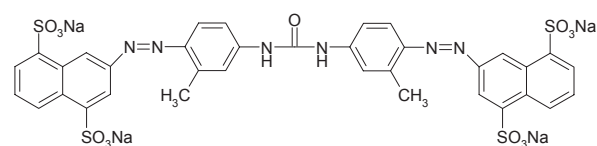
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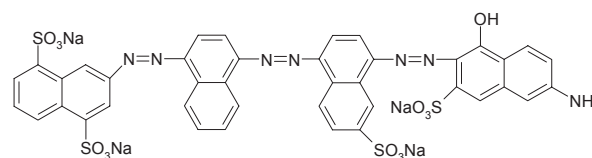
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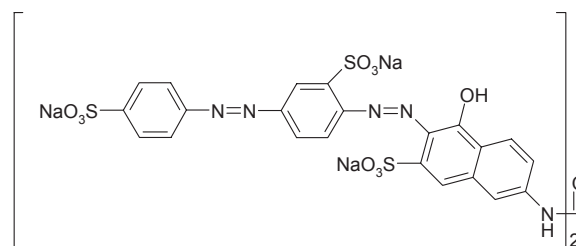
Direct Red 80

Fig. 1. Selected dyes for the adsorption study.

Table 1. Results of direct dyes characterization.

Dye	CAS No	Colour index No	F.W. (gmol^{-1})	λ_{max} (nm)*	ε (dm^3/mol.cm)*
Direct yellow 50 (DY50)	3214-47-9	29025	956.83	398	29878
Direct red 80 (DR80)	2610-10-8	35780	1373.09	527	34828
Direct blue 71 (DB7)	4399-55-7	34140	1029.88	587	44657

*Measured experimentally

sorbents was attained within 40 min. Therefore, a 40 min shaking time was found to be appropriate for maximum adsorption and was used in all subsequent experiments.

The removal of direct dyes by adsorption increased with time and attained a maximum value in 40 min and thereafter it remained constant for all the concentrations studied. It can be seen from Fig. 2 that equilibrium time was independent of dye concentration.

The distribution between the adsorbent and dye solution, when the system was at equilibrium; is defined by the adsorption isotherm and it helps to establish the capacity of the RAC, HAC, KC and MC for the direct dyes.

Graphs obtained plotting Ce (equilibrium concentration, mg/dm^3) versus Ca (amount of adsorbed dye, mg/g) for direct dyes on RAC, HAC, KC and MC samples are given in Fig. 3.

To quantify the adsorption capacity of adsorbents in relation to the dye, the experimental data points were fitted to the linear form of the Langmuir adsorption equation:

$$C_e/C_a = 1/(bC_m) + C_e/C_m \qquad (1)$$

Where, C_e is concentration of dye in the equilibrium solution. C_a is the amount of dye adsorbed per gram of adsorbents. C_m is the maximum amount of dye that can be adsorbed in a monolayer (adsorption capacity) and b is Langmuir isotherm constant related to the enthalpy of adsorption

Figure 4 shows, respectively, the straight lines obtained plotting C_e/C_a versus C_e for acid dye on RAC, HAC, KC and MC samples studied, correlation coefficients (r^2) being in all cases greater than 0.95 (all correlations were significant at the 0.005 probability level). C_m and b parameters were calculated from the least squares method applied to the straight lines and their values for direct dyes are summarized in Table 2.
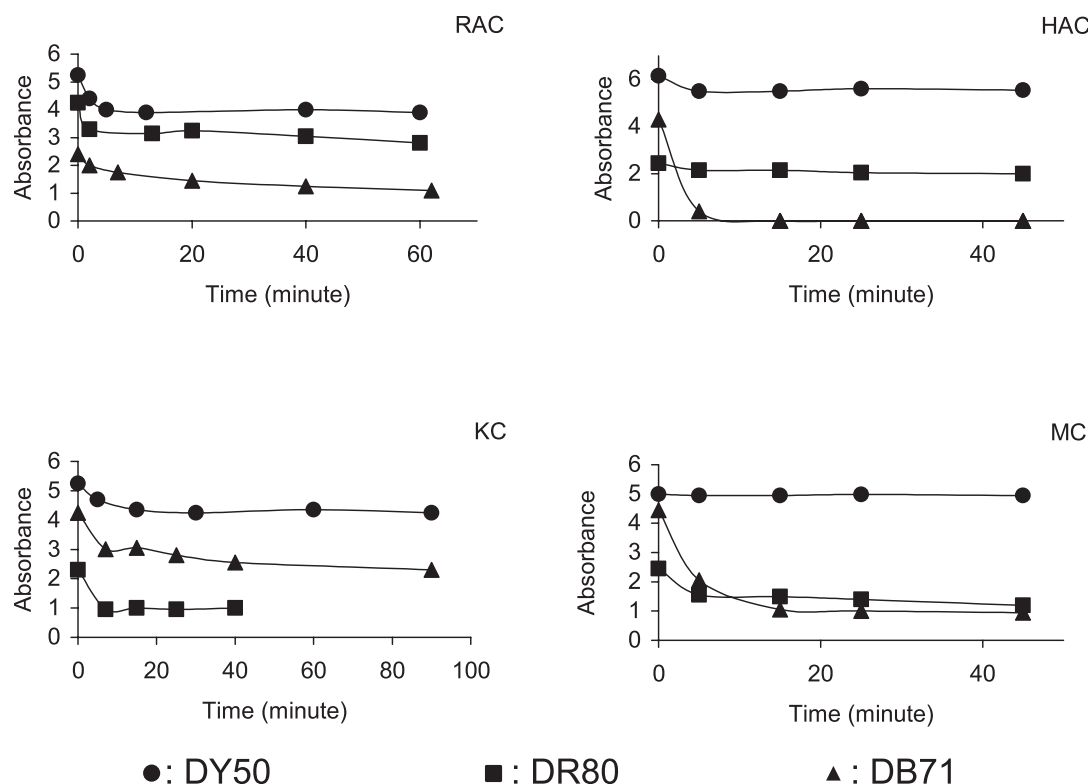

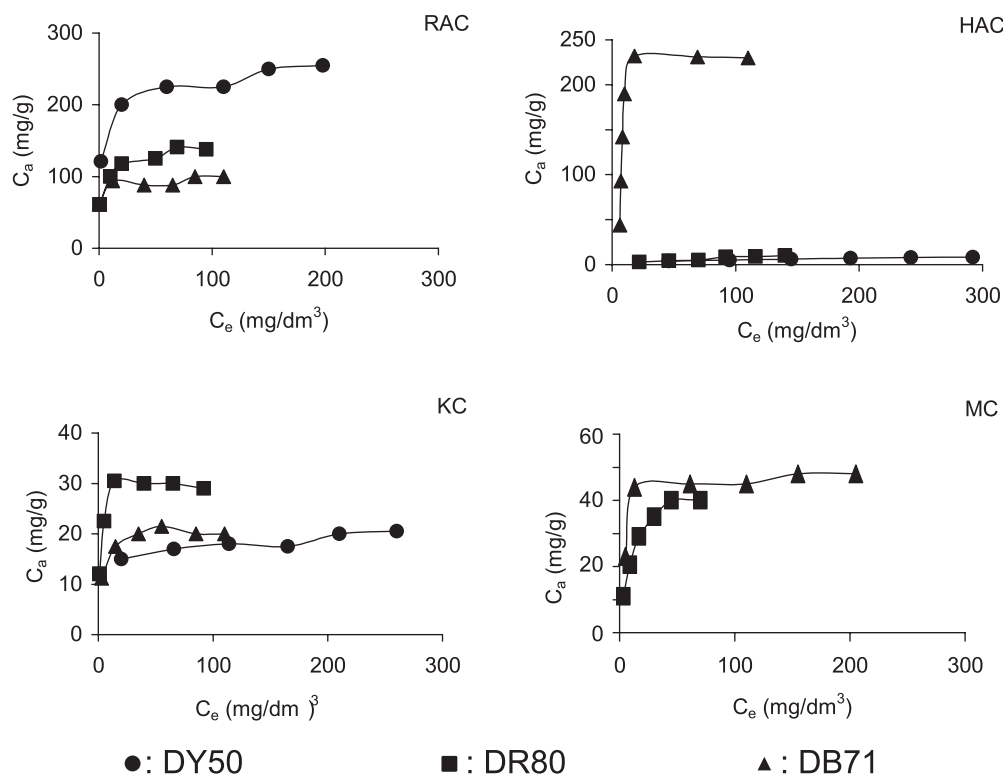Fig. 2. The effect of time on the adsorption of the studied dyes at 25°C.

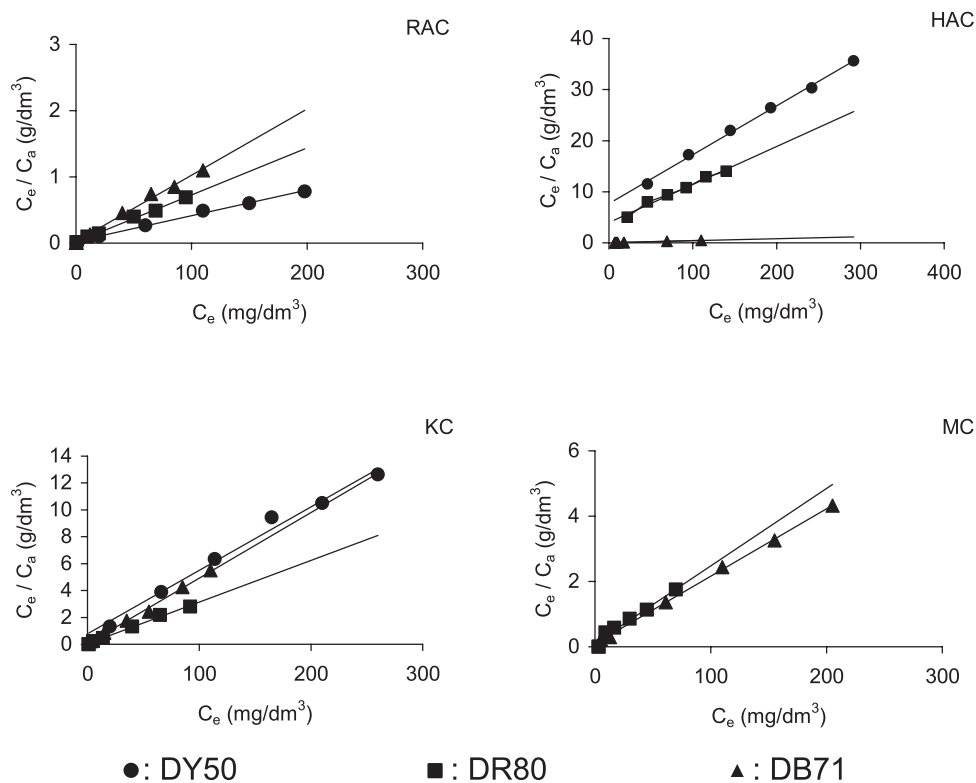Fig. 3. Adsorption isotherms for the studied direct dyes onto the adsorbents at 25°C.

Fig. 4. Langmuir plots corresponding to the adsorption of the studied direct dyes onto the adsorbents at 25°C.

Table 2. Langmuir equation parameters, correlation coefficients and removal efficiency for the adsorbents used in adsorption of the direct dyes.

Adsorbents	Dyestuffs	C_m (mg/g)	b (dm³/mg)	Removal (R, %)	r²
RAC	DY50	256	0.155	97	0.995
	DR80	141	0.441	98	0.995
	DB71	100	0.368	99	0.992
HAC	DY50	11	0.011	8	0.997
	DR80	14	0.019	12	0.981
	DB71	26	0.866	88	0.947
KC	DY50	21	0.061	30	0.988
	DR80	29	0.034	48	0.999
	DB71	22	1.054	50	0.995
MC	DY50	no adsorption	-	-	-
	DR80	42	0.228	44	0.969
	DB71	48	0.230	45	0.999

As seen in Table 2, the parameter Cm shows that activated carbon adsorbed the dye to a greater extent than kaolinite and montmorillonite. Adsorption capacity of RAC, HAC, KC and MC increased in the following order: DY50>DR80>DB71, DB71>DR80>DY50, DR80>DB71>DY50 and DB71>DR80 (DY50 shows no absorption) for the direct dyes, respectively.

Maximum adsorption capacities of the adsorbents increased and followed the order: RAC>KC>HAC>MC (no absorption),RAC>MC>KC>HAC and RAC>MC>HAC> KC for DY50, DR80 and DB71, respectively. RAC had a large surface area than the other adsorbents and mesoporosity [19]. This fact might be explained by the method of manufacture of activated carbon. The activation
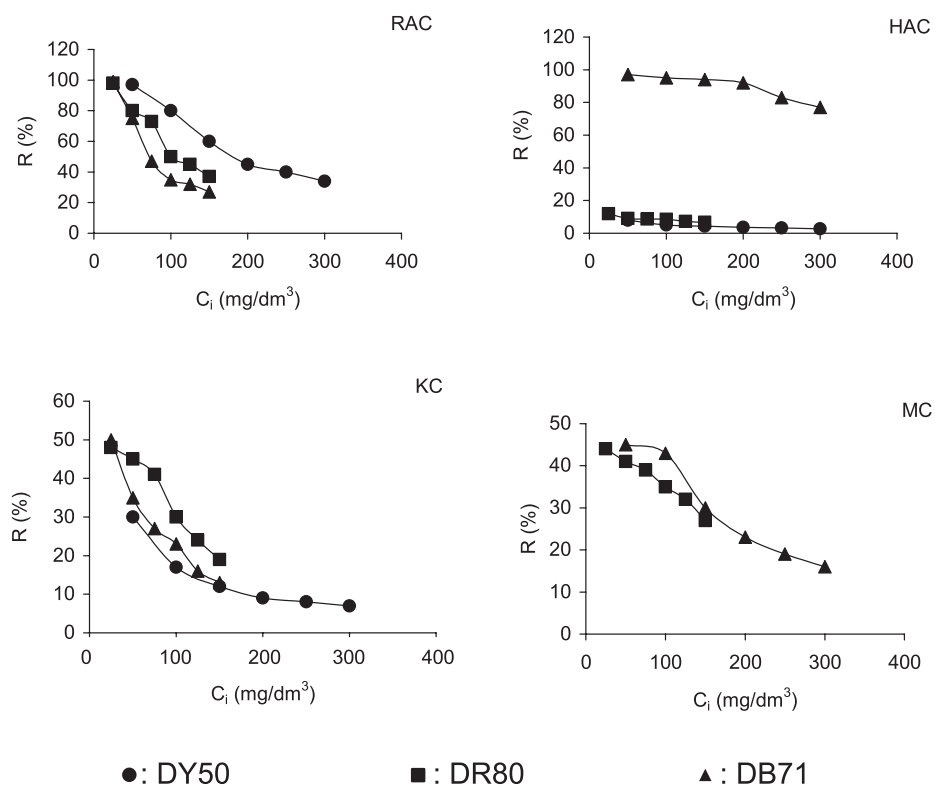

Fig. 5. Plots of per cent removal of direct dyes on the various adsorbents at 25°C.

procedure determines mainly the nature of the surface oxides and the surface area of the product. As explained earlier, activated carbons produced by wet chemical route contain essentially a macroporous pore-size distribution. These products (HAC) therefore generally have a smaller surface area than thermally activated product (RAC). So, adsorption capacity of RAC is larger than HAC. HAC showed less adsorption capacity than MC and KC.

The minerals of kaolinite groups consist of a single silica tetrahedral sheet and a single alumina octahedral sheet combined in a unit so that the type of the silica tetrahedrons and one of the octahedral sheet form a common layer.

Montmorillonite minerals are characterized by a three-layer structure of two silicate layers enveloping an aluminate layer. In such a structure, the replacement of tetravalent silica with trivalent aluminium with divalent magnesium leads to an unfilled vacant position, which contributes to excess negative charge on the lattice.

The removal efficiency (R) is defined as :

$$R = (C_i - C_e/C_i) \times 100 \qquad (2)$$

Where C_i is the initial concentration of the dye of aqueous solution placed in a conical flask and shaken for 40 minutes with 1.0 g of the adsorbents, and C_e is the equilibrium solution concentration. R is expressed in terms of percentages in Table 2.

The removal efficiency depended on initial concentration of the dye. Dependence of removal efficiency with initial concentration of the direct dyes is presented in Fig. 5. The removal efficiency of the dye increased at dilute concentrations, whereas it decreased at high concentrations. Removal efficiency of the adsorbents increased and followed this order: RAC>KC>HAC>MC (no adsorption), RAC>KC>MC>HAC and RAC>HAC> >KC>MC for DY50, DR80 and DB71, respectively.

The removal of dyes from aqueous solution by adsorption is dependent on pH of the solution, which affects the surface charge of the adsorbent, and degree of ionization and speciation of adsorbate [20].

The adsorption of the direct dyes on the adsorbents were studied at original pH. Original pH of the direct dyes are 5.6, 6.8 and 6.4 for DY50, DR80 and DB71, respectively. The pH of the solution decrease from 5.6, 6.8 and 6.4 to 4.4, 5.7 and 5.8 and, 4.8, 6.3 and 6.1 for RAC and HAC, respectively. It can be suggested when direct dyes adsorbs on activated carbon (RAC and HAC) which have acidic properties. However, when the direct dyes adsorb on kaolinite and montmorillonite, the pH of the solutions increase from 5.6, 6.8 and 6.4 to 6.7, 6.9 and 6.8 for kaolinite and no adsorption was observed for DY50 (Table 2), 7.2 and 6.7 for montmorillonite, respectively. The pH of the solutions increases due to negative charge on the clay surface (KC and MC).

Conclusions

Removal efficiency and adsorption capacity was found to be the highest for RAC (Commercial activated carbon). RAC is the most popular adsorbent and has been used with great success, but is expensive. Experimental results have shown that adsorption capacity of HAC obtained from shell of hazelnut was comparatively lower than those of clays such as raw kaolinite (KC) and montmorillonite (MC). These experiments indicate that raw kaolinite and montmorillonite were effective in removing direct dyes from aqueous solution in the range of the concentrations investigated. Because these types of clays are plentiful and inexpensive adsorbents, these could be considered for removing direct dyes from an aqueous solution.

Nomenclature

C_e - Equilibrium liquid-phase concentration (mg/dm^3)
C_a - Amount of the dye adsorbed per gram of the used adsorbents
C_i - Initial liquid-phase concentration (mg/dm^3)
C_m - Maximum amount of dye that can be adsorbed on the adsorbents (mg/g)
b - Parameter of Langmuir isotherm (dm^3/mg)
R - Dimensionless parameter, defined by equation (2)
r^2 - correlation coefficient

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