BIOSORPTION OF METHYLENE BLUE BY WASTE APRICOT SHELLS FROM FOOD INDUSTRY

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Abstract

In this paper, the removal of methylene blue (MB) from aqueous solution by biosorption onto apricot shells has been investigated through batch experiments. Apricot shells were chosen as a locally available and abundant waste from fruit juice industry. Methylene blue is common pollutant of waste waters from textile industry.

The influence of initial MB concentration on biosorption process has been studied. The experimental data have been analysed using Langmuir and Freundlich isotherm models. The Langmuir model better fits to experimental data, which explain monolayer adsorption. Maximum biosorption capacity is 24.31 mg/g. A comparison of the biosorption capacity of waste apricot shells with biosorption capacities of similar adsorbents previously investigated indicates that apricot shells could be a promising biosorbent for removal of MB from aqueous solution.

Keywords: biosorption, apricot shells, methylene blue.

1. INTRODUCTION

Industries such as textile, leather, paper, plastic etc., use dyes in order to color their products and in the same time generate a large amount of colored wastewater [1]. Even a very small amount of dyes in water (less than 1ppm) is visible [2,3].
One of the most commonly used chemical for dying cotton, wood and silk is Methylene Blue (MB) [4]. Molecular structure of MB is illustrated in Figure 1.

![Figure 1. Molecular structure of Methylene Blue](image)

Many methods have been used for wastewater cleaning, including physiochemical, chemical and biological methods such as coagulation and flocculation, ozonation, electrochemical methods, fungal decolonization [5-8] etc. Amongst these methods, adsorption gives the best results [9-11]. Recently, many attempts have been done to develop economic and environmental friendly alternative for wastewater cleaning from this pollutant. Many low-cost adsorbents such as waste materials from agriculture and industry have been proposed by several workers and they showed very good performance for removal of MB [12-16].

The aim of this paper is to investigate applicability of low cost and locally available apricot shells classified as a waste in fruit industry, for MB removal from aqueous solution by process of biosorption.

2. MATERIALS AND METHODS

2.1 Biosorbent Preparation

Apricot stones were obtained from the juice factory “Vino Župa” Aleksandrovac in Serbia. The waste apricot stones were air dried, separated from kernels, milled (KHD Humbolt Wedag AG) and <1 mm fraction of apricot shells was chosen for the biosorption tests. After that, biomaterial was washed with deionized water and dried at 60°C and stored in dry plastic containers.

2.2 Preparation of Stock Solution

Stock solution was prepared by dissolving exact amount of MB (p.a. grade) in deionized water. Solutions of different MB concentrations were prepared by diluting of stock solution to the various concentrations.
2.3 Batch Experiments

Batch experiments were performed by mixing of 0.01 g of biosorbent in 50 mL of MB solution of various concentration (from 1.2 to 12 mg/L). The mixtures were shaken during 48 h in shaker at 250 rpm at ambient temperature and at pH 5.0. Afterwards, the mixture was filtrated and the concentration of MB remaining in the filtrate was analysed by spectrophotometer Spekol 1300 at 620 nm.

The amount of MB sorbed per gram of sorbent (q, mg/g) of MB adsorbed by the biosorbent was obtained by the following equation:

$$q = \frac{(C_i - C_{eq}) \cdot V}{m}$$

(1)

where $V$ is solution volume (L), $m$ is mass of the sorbent (g), and $C_i$ and $C_{eq}$ (mg/L) are the initial and final concentration of the MB in the solution, respectively.

3. RESULT AND DISCUSSION

3.1 Effect of initial MB concentration

Figure 2 shows the effect of various initial MB concentrations on biosorption capacity and biosorption efficiency. As can be seen biosorption efficiency decreases with increase of dye concentration but the amount of MB adsorbed per unit mass of biosorbent increases with increase of MB concentration. Previous studies are in correlation with obtained results: as the MB concentration increases, the number of available sites on the surface of biosorbent decreases. When the concentration of MB is low, molecules of the adsorbat have more chance to react with the available active sites on biosorbent resulting in increased adsorption rate [17].
3.2 Adsorption isotherms

The adsorption isotherm illustrates the correlation among the quantity of adsorbate taken by the biosorbent and the adsorbate residual concentration in solution [18]. Experimental data were fitted to the two isotherm models (Figure 3): Langmuir (1) and Freundlich (2).

\[ q = \frac{q_m K_c}{1 + K_c C} \]  
(1)

Where \( q \) (mg/g) is amount of MB adsorbed per mass of adsorbent, \( C \) (mg/L) is equilibrium concentration, \( q_m \) (mg/g) is the maximum adsorption capacity of the biosorbent and \( K_L \) (L/mg) are the Langmuir constants.

The Freundlich adsorption isotherm is an indication of the surface heterogeneity of biosorbent [19].

\[ q = K_F C^{n/\alpha} \]  
(2)

Where \( q \) (mg/g) is amount of metal ions adsorbed per mass of adsorbent, \( C \) (mg/L) is equilibrium concentration \( n \) is the Freundlich constants related to adsorption capacity and \( K_F \) is the adsorption coefficient.

The constants for both isotherms are given in Table 1. According to correlation factor (\( R^2=0.997 \)) adsorption isotherm better follows the Langmuir model than Freundlich, which means that the surface of this biosorbent is homogenous. As can be seen from Table 1 maximum biosorption capacity value is 24.31 mg/g.
Table 1. Langmuir and Freundlich isotherm constants

<table>
<thead>
<tr>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Experimental value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_m$ (mg/L)</td>
<td>$K_L$ (L/g)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>24.31</td>
<td>1.95</td>
<td>0.997</td>
</tr>
</tbody>
</table>

Figure 3. Langmuir and Freundlich isotherms

Table 2 presents a comparison of several adsorbents employed for MB biosorption. Waste apricot shells present very good adsorption capacities for the chosen adsorbat when compared with several different adsorbents.

Table 2. Biosorbent capacity of MB

<table>
<thead>
<tr>
<th>Biosorbents</th>
<th>Biosorbent capacity (mg/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hazelnut shell</td>
<td>38.22</td>
<td>[12]</td>
</tr>
<tr>
<td>Rice husk</td>
<td>28</td>
<td>[13]</td>
</tr>
<tr>
<td>Cotton waste</td>
<td>24</td>
<td>[13]</td>
</tr>
<tr>
<td>Banana peel</td>
<td>20.8</td>
<td>[14]</td>
</tr>
<tr>
<td>Orange peel</td>
<td>18.6</td>
<td>[14]</td>
</tr>
<tr>
<td>Wheat shells</td>
<td>16.56</td>
<td>[15]</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>2.23</td>
<td>[16]</td>
</tr>
</tbody>
</table>
4. CONCLUSION

The presented results revealed possibility to use apricot stones as a biosorbents for the removal of MB from aqueous solution. A usage of this non-treated biosorbent (biosorbent is prepared without energy consumption) is economically and environmentally significant. Langmuir isotherm model better fits to experimental data and the monolayer adsorption capacity of waste apricot shells for MB was found to be 24.31 mg/g. The waste apricot shells are an effective alternative biomaterial for the removal of MB from aqueous solution.

Acknowledgement

This study is part of the project TR 31003, “Development of technologies and products based on mineral raw materials and waste biomass for protection of natural resources for safe food production”, supported by the Ministry of Education and science of the Republic of Serbia.

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DOI: 10.7251/JEPMEN1507107S
UDK: 54.43:634.21

Naučni rad

BIOSORPCIJA METILEN PLAVOG UPOTREBOM OTPADNE BIOMASE (LJUSKE KAJSIJA) POREKLOM IZ PREHRAMBENE INDUSTRIJE

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Izvod

U radu je ispitivana biosorpncija metilen plavog(MB) iz vodenih rastvora u šaržnom sistemu, upotrebom otpadne biomase- ljuske kajsija. Ova biomasa poreklom iz fabrike sokova je odabrana zbog svoje dostupnosti i značajnih količina koje se generišu na godišnjem nivou. Metilen plavo je čest zagađivač koji se javlja u otpadnim vodama i poreklom je iz tekstilne industrije.


Poređenje biosorpcioni kapaciteta ranije ispitanih sličnih biomaterijala i otpadne biomase opisane u ovom radu, pokazuje da ljuske kajsija mogu biti dobar biosorbet MB iz vodenih rastvora.

Ključne reči: biosorpncija, ljuske kajsija, metilen plavo