ADSORPTION OF BASIC YELLOW 28 (BY 28) AND ACID YELLOW 23 (AY 23) DYES ONTO CHITIN

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Abstract

The present study investigated the sorption of Basic Yellow 28 (BY 28) and Acid Yellow 23 (AY 23) by chitin flakes. The study determined the influence of pH value on adsorption effectiveness and the adsorption capacity of chitin flakes. The results were described with Freundlich, Langmuir, Sips and double Langmuir isotherms. Similar values of adsorption capacities were achieved for both tested dyes using Langmuir, Sips and Langmuir2 models, i.e. 16.804, 17.740 and 18687 mg/g d.m. for BY28 as well as 24.195, 27.930 and 24.196 mg/g d.m. for AY23, respectively. The isotherms were compared with the use of average relative error (ARE) of approximation. In the case of both dyes, the best fit to experimental data was achieved with the use of tri-parametric Sips equilibrium isotherm, which was indicated by ARE values of 3.10% (BY 28) and 5.26% (AY 23).

Key words: *adsorption, dyes, chitin flakes, isotherm models, ARE*

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1. Introduction

An important group of organic pollutants of the aquatic environment includes dyes and pigments. They are discharged to wastewater from various branches of the industry, like dyeing, textile, cosmetic and cellulose industries [1]. Even at low concentrations, they may color significant volumes of water. The introduction of color wastewater to the environment is undesirable not only because of their color, but also because of products of their degradation that may be toxic or carcinogenic. The textile industry is developing in response to a growing demand for fabrics, which generates increasing volumes of wastewater. It makes this industry one of the key sources of contaminants that pose a serious global problem [2].

Literature data indicate that treatment of wastewater containing synthetic dyes with conventional biological methods, e.g. in activated sludge systems, is little effective [3, 4] The complex chemical structure of dyes makes their removal from wastewater a multi-stage and expensive process.

It seems advisable, therefore, to apply the treatment methods at the site of wastewater generation as it would allow reducing the load of contaminants discharged to the natural environment.

Among various methods for dyes removal, adsorption is acknowledged as not requiring high investment costs.

According to literature data, the most popular adsorbents include zeolites [5, 6], silica gels [8, 9], and activated carbons [9, 10]. New materials of biological origin are, however, sought after that would be economic, effective and easily available sorbents in dye removal process.

Biosorbents applied for dyes adsorption may include materials commonly occurring in the natural environment like algae, moss, biomass of microorganisms being a waste product, as well as microorganisms that are specially cultured, then rinsed in acids or bases, dried and granulated.

Such biological materials like chitin, chitosan, peat, yeast or biomass are increasingly often successfully applied as adsorbents for the removal of dyes from solutions. Biosorbents and their derivatives contain different functional groups that may complexate dyes. In addition, they are often more selective than the traditional ion-exchange resins and commercial activated carbons, and may reduce dye concentration to the level of micrograms per dm^3.

2. Materials and Methods

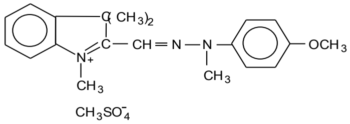
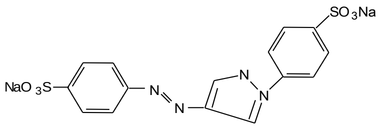
2.1. Characteristics of chitin flakes

Chitin in the form of flakes with a deacetylation degree DD = 35% originated from BioLog company, which uses shrimp shells from the seafood processing industry.

2.2 Characteristics and preparation of dyes

Experiments were conducted with two reactive dyes: Basic Yellow (BY28) and Acid Yellow (BY23), produced by ZPB “Boruta”SA in Zgierz. The structure of reactive dyes is presented in Table 1.

Table 1. Characteristics of the dyes examined

Structural formula	**Name**	**λ_{max} (nm)**	**Molecular weight**
	Basic Yellow (BY28)	450	433
	Acid Yellow (BY23)	425	534

A stock solution of dye was prepared by weighing 1.00 g of pure powdered dye. The dye was quantitatively transferred into a 1dm3 measuring flask which was then filled up with distilled water. Dye concentration in the solution reached 1000 mg/dm3. The stock solution was used to prepare working solutions.

2.3 Determination of the optimal pH value of adsorption process

In order to determine the optimal pH value of the adsorption process, aqueous solutions were prepared with dye concentration of 100 mg/dm3 and pH from 1 to 12. Adsorbent in the quantity of 1 g d.m./dm^3 and 100 cm^3 of dye solutions with pH from 1 to 12 were added to each of the conical flasks (200 cm3). Next, the flasks were placed on a magnetic stirrer, and the concentration of adsorbate in the solution was determined after 2 h of adsorption.

2.4 Determination of the maximum adsorption capacity

In order to determine the adsorption capacity of chitin flakes, 1 g d.m./$dm^3$of the sorbent was weighed into 200 cm^3 Erlenmeyer flasks and supplemented with 100 cm^3 of the working solution of the dye at an appropriate concentration. Samples were fixed on a shaker and shaken for 2 hours at a constant rate of 200 r.p.m.

2.5 Analytical methods

The concentration of dye left in the aqueous solution was determined spectrophotometrically in each sample. Samples to be analyzed were collected (10 cm3), decanted and centrifuged for 15 min at 10,000 rpm. To assay dye concentration, the solution was adjusted to pH 6. The concentration of the remaining dye was determined acc. to standard curves in a UV-VIS Spectrophotometer SP-3000.

A wave length at which absorbance was measured was determined for each of the two dyes examined (Table 1).

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2.6 Computation methods

The effectiveness of dyes adsorption from the solution was analyzed based on changes in their concentration in the solution.

The quantity of adsorbed basic and acid yellow was calculated from the formula (1):

$$Q = \frac{C_0 - C_s}{m} \tag{1}$$

where: Qs – weight of adsorbed dyes [mg/g.d.m.]; C_0 – initial concentration of dyes [mg/dm3]; Cs – dyes concentration after adsorption [mg/dm3]; m – weight of adsorbent [g.d.m.].

Experimental data were described using four models – the Freundlich model, Langmuir model, heterogeneous Langmuir model (double Langmuir equation) and Sips model.
The Freundlich, Langmuir, Sips and double Langmuir isotherms (equations 2-5, respectively) were examined to model the equilibrium sorption data.

Table 2 Models and equations

Model	Equation		Literature
Freundlich	$Q = K_F C^{1/n}$	(2)	[11]
Langmuir	$Q = \frac{K \cdot b \cdot C}{1 + K \cdot C}$	(3)	[11]
Sips	$Q = \frac{b \cdot K \cdot C^{1/n}}{1 + K \cdot C^{1/n}}$	(4)	[11]
double Langmuir	$Q = \frac{K_1 \cdot b_1 \cdot C}{1 + K_1 \cdot C} + \frac{K_2 \cdot b_2 \cdot C}{1 + K_2 \cdot C}$	(5)	[12]

where K_F, n, K, b, K_1 K_2, b_1, b_2 are constants of isotherms and C are dye concentration in the solution after adsorption, Q mass of dye adsorbed/desorbed by/from the biosorbent.

Program STATISTICA 10.0 was applied to determine the fit of the curves (with the determined constant) to the experimental data with the use of non-linear estimation by the method of least squares, at a significance level of $p<0.05$.

3. Results and discussion

3.1. Analyses of dye biosorption depending on the pH value

Fig. 1 depicts the effect of pH value on the effectiveness of dyes adsorption onto chitin. The highest effectiveness of dyes removal from aqueous solutions onto chitin flakes (about 55%) was achieved for acid yellow AY 23 at pH 1-3. An increase in pH value diminished the effectiveness of acid dye anions removal by chitin flakes to about 21%.

It was linked with protonation of adsorbent surface, which caused a change in adsorbent properties making it more capable of binding Acid Yellow 23 dye ions.

The effectiveness of BY28 dye adsorption was maintaining at a similar level of 31% on average in the pH range from 4.0 to 12.0. A decrease in the pH value below 4.0 caused a reduction in BY28 adsorption effectiveness to ca. 17%. The analysis of experimental results enabled concluding that the pH value had a greater impact on adsorption effectiveness in the case of Acid Yellow 23 dye (AY 23).

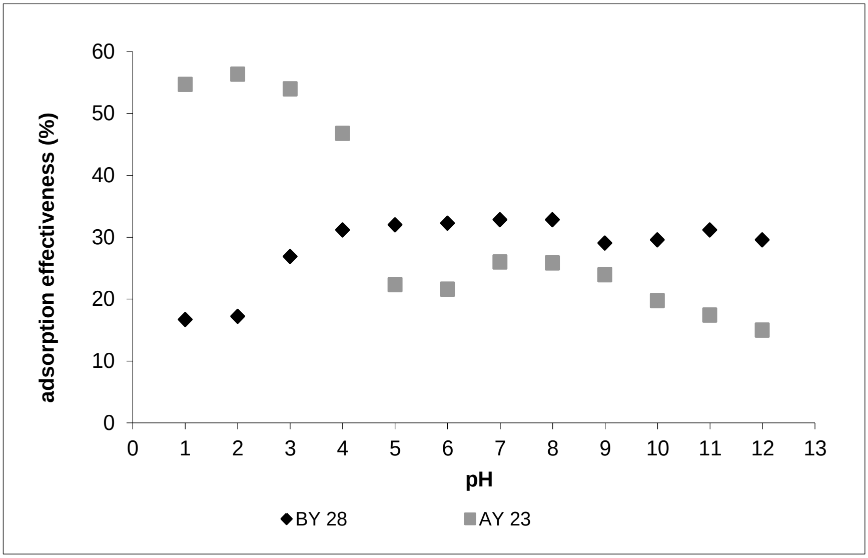

Figure 1. Effect of pH value on AY23 and BY28 adsorption effectiveness

3.2 Analysis of adsorption capacity

Experimental results of Basic Yellow (BY 28) dye adsorption from the aqueous solution and isotherms determined from Freundlich, Langmuir, Sips and Langmuir2 equations were presented in Fig. 2.

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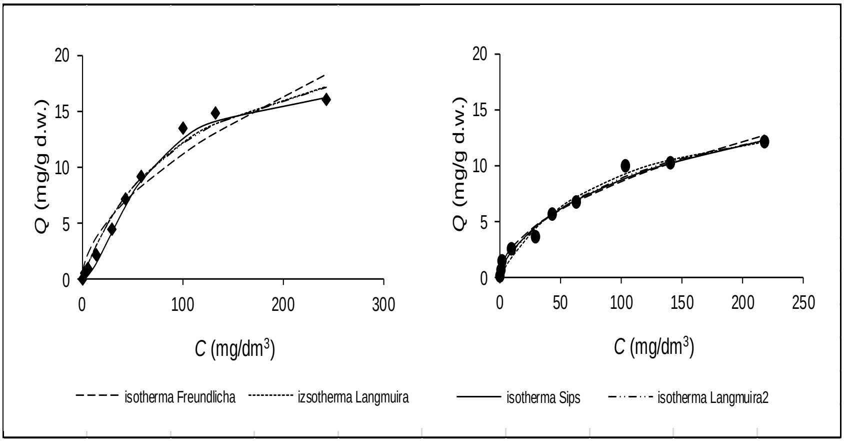

Figure 2. Experimental results of adsorption onto chitin: a. Basic Yellow 28, b. Acid Yellow 23; and adsorption isotherms determined from Freundlich, Langmuir, Sips and Langmuir2 equations

Table 3 presents constants determined from the four selected adsorption models.

Results obtained indicate the lowest fit of the Freundlich model to experimental data of basic dye BY28 adsorption. In the case of the acidic dye AY23, all isotherms were characterized by high fit to experimental data.

Similar values of adsorption capacity were obtained for both dyes in Langmuir, Sips and Langmuir2 models, i.e. 16.804, 17.740 and 18687 mg/g d.m. for BY28 and 24.195, 27.930 and 24.196 mg/g d.m. for AY23, respectively. Adsorption affinity determined from the Langmuir, Sips and double Langmuir models was similar and ranged from 0.001 to 0.012 dm^3/mg. Only the value of K_2 constant was significantly higher in the double Langmuir equation.

3.3. The average relative error (ARE) of approximation

The value of the average relative error (ARE) of approximation, defined with equation (6), enabled determining prediction accuracies of particular equilibrium models and their comparison.

$$\mathrm{ARE}\,(\%) = \frac{100}{z}\sum_{i=1}^{z}\left(\frac{\left|q_{exp} - q_{calc}\right|}{q_{exp}}\right)_i \qquad (6)$$

where: z is the number of given points; q_{exp} and q_{calc} indicate adsorption capacity determined from experimental data and from theoretical models [13].

Table 3. Basic Yellow 28 adsorption constants determined from Freundlich, Langmuir, Sips and Langmuir2 models for the tested biosorbents

Models			Dyes	
			Basic Yellow 28	Acid Yellow 23
2-parametric	Freundlich	K_F	0.856	0.830
		n	0.557	0.507
		R^2	0.969	0.992
	Langmuir	b	16.804	24.195
		K	0.010	0.012
		R^2	0.991	0.991
3-parametric	Sips	b	17.740	27.930
		K	0.001	0.018
		n	1.690	0.700
		R^2	0.998	0.994
4-parametric	Langmuir2	b_1	17.638	14.003
		K	0.010	0.008
		b_2	1.049	10.193
		K_2	0.010	1.764
		b_1+b_2	18,687	24.196
		R^2	0.991	0.995

The values of ARE presented in Fig. 4 demonstrate the worst fit to experimental data for Freundlich equilibrium isotherm in the case of BY28 (ARE=15.93%).

In the case of both dyes, the best fit to experimental data was achieved for the three-parametric Sips equilibrium isotherms. The average relative error for this model reached 3.10% (BY28) and 5.26% (AY23). The lowest value of ARE (2.42%) was determined for the acidic dye AY23 and four-parametric Langmuir2 equilibrium isotherm.

Results obtained in the study indicate that the three-parametric Sips equation of adsorption isotherm may be successfully applied in mathematical modeling of the dye removal process (both acidic and basic dyes) from aqueous solutions on chitin flakes.

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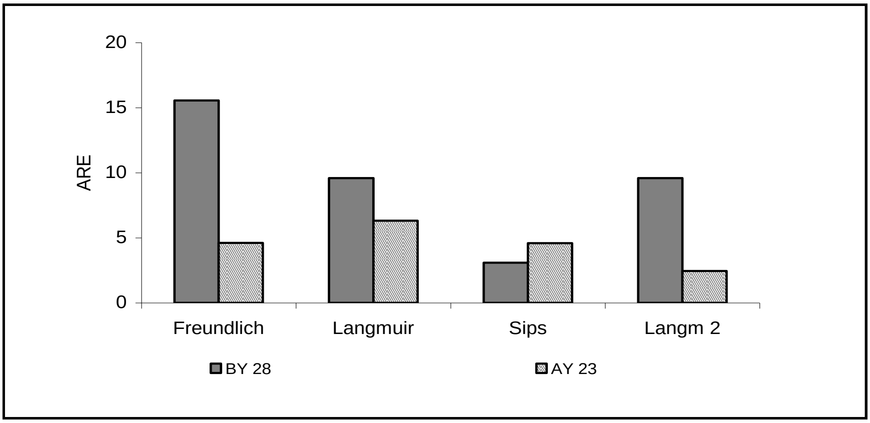

Figure 3. Values of average relative error (ARE)

The effectiveness and universal character of the Sips model were confirmed in a study by Ho et al. [14], who analyzed adsorption of three bivalent metal ions: copper, nickel and lead, from a water solution on peat. Experimental data were analyzed with the following models: Langmuir, Freundlich, Redlich-Peterson, Toth, Temkin, Dubinin-Radushkevich and Sips. The values of ARE demonstrated that Sips equation ensured the best fit of the model to experimental data obtained for the three investigated metals.

4. Conclusions

Adsorption effectiveness of the analyzed dyes onto chitin flakes depended on dye type. For the basic dye: Basic Yellow 28, the optimal pH range was found at pH 5-12, whereas for the acidic dye: Acid Yellow 23 – the pH range of 1-3. Adsorption capacity determined from Langmuir, Sips and double Langmuir models for both dyes was similar. Adsorption isotherms demonstrated high fit to experimental data of dyes adsorption by the tested biosorbent for all models except for Freundlich model. The best fit of the model to experimental data was obtained upon the use of Sips isotherm, followed by Langmuir and Langmuir2 isotherms. The lowest average relative error of approximation (ARE) was determined in the case of Sips model (2.8%) and Langmuir2 model (4.9%).

5. References

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