GORDON McKAY*, BUSHRA AL DURI*

# COMPARISON OF METHODS TO PREDICT MULTICOMPONENT ADSORPTION ISOTHERMS FOR DYE ADSORPTION ONTO CARBON

The adsorption of three basic dyes (Basic Red 22 — BR22, Basic Yellow 21 — BY21 and Basic Blue 69 — BB69) onto activated carbon has been studied as single, double and triple component systems. Several models have been used to predict and correlate the equilibrium data. The ideal adsorbed solute (IAS) theory enabled multicomponent isotherm data to be predicted using single component data with excellent agreement between experimental and theoretical data. Due to the extensive computational work involved in applying the IAS theory, three empirical methods were tested. Two methods, based on extended Langmuir and Redlich–Peterson equations, even incorporating an interaction factor, did not correlate experimental multicomponent isotherms well for using single solute data. However, and extended general Freundlich expression was used with considerable success.

## NOMENCLATURE

$A$ — surface area of adsorbent (dm²),
$a$ — constant in Freundlich isotherm,
$a_L$ — Langmuir isotherm constant (dm³/mg),
$b$ — exponent in Freundlich isotherm,
$c$ — constant of equation (7),
$Kj$ — Jossens isotherm constant,
$K$ — Langmuir isotherm constant (dm³/g),
$m$ — Jossens isotherm constant,
$R$ — Universal Gas Constant,
$T$ — absolute temperature (K),
$X$ — dye concentration in liguid (mg/dm³),
$Y$ — dye concentration on solid adsorbent (mg/g).

* Department of Chemical Engineering, Queen's University, Belfast BT9 1NN, Northern Ireland.

## GREEK LETTERS

$\pi$    — spreading pressure,
$\gamma$    — exponent in Jossens isotherm,
$\eta$    — interaction term.

## SUBSCRIPTS

1    — component 1,
2    — component 2,
A, B — components A and B,
$i$    — general component, $i$,
$j$    — components in a system,
$k$    — concentration range,
$r$    — number of components.

## SUBSCRIPT

$o$    — pure component dye.

# 1. INTRODUCTION

Adsorption processes are continually gaining prominence as methods of purifying textile effluents, industrial and municipal waste waters. Although a considerable amount of information is available on single solute adsorption, most companies discharge effluents containing several components. Experimental results for binary mixtures were reported many years ago (Amiot, 1934; Kolthoff and Van der Groot, 1929) but no attempt was made to analyse the results.

This paper reports the adsorption of three single component dyes, the three possible binary mixtures and the one triple component mixture onto carbon have been studied. The equilibrium isotherms have been determined experimentally and several models have been tested to assess their ability to predict bisolute equilibrium data using single component data. The model tested fall into the following categories:

(i) ideal adsorbed solute theory,
(ii) empirical equations using single solute data based on extended conventional isotherms, such as Langmuir, Freundlich and Redlich–Peterson,
(iii) modified extended isotherms,
(iv) empirical correlations for multicomponent data.

# 2. EXPERIMENTAL

Adsorption isotherms were determined by shaking a fixed mass of carbon ($d_p = 355$–$500\mu m$) type Filtrasorb 400 (supplied by Chemviron Ltd) with fixed volumes of dye solutions having different initial concentrations. The three dyes used

in this work were Basic Blue 69 (BB69), Basic Red 22 (BR22) and Basic Yellow 21 (BY21), all supplied by Bayer Ltd. Analysis of dye mixture concentrations was undertaken by measuring adsorbances on a Perkin Elmer 550S spectrophotometer at wavelengths corresponding to the maximum absorbance band for each of the dyes.

## 3. THEORY

The most thermodynamically acceptable model for multicomponent adsorption is the ideal adsorbed solute theory (IAS theory), proposed by MYERS and PRAUSNITZ [11], and analagous to Raoult's law. The theory was extended for dilute solutions by RADKE and PRAUSNITZ [12] and only single solute data are required. The model is based on calculating the spreading pressure $\pi$ using equation (1)

$$\frac{\mu A}{RT} = \int_0^{X_i^0} \frac{Y_i^0(X_i^0)}{X_i^0} dX_i^0. \tag{1}$$

The spreading pressure is then used to determine the fractional surface coverage of the adsorbent particle by the solute, and then this fractional coverage is used to predict multicomponent adsorbtion data. The method of solution is complex requiring extensive iteration and computation. Therefore simplifying assumptions for the term $Y_i^0(X_i^0)$ have been proposed (KIDNAY and MYERS [7], JAIN and SNOEYINK [6], Di GIANO et al., 1978, FRITZ and SCHLÜNDER [4]) and found to be useful for certain systems.

In addition to the IAS theory for the prediction of multicomponent isotherm data, a number of empirical equations have been proposed and summarized in tab. 1.

Table 1

Summary of isotherm equations studied in the work

| Isotherm type | Single component | Extended type | Modified extended |
|---|---|---|---|
| Langmuir | $Y_i = \dfrac{K_i X_i^0}{1 + a_{L_i} X_i^0}$ (2) | $Y_i = \dfrac{K_i X_i^0}{1 + r \displaystyle\sum_{j=1}(a_{L_j} X_j^0)}$ (3) | $Y_i = \dfrac{(K_i X_i^0/\eta_i)}{1 + r \displaystyle\sum_{j=1} \dfrac{(a_{L_j} X_j^0)}{\eta_j}}$ (4) |
| Freundlich | $Y_i = a_i X^{ob_i}$ (5) | $Y_1^* = \dfrac{a_1 X^{ob_1 + b_{11}}}{X_1^{b_{11}} + a_{12} X_2^{b_{12}}}$ (6) | $Y_i = \dfrac{a_{io} X_i^{b_{io}}}{c_i + r \displaystyle\sum_{j=1} a_{ij} X_j^{b_{ij}}}$ (7) |
| Redlich–Peterson | $Y_i = \dfrac{K_{Ji} X_i^0}{1 + m_i X_i^{o\gamma i}}$ (8) | $Y_i = \dfrac{K_{Ji} X_i^0}{1 + r \displaystyle\sum_{j=1} m_j X_i^{o\gamma i}}$ (9) | $Y_i = \dfrac{(K_{Ji} X_i^0/\eta_i)}{1 + r \displaystyle\sum_{j=1} \dfrac{m_j X_j^{o\gamma j}}{\eta_j}}$ (10) |

\* For bisolute systems.

G. McKay, B. Al Duri

Markham and Benton [9] proposed equation (3) but when it was found inapplicable to several systems, Schay et al. [14] modified the equation by accommodating molecular interactions in the adsorbed phase, depicted by equation (4). Fritz and Schlunder [4] extended the Freundlich equation (5) to produce equation (6) which is a simplification of the general isotherm equation (7), setting $c_1 = 0$. It is for bisolute systems and does incorporate some multicomponent correlation factors in evaluating its constants. Mathews [10] and Crittenden [2] used a Redlich–Peterson [13] equation (8) and applied an extended form, equation (9), and a modified form, equation (10), incorporating a molecular interaction factor (Yon and Turnock [15]) to a number of bisolute systems.

## 4. RESULTS AND DISCUSSION

The aim of this paper is to develop and test the suitability of a range of models to predict multicomponent equilibrium isotherms for the adsorption of basic dyes onto activated carbon. Figure 1 shows the isotherms for the adsorption of BR22 dye as
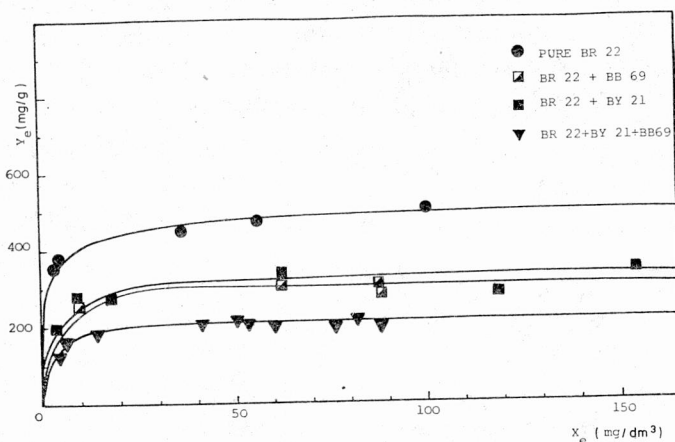


Fig. 1. Comparison between adsorption isotherms of BR22 in single component with several multi-component systems

a pure single component, in its bisolute mixtures with BY21 and BB69, and in its triple mixture. The capacity of the dye for carbon is seen to decrease as the competition for carbon from other dyestuffs increases. The saturation monolayer adsorption capacities for BR22 dye onto carbon are 500 mg dye/g carbon for single component, 320, 300, and 200 in BY, BB and the triple component system, respectively.

The IAS theory, in general, gave the best correlation between experimental and theoretical data, and fig. 2 shows such a comparison for the adsorption of BR22 in a mixture of BR22 and BY21. The application of the IAS theory to the other dye mixtures gave similar excellent correlations between experimental and theoretical results. Due to extensive computational time, however, several other approaches, using simplifying assumptions or empirical correlations, were then proposed and tested.
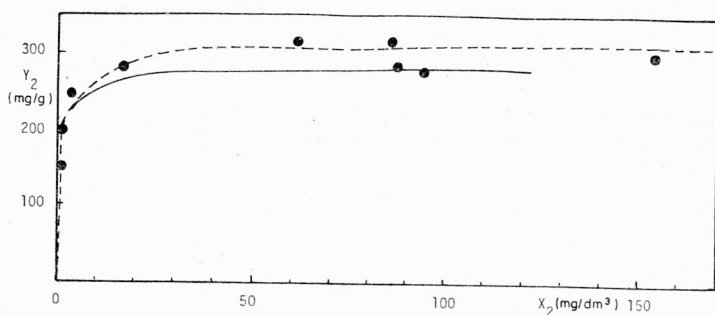


Fig. 2a. Comparison of experimental points with theoretically predicted equilibrium isotherm for BY21 in a mixture of BR22 and BY21
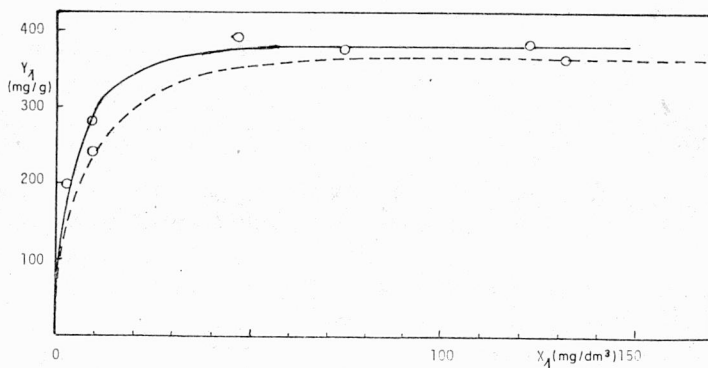


Fig. 2b. Comparison of experimental points with theoretically predicted equilibrium isotherm for BR22 in a mixture of BR22 and BY21

Figures 3, 4 and 5 show predicted and experimental data using; the extended Langmuir (equation 3) for the adsorption of BR22 in a mixture of BR22 and BY21, the extended Freundlich (equation 6) for the adsorption of BB69 in a mixture of BB69 + BR22, and the extended Redlich–Peterson (equation 9) for the adsorption of BY21 in a mixture of BB69 and BY21. It was found that for the BR22 and BY21
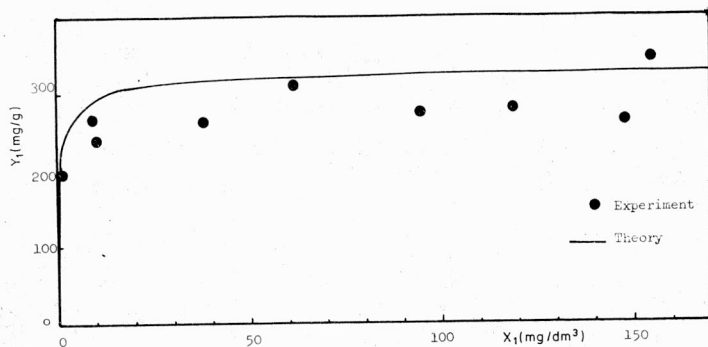
G. McKay, B. Al Duri



Fig. 3. Predicted and experimental data using the empirical extended Langmuir formula for the adsorption of BR22 in a mixture of BR22 + BY21 on carbon
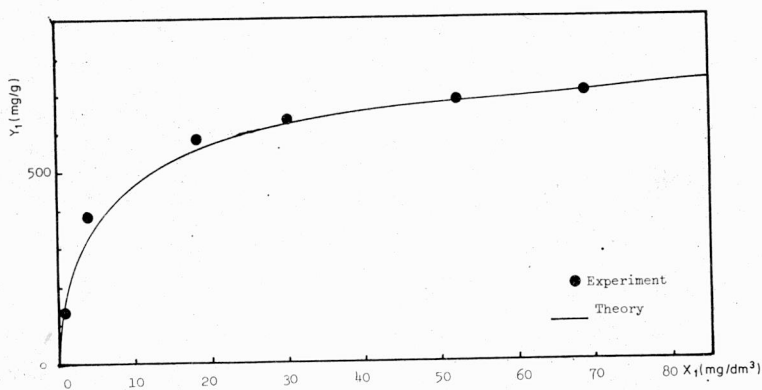


Fig. 4. Predicted and experimental data using the empirical Freundlich formula for bisolute mixtures for the adsorption of BB69 in a mixture of BB69 + BR22 on carbon
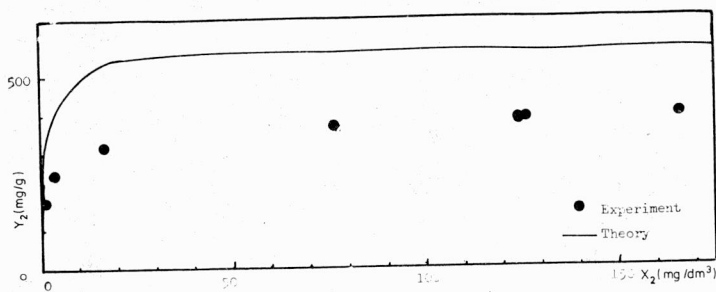


Fig. 5. Predicted and experimental data using the empirical Redlich–Peterson formula for the adsorption of BY21 in a mixture of BB69 + BY21 on carbon

system, the three equations gave predictions only moderately close to experimental data. However, for any mixture involving BB69 dye, the correlation between experimental and theoretical results was very poor and this method was unsatisfactory. That is because the above mentioned equations assume independent component adsorbtion regardless of interactions and competition.

The application of the modified extended Langmuir (equation (4)) and Redlich–Peterson (equation (10)) expressions are represented in figs. 6 and 7. These
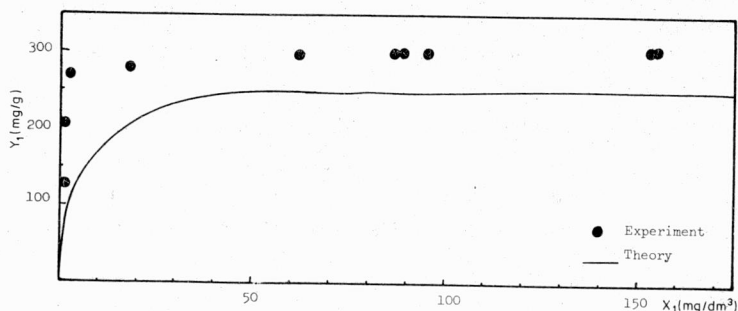


Fig. 6. Application of the empirical extended Langmuir formula with interaction term $\eta$ to the adsorption of BR22 in (BR22 + BB69)
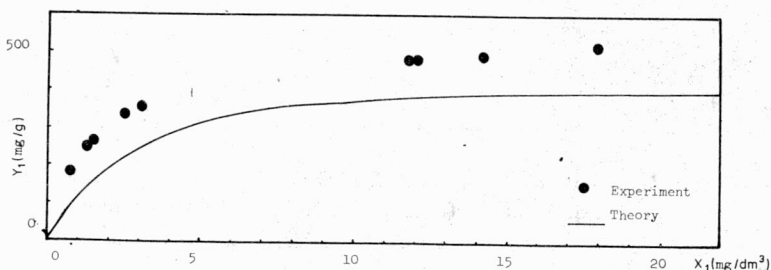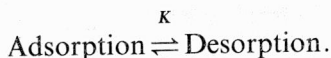


Fig. 7. Application of the empirical extended Redlich–Peterson formula with interaction term $\eta$ to the adsorption of BB69 in (BB69 + BR22 + BY21) trimixture

results were optimized using a minimization subroutine programme from the computer library file and although better fits were obtained using the interaction factor $\eta$ than using equations 3, 6 and 9; the results were still relatively poor except for the BR22 and BY21 system. Figure 6 shows the adsorbtion of BR22 in a BR22 and BB69 mixture and fig. 7 shows the adsorbtion of BB69 in the triple mixture.

It is apparent from the application of equations (3)–(10) that extended equilibrium isotherms and the modified expressions are not sufficient for all mixtures. The previous equations are derived for competitive adsorption and dye–dye interaction.

It would appear, however, that BB69 dye adds an additional complication to the adsorption mechanism by creating a dye–carbon surface–dye interaction or by perhaps 'swamping' competition and interaction effects in the early stages of adsorption. The BB69 dye has the highest capacity in all the systems in which it is a component. Consequently, it is necessary to consider a different empirical approach for the systems containing BB69 dye. The high adsorptive capacity of BB69 ($Q_{max}$ 800 mg/g) is related to these interactions whose presence adds further complications to the system equilibrium conditions making equations (4) and (10) partially successful for multicomponent isotherm calculations of BB69 systems as it does not correlate $K$ values which are directly related to equilibrium

$$\text{Adsorption} \overset{K}{\rightleftharpoons} \text{Desorption}.$$

Equation 10 was derived basing on the analysis of multicomponent data and has been applied to all the dye mixtures. Figure 8 shows the agreement between experimental
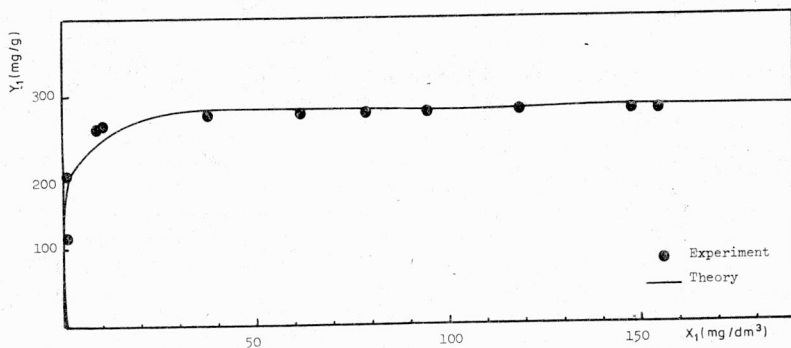


Fig. 8. Application of the extended empirical Redlich–Peterson formula with interaction term $\eta$ to the adsorption of BR22 in a (BR22 + BY21) mixture
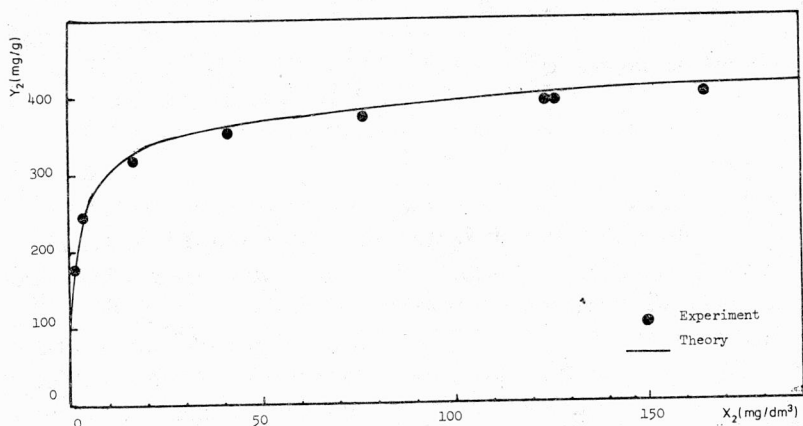


Fig. 9. Application of equation (6) to the adsorption of BY21 in (BB69 + BY21) bisolute system

and theoretical data for the adsorption of BR22 on carbon in a mixture of BR22 and BY21. Excellent agreement was obtained for all the dye mixtures using equation (6) because both its constants are correlated with multicomponent data and this takes all interactions into account. Tables 2 and 3 give a statistical comparison of the approaches in this paper in terms of the variance $\sigma^2$

$$\sigma^2 = \sum_{j=1}^{n} \left[ \frac{Q_{exp} - Q_{cal}}{Q_{exp}} \right]^2 \Big/ n.$$

Table 2

Comparison of variances $\sigma^2$ using different equations for the bisolute mixture (BB69 and BR22)

| Compo-nents Formulae | Empirical extended | | Empirical extended $\eta$ | | Empirical |
|---|---|---|---|---|---|
| | Langmuir | Redlich–Peterson | Langmuir | Redlich–Peterson | Freundlich |
| BB69 | 0.755 | 0.783 | 0.198 | 0.158 | 0.0891 |
| BR22 | 0.405 | 0.462 | 0.266 | 0.268 | 0.0928 |

Table 3

Comparison of variances $\sigma^2$ using different formulae for the prediction and correlation of bisolute mixture (BB69 and BY21)

| Compo-nents Formulae | Empirical extended/without $\eta$ | | Empirical extended/with $\eta$ | | Empirical |
|---|---|---|---|---|---|
| | Langmuir | Redlich–Peterson | Langmuir | Redlich–Peterson | Freundlich |
| BB69 | 0.687 | 0.713 | 0.197 | 0.203 | 0.0871 |
| BY21 | 0.338 | 0.278 | 0.128 | 0.0986 | 0.0897 |

## 5. CONCLUSIONS

Several models have been tested with regard to their ability to predict multicomponent equilibria for the adsorption of basic dyes onto carbon. The ideal adsorbed solute theory, based on classical thermodynamic consideration, enables multicomponent equilibria data to be predicted using pure single component data. An extended Freundlich isotherm, using limited multicomponent factors, also gave excellent correlation between theoretical and experimental equilibrium data. Other empirical correlations based on Langmuir and Redlich–Peterson single component

data only correlated multicomponent data well when the adsorption capacities of the individual components in the mixture were of a similar order of magnitude, these are systems with similar equilibrium behaviours.

## REFERENCES

[1] Amiot M. R., Comptes Rendu, 199, 638 (1934).
[2] Crittenden J. C., Thesis, University of Michigan, 1976.
[3] Di Giano F. A., Weber W. J., J. Wat. Pollut. Contr. Fed., 45, 713 (1973).
[4] Fritz W., Schlünder E. U., Chem. Eng. Sci., 29, 1279 (1974).
[5] Fritz W., Schlünder E. U., Chem. Eng. Sci., 36, 731 (1981).
[6] Jain J. S., Snoeyink V. L., J. Wat. Pollut. Contr. Fed., 45, 2463 (1973).
[7] Kidnay, A. J., Myers A. L., A. I. Ch. E. J., 12, 981 (1966).
[8] Kolthoff, I. M., Van der Groot E., Rec. Trav. Chim., 48, 265 (1929).
[9] Markham E. C., Benton A. F., J. Am. Chem. Soc., 53, 497 (1931).
[10] Mathews A. P., Thesis, University of Michigan, 1975.
[11] Myers A. L., Prausnitz J. M., A. I. Ch. E. J., 11, 121 (1965).
[12] Radke C. J., Prausnitz J. M., A. I. Ch. E. J., 18, 761 (1972).
[13] Redlich O., Peterson D. L., J. Phys. Chem., 63, 1024 (1959).
[14] Schay G. J., Fejeo F. P., Szethmary J., Acta. Chim. Acad. Sci. Hung., 12, 299 (1957).
[15] Yon C. M., Turnock P. H., A. I. Ch. E. Symp. Ser., No. 117, 67, 74 (1981).

## PORÓWNANIE METOD PROGNOZOWANIA PRZEBIEGU WIELOSKŁADNIKOWYCH IZOTERM ADSORPCYJNYCH PODCZAS ADSORPCJI BARWNIKA NA WĘGLU

Adsorpcja trzech podstawowych barwników (czerwień zasadowa, żółć zasadowa i błękit zasadowy) na węglu aktywnym była badana w układzie jedno-, dwu- i trójskładnikowym. Zastosowano kilka modeli, aby przewidzieć i skorelować dane odnoszące się do stanu równowagi. Teoria idealnego roztworu adsorpcyjnego (IAS) umożliwia przewidywanie przebiegu wieloskładnikowych izoterm na podstawie danych dotyczących jednoskładnikowego układu. Dane doświadczalne i teoretyczne są w tym przypadku zgodne. Ponieważ zastosowanie teorii IAS wymaga czasochłonnych obliczeń komputerowych, przetestowano więc trzy metody doświadczalne. Dwie z nich, bazujące na rozszerzonych równaniach Langmuira i Redlicha–Patersona, chociaż uwzględniają wzajemne oddziaływanie, nie korelowały zadowalająco doświadczalnych izoterm wieloskładnikowych z danymi dla jednej substancji rozpuszczonej, użycie jednak rozszerzonego ogólnego równania Freundlicha dało zadowalające wyniki.

## СРАВНЕНИЕ МЕТОДОВ ПРОГНОЗИРОВАНИЯ ХОДА МНОГОКОМПОНЕНТНЫХ АДСОРБЦИОННЫХ ИЗОТЕРМ ВО ВРЕМЯ АДСОРБЦИИ КРАСИТЕЛЯ НА УГЛЕ

Адсорбция трех основных красителей (основного красного, основного желтого и основного голубого) на активном угле исследовалась в одно-, двух- и трехкомпонентной системах. Применили несколько моделей, чтобы предусмотреть и коррелировать данные, относящиеся к состоянию равновесия. Теория идеального адсорбционного раствора (IAS) дает возможность

предусмотреть ход многокомпонентных изотерм на базе данных, касающихся однокомпонентной системы. Экспериментальные и теоретические данные в этом случае согласны друг с другом. Из-за того, что применение теории IAS требует трудоемких компьютерных расчетов, протестированы три экспериментальных метода. Два из них, базирующие на расширенных уравнениях Лангмуара и Редлиха–Патерсона, хотя учитывают взаимовоздействие, не коррелировали удовлетворительно экспериментальных многокомпонентных изотерм с данными для одного растворенного вещества. Однако, употребление расширенного общего уравнения Фройндлиха дало удовлетворительные результаты.