Elwira TOMCZAK¹ and Paweł TOSIK¹

SORPTION EQUILIBRIUM OF AZO DYES DIRECT ORANGE 26 AND REACTIVE BLUE 81 ONTO A CHEAP PLANT SORBENT

Abstract: Azo dye-plant sorbent system was investigated in the paper. Direct Orange 26 and Reactive Blue 81 azo dyes were sourced from Boruta-Zachem Kolor Sp. z o.o. Mechanically and chemically modified rye straw was used as a “low-cost” biosorbent. During experiments, dye concentration changes in the solution and sorbent in time were measured at constant temperature until equilibrium was reached. Sorption equilibrium was described by 2-parameter (Freundlich, Langmuir) and 3-parameter (Redlich-Peterson and Radke-Prausnitz) equations widely used in adsorption studies. Characteristic coefficients of equations were determined and the proposed approximations of the results of experimental studies were evaluated statistically. Higher sorption capacity was obtained for Direct Orange 26 than for Reactive Blue 81.

Keywords: azo dyes, rye straw, sorption isotherms

Introduction

Textile wastewater poses a potential threat to surface waters. It has a complex chemical composition and in most cases dyes are the dominant compounds. An estimated 2% of dyes generated annually are discharged to wastewater from manufacturing operations whereas 10% are discharged from textile and related industries [1]. Dyes in water impede light penetration, interfere with the photosynthetic process in plants, negatively affect the growth of flora and fauna, and inhibit oxygen dissolution and water self-purification, while their direct effect results from toxic properties of some of the dyes. Dyes are a particular threat to environmental even if they are in small amount. Therefore the removal of dyes from aqueous solutions is of critical importance both from the technological and most importantly from environmental point of view.

A number of methods such as anaerobic decomposition, coagulation, filtration or membrane separation as well as biological methods are used to remove dyes from industrial

¹ Faculty of Process and Environmental Engineering, Lodz University of Technology, ul. Wolczanska 213, 90-924 Lodz, Poland, phone +48 42 631 37 88
*Corresponding author: tomczak@wipos.p.lodz.pl
Adsorption is very effective at reducing dye concentration in effluents. Experiments aim at increasing efficiency of dye removal from aqueous solutions particularly by selecting suitable process parameters were carried out. It is important that the process be cost-effective and innovative natural materials were used. Industrial by-products are investigated for this purpose.

Activated carbons, ion-exchange polymers, synthetic zeolites are well known and commercially used sorbents for removing contaminants from water. Due to the relatively high cost and not always high sorption efficiency of conventional sorbents scientists have been searching for new sorption materials eg chitosan [3]. Promising sorbents of this type are natural materials especially pant. The process based on the plant sorbents due to their natural ability to bind water contaminations and their chemical and surface structure are used for water purification. Sorbents derived from plant tissue are composed of cellulose-lignin complex which facilitates the sorption. In the subject literature there are numerous number of publications concerning that topic. Over the last ten years more than 15,000 papers have been published worldwide with keywords such as “sorption application”, “sorption onto natural sorbent” and “water purification”, which confirms the importance of adsorption in waste water treatment and water purification for consumption.

Taking into account the origin of the sorbent, the process in the world literature was named biosorption [4]. Currently, biosorption is an alternative to physicochemical separation processes [5-7].

Commonly used biosorbents are locally available materials. Bioadsorbents may include organic, cellulose materials such as tree leaves [8], wheat straw [9], nut hulls [10], seagrass [11], cassava straw [12].

In the paper [13] use of palm kernel fibre, a readily available agricultural waste product for the sorption of Methylene Blue from aqueous solution and the possible mechanism of sorption was investigated at various fibre doses. The intraparticle diffusion and mass transfer rate constants were observed. It was found that at low sorbent dose the mass transfer rate is the main controlling parameter. However at high sorbent dose, intraparticle diffusion becomes controlling factor. In that study high sorption capacity about 672 mg/g was reached.

Spruce wood shavings from Picea abies were used for an adsorptive removal of dyes from waters [14]. The sorption properties of the sorbents were modified with HCl, Na₂CO₃ and Na₂HPO₄. The maximum sorption capacities estimated from the Langmuir-Freundlich isotherms ranged from 0.060 to 0.165 mmol/g for the sorption of Methylene Blue, and from 0.045 to 0.513 mmol/g for the sorption of Egacid Orange.

The mineral absorbents are also used for removal dyes [15]. Furnace Bottom Ash and Granulated Blast Furnace Slag have been tested experimentally in the removal of two acid dyes (Acid Red 183 and Acid Yellow 99) from aqueous solutions [16]. It was found that only FBA can be used as an efficient sorbent for the removal of Acid Yellow 99 and Acid Red 183 from wastewater. Dye removal efficiencies can reach up to 50%.

The scientific articles often compared natural sorbents adsorption to adsorption on activated carbon [17]. The ability of P. oceanica to remove the dye C.I. Acid Yellow 59 from an aqueous solution was compared to that of two commercial activated carbon forms: powdered (PAC) and granular (GAC) activated carbon [18]. Posidonia oceanica, an endemic marine magnoliophyta found in the Mediterranean Sea, was used as a biosorbent for dye wastewater treatment. This comparative study indicates that sorption onto
P. oceanica is an effective, cheaper alternative for dye removal. The best dye retention was found to be respectively onto the PAC, the Posidonia and finally onto GAC. Similarly, the work [19] shown the better properties activated carbon than prepared sawdust. Adsorbents prepared from Prosopis Cineraria sawdust - an agro-industry waste - were successfully used to remove the malachite green from an aqueous solution. The adsorption efficiency of different adsorbents was in the order GAC > formaldehyde-treated sawdust > sulphuric acid-treated sawdust.

Advantages and disadvantages of natural adsorbents, favourable conditions for particular adsorbate-adsorbent systems, and adsorption capacities of various low-cost adsorbents and commercial activated carbons as available in the literature are presented in paper [20]. The review [21] presents a critical analysis of low-cost materials; describes their characteristics, advantages and limitations; and discusses various mechanisms involved. The literature presents different values of sorption capacity for the same systems sorbent-sorbate. It depends on the origin, physical and chemical processing of the sorbent and the pH and temperature of the process. The most commonly reported in the literature is the adsorption of the Methylene Blue onto various natural sorbents. The other hand the type of used biosorbent depends on opportunities and the place of its acquisition. Examples are summarized in Table 1.

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Sorbent</th>
<th>Maximum sorption capacity [mg/g]</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bismarck Brown</td>
<td>Activated rubberwood sawdust</td>
<td>2000</td>
<td>[22]</td>
</tr>
<tr>
<td>Direct Red 80</td>
<td>Soy meal hulls</td>
<td>178.57</td>
<td>[23]</td>
</tr>
<tr>
<td>Direct Red 81</td>
<td></td>
<td>120.48</td>
<td></td>
</tr>
<tr>
<td>Acid Blue 92</td>
<td></td>
<td>114.94</td>
<td></td>
</tr>
<tr>
<td>Acid Red 14</td>
<td></td>
<td>109.89</td>
<td></td>
</tr>
<tr>
<td>Methylene Blue</td>
<td>Duckweed</td>
<td>112.36</td>
<td>[24]</td>
</tr>
<tr>
<td>Methylene Blue</td>
<td>Palm kernel fibre</td>
<td>671.59</td>
<td>[13]</td>
</tr>
<tr>
<td>Methylene Blue</td>
<td>Wheat shells</td>
<td>21.50</td>
<td>[25]</td>
</tr>
<tr>
<td>Methylene Blue</td>
<td>Neem leaf powder</td>
<td>8.76</td>
<td>[26]</td>
</tr>
<tr>
<td>Methylene Blue</td>
<td>Rice husk</td>
<td>40.58</td>
<td>[27]</td>
</tr>
<tr>
<td>Methylene Blue</td>
<td>Jute waste</td>
<td>22.47</td>
<td>[28]</td>
</tr>
<tr>
<td>Methylene Blue</td>
<td>Banana peel</td>
<td>20.80</td>
<td>[29]</td>
</tr>
<tr>
<td>Methylene Blue</td>
<td>Orange peel</td>
<td>18.60</td>
<td></td>
</tr>
<tr>
<td>Direct Red 23</td>
<td>Orange peel</td>
<td>10.72</td>
<td>[30]</td>
</tr>
<tr>
<td>Direct Red 80</td>
<td></td>
<td>21.05</td>
<td></td>
</tr>
<tr>
<td>Reactive Orange 16</td>
<td>Corn cob</td>
<td>25.25</td>
<td>[31]</td>
</tr>
<tr>
<td>Acid Yellow 36</td>
<td>Rice husk</td>
<td>86.90</td>
<td>[32]</td>
</tr>
</tbody>
</table>

Azo dye-plant sorbent system was investigated in the paper. Rye straw obtained from areas in the vicinity of Lodz in 2012 was the biosorbent used. The aim was to determine sorption capacity of chemically modified rye straw for removing selected azo dyes from aqueous solutions and provide a mathematical description of the process with sorption isotherms.
After initial studies with raw straw, further experiments involved chemically pretreated straw with a view to increasing its sorption capacity. Experiments were carried out to determine sorption kinetics based on the changes of dye concentration in the solution and in the sorbent in time.

Subsequently kinetic and equilibrium parameters [23, 33] were determined for the sorption process, necessary for calculations related with the dynamics of process carried out in adsorption column, which will comprise the next stage of the studies.

**Research method**

Dyes used for the purposes of this study were supplied by Boruta-Zachem Kolor Sp. z o.o. in Zgierz. They are used for coloring home cleaning products, cosmetics and have several other applications (Order of the Minister of Health of 30th March 2005, Journal of Laws of 2005 No. 72 Item 642), and represent the azo compound group. Chemical structure and properties of azo dyes have been presented in Figures 1 and 2.

**Fig. 1.** Molecular structure of Direct Orange 26, molecular formula: C_{33}H_{22}N_{6}O_{9}Na_{2}S_{2}, MW = 756.67

**Fig. 2.** Molecular structure of Reactive Blue 81, molecular formula: C_{25}H_{17}Cl_{2}N_{7}O_{10}S_{3}Na_{3}, MW = 811.51

Rye straw was used as a sorbent. The straw was mechanically cut into 1 cm pieces, washed and boiled in a pressure cooker at 130°C for 2 hours. To increase its sorption capacity, the straw was etched with 10% H_{2}SO_{4} for 5 hours at 60°C. Following chemical pretreatment, the straw was dried at 105°C for 2 hours. The procedure of chemical pretreatment was developed based on the previous experience with straw that had only been washed. Sorption equilibrium and kinetics studies were carried out at T = 25°C, pH = 5-6. Five grams of dry weight sorbent were placed in glass flasks and 200 cm³ solution of dye concentration of 100-800 mg/dm³ was added. Flasks with the mixture were shaken.
mechanically in a water bath until adsorption equilibrium was reached. During the process, dye concentration in the water phase was measured using UV-vis Jasco V630 spectrophotometer at wavelength of 494 nm for Direct Orange 26 and 583 nm for Reactive Blue 81.

**Mathematic description of sorption equilibrium**

Sorption equilibrium mathematical modeling is useful for analyzing and designing adsorption systems. It can also be applied for theoretical considerations and interpretation of thermodynamic parameters. In spite of several literature reports, there still are no comprehensive and clear comparative studies for the various models. Some conclusions concerning this issue can be found in literature [34-36].

Based on experimental data, with known initial concentration \( c_0 \) and equilibrium concentration \( c_e \), sorption capacity \( q_e \) was determined for the solution using the following formula:

\[
q_e = \frac{V}{m} (c_0 - c_e)
\]

where: \( c_0 \) and \( c_e \) - initial and equilibrium concentration of dye in a solution [mg/dm\(^3\)], \( q_e \) - equilibrium concentration of dye in an adsorbent, sorption [mg/g], \( V \) - solution volume [dm\(^3\)], \( m \) - adsorbent mass [g].

The measurement results were described using two-parameter adsorption isotherm equations:
- **Freundlich**

\[
q_e = K_F c_e^a
\]

- **Langmuir**

\[
q_e = \frac{q_m K_L c_e}{1 + K_L c_e}
\]

The results were compared with three-parameter isotherm equations
- **Redlich-Peterson**

\[
q_e = \frac{q_m K_{RP} c_e}{1 + K_{RP} c_e^a}
\]

- **Radke-Prausnitz**

\[
q_e = \frac{K_{RP} c_e}{1 + A \cdot c_e^{3-a}}
\]

where: \( q_m \) - adsorption capacity; \( K_L \) [dm\(^3\)/g], \( K_F \) [dm\(^3\)/g], \( K_{RP} \) [mg/g], \( K_{RP} \) [mg/g], \( A \) - constants for the respective equations.

Two-parameter models, though very simple, have been very useful and convenient tools for quantitative comparison of results. Therefore, the vast number of studies is based on fitting Langmuir and/or Freundlich models to experimental data. Langmuir model was successfully applied to describe adsorption of a number of dyes onto crosslinked and grafted chitosan [37-39]. Three-parameter equations for the Redlich-Peterson or
Radke-Prausnitz sorption isotherms, based on modifications of the Langmuir and Freundlich equations should be taken into consideration when two-parameter equations fail. Radke-Prausnitz equation at low concentrations approximates to a linear isotherm, at high concentrations it approaches Freundlich isotherm, and for $n = 0$ it becomes Langmuir isotherm. This model provides a good fitting across a wide range of concentrations and should be preferred over Langmuir and Freundlich models.

**Interpretation of results**

During the studies, a decrease in dye concentration $c$ [mg/dm$^3$] in a solution and the corresponding increase in dye concentration in adsorbent $q$ [mg/g] were observed, calculated using formula (1). The results are shown in Figures 3 and 4 for DO 26 and RB 81 azo dyes, respectively.

![Fig. 3. Sorption kinetics for rye straw - Direct Orange 26 system](image)

![Fig. 4. Sorption kinetics for rye straw - Reactive Blue 81 system](image)

Given the initial and equilibrium concentration in a solution, dye removal rate $R$ [%] was calculated for rye straw depending on the initial concentration (Fig. 5). The results were
better for Direct Orange 26. In this case $R$ was between 62 and 95%, while for Reactive Blue 81 it was between 45 and 84%.

Fig. 5. Dye removal rate

Next, sorption isotherms were calculated using the two- and three-parameter equations. Figures 6 and 7 compare the approximation of experimental data for the DO 26 and the RB 81 dyes, respectively. Points reflect experimental data and lines are generated from the models. Approximation of the experimental data using selected equations in all cases was similar. The calculations were performed using the program Origin and Levenberg-Marquardt optimization procedure.
Table 2 summarizes the calculated coefficients for equations (2)-(5) and statistical evaluation expressed as coefficient of determination $r^2$.

Table 2

<table>
<thead>
<tr>
<th>Equation</th>
<th>Direct Orange 26</th>
<th>Reactive Blue 81</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K$</td>
<td>$q_m$ or $A$</td>
</tr>
<tr>
<td>Freundlich</td>
<td>0.941</td>
<td>0.981</td>
</tr>
<tr>
<td>Langmuir</td>
<td>4.95E-3</td>
<td>5.21E-3</td>
</tr>
<tr>
<td>Redlich-Peterson</td>
<td>69.79</td>
<td>0.489</td>
</tr>
<tr>
<td>Radke-Prausnitz</td>
<td>93.63</td>
<td>0.513</td>
</tr>
</tbody>
</table>

Summary and conclusion

The aim of the present paper was to determine sorption capacity of pretreated rye straw as potential natural adsorbent to remove azo dyes from aqueous solutions. Sorption kinetics of two azo dyes onto natural plant sorbent was discussed. It was determined that sorption was more favorable for Direct Orange 26 comparing to Reactive Blue 81, reaching sorption values for the highest initial concentrations of 22 and 14 mg per gram of dry sorbent, respectively. Initial studies with the use of rye straw not subjected to pretreatment demonstrated that sorption capacity was lower i.e. 14.3 and 12.8 mg, respectively.

To describe sorption equilibrium, two- and three-parameter equations were proposed. Mathematical description with Freundlich, Langmuir, Redlich-Peterson and Radke-Prausnitz isotherms was compared. Experimental data approximation in all of the analyzed cases was effective, which was confirmed by statistical evaluation. It must be
stated, however, that the description of sorption isotherms by Langmuir equation showed worse results. Therefore the equation is not recommended as suitable for describing equilibrium experiments, though it is most widely used in the literature concerning this field.

Mechanically and chemically modified rye straw is suitable for sorption of azo dyes: Direct Orange 26 and Reactive Blue 81 from water solutions.

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References


Sorption equilibrium of azo dyes Direct Orange 26 and Reactive Blue 81 onto a cheap plant sorbent

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Wydział Inżynierii Procesowej i Ochrony Środowiska, Politechnika Łódzka


Słowa kluczowe: barwniki azowe, słoma żytnia, izotermę sorpcji