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***Fixed-bed-column studies in laboratory and pilot scale for Methylene Blue removal and recovery by untreated, autohydrolized and brine hydrolized spruce***



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**ABSTRACT**

This work reports the practicability of using spruce to remove widely used basic dyes like Methylene Blue from wastewaters. In continuous fixed-bed column systems, the effects of parameters such as bed-depth, flow rate and initial dye concentration were examined. The results revealed that the Methylene Blue is fairly adsorbed on spruce. This process could be a low cost technique for the removal of basic dyes from aqueous systems.

**Keywords:** adsorption, desorption, column, methylene blue, spruce, wastewaters

1. **Introduction**

This work aims at the analytical presentation of the fixed-bed or packed-column biomass adsorption systems and reactors and their design methods. Initially the definitions are given about fixed-bed or packed-bed systems and/ or reactors. Then, the physical characteristics of the fixed-bed columns are presented. Both ends, low, medium and high scale (laboratory and pilot) individual experiments are combined to provide a basis for scale up modeling. Next, the scale up or modeling of dye removal systems is thoroughly analyzed. The vast majority of existing mathematical models for similar systems are referring to the removal of heavy metals, organic toxicants etc. from wastewater or from natural water systems (lake, river, sea, surface, underground). In this study continuous fixed-bed-column systems were investigated. The adsorbents which we use are: spruce (*PiceaAbies*) untreated, spruce modified by autohydrolysis. The column systems were filed with biomass at various initial dye concentrations, flow rates and bed-depths.

**2. Materials and Methods**

*2.1 Adsorbents*

The Spruce (*PiceaAbies*) sawdust used was obtained from a local furniture manufacturing company, as a suitable source for full-scale/industrial applications. The moisture content of the material when received was 9% (w/w); after screening, the fraction with particle sizes between 0.2 and 0.9 mm was isolated.

*2.2 Adsorbate*

The dye used herein in batch and column experiments was Methylene Blue (C16H18ClN3S. 3H2O, molecular weight = 373.90 10-3 kg mol-1) supplied by Sigma-Aldrich. A stock solution was prepared by dissolving a specific amount of MB (humidity 22%) in distilled water. Working solutions were 3 - 140 mg L-1. MB concentrations were determined by measuring the absorbent values in each experiment with HACH DR4000U UV-VIS spectrophotometer at *λ=664nm.*

*2.3 Pretreatments*

*2.3.1 Pretreatment by autohydrolysis*

The autohydrolysis process was performed in a 3.75-L batch reactor PARR 4843. The isothermal autohydrolysis time was t = 0, 10, 20, 30, 40 and 50 min (not including the non-isothermal preheating and the cooling time-periods); the reaction was catalyzed by the organic acids produced by the pine sawdust itself during autohydrolysis at a liquid-to-solid ratio of 10:1; the liquid phase volume (water) was 2000 mL and the solid material dose (pine sawdust) was 200 g; stirring speed 150 rpm. The reaction ending temperature values were T = 160 °C, 200 °C and 240 °C, reached after t = 42, 62 and 80 min preheating time values, respectively. The autohydrolysis product was filtered using a Buchner filter with Munktell paper sheet (grade 34/N) to separate the liquid phase and from the solid phase. The solid residue was washed with water until neutral pH (the initial filtrate pH was 2.90–4.76depending on the autohydrolysis severity). The solid residue was dried at 110 °C for 10 days at room temperature to reach the humidity of the untreated material. Then it was used as adsorbent.

Table 6: Adsorption by autohydrolized spruce

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **T (oC)** | **t (min)** | **Ci** | **Q (mL/min)** | **m (g)** | **N** | **K** | **R** | **qo (mg/g)** |
|  |  |  |  |  |  |  |  |  |
| **160** | 0 | 165 | 20 | 20 | 9643 | 0,000146 | -0,9313 | 43,01 |
| **160** | 0 | 165 | 20 | 20 | 6492 | 0,000541 | -0,9651 | 28,96 |
| **160** | 20 | 165 | 20 | 20 | 6362 | 0,000449 | -0,9573 | 28,38 |
| **160** | 30 | 165 | 20 | 20 | 7176 | 0,000381 | -0,9325 | 32,01 |
| **160** | 40 | 165 | 20 | 20 | 6092 | 0,000596 | -0,9779 | 27,17 |
| **160** | 50 | 165 | 20 | 20 | 10412 | 0,000193 | -0,8966 | 46,44 |
| **180** | 10 | 165 | 20 | 20 | 6926 | 0,000371 | -0,9740 | 30,89 |
| **240** | 30 | 165 | 20 | 20 | 7355 | 0,000229 | -0,9551 | 41,06 |
| **240** | 50 | 165 | 20 | 20 | 5389 | 0,000275 | -0,9813 | 28,38 |

*2.3.2 Pretreatment by brine - hydrolysis*

The brine treatment process was performed in a 3.75-L batch reactor PARR 4843. The isothermal autohydrolysis time was t = 0, 10, 20, 30, 40 and 50 min (not including the non-isothermal preheating and the cooling time-periods); the reaction was catalyzed by the organic acids produced by the pine sawdust itself during autohydrolysis at a liquid-to-solid ratio of 10:1; the liquid phase volume (water) was 2000 mL and the solid material dose (pine sawdust) was 200 g; stirring speed 150 rpm. The reaction ending temperature values were T = 160 °C, 200 °C and 240 °C, reached after t = 42, 62 and 80 min preheating time values, respectively. The autohydrolysis product was filtered using a Buchner filter with Munktell paper sheet (grade 34/N) to separate the liquid phase and from the solid phase. The solid residue was washed with water until neutral pH (the initial filtrate pH was 2.90–4.76 depending on the autohydrolysis severity). The solid residue was dried at 110 °C for 10 days at room temperature to reach the humidity of the untreated material. Then it was used as adsorbent.

Table 7: Adsorption by brine hydrolyzed spruce

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Conc. X Times** | **T (oC)** | **t (min)** | **Ci** | **Q (mL/min)** | **x (cm)** | **m (g)** | **N** | **K** | **R** | **qo (mg/g)** |
| **1** | 180 | 50 | 165 | 20 | 15 | 20 | 4948 | 0,000353 | -0,9481 | 18,21 |
| **2** | 180 | 50 | 165 | 20 | 15 | 20 | 6975 | 0,000242 | -0,9683 | 25,67 |
| **4** | 140 | 0 | 165 | 20 | 15 | 20 | 8461 | 0,000153 | -0,9616 | 51,42 |
| **4** | 160 | 0 | 165 | 20 | 15 | 20 | 4304 | 0,000694 | -0,9946 | 27,07 |
| **4** | 160 | 50 | 165 | 20 | 15 | 20 | 5834 | 0,000300 | -0,9662 | 21,47 |
| **4** | 180 | 0 | 165 | 20 | 15 | 20 | 6054 | 0,000257 | -0,9744 | 38,41 |
| **4** | 180 | 50 | 165 | 20 | 15 | 20 | 5666 | 0,000444 | -0,9479 | 20,85 |
| **4** | 200 | 0 | 165 | 20 | 15 | 20 | 4682 | 0,000866 | -0,9667 | 28,01 |
| **4** | 200 | 50 | 165 | 20 | 15 | 20 | 9259 | 0,000132 | -0,9390 | 46,67 |
| **4** | 200 | 50 | 165 | 20 | 15 | 20 | 7713 | 0,000157 | -0,9232 | 28,38 |
| **4** | 220 | 50 | 165 | 20 | 15 | 20 | 5840 | 0,000235 | -0,9863 | 35,82 |
| **4** | 200 | 50 | 165 | 20 | 15 | 20 | 9233 | 0,000181 | -0,9466 | 33,97 |
| **4** | 240 | 50 | 165 | 20 | 15 | 20 | 1358 | 0,000899 | -0,9237 | 7,69 |
| **4** | 240 | 50 | 165 | 20 | 15 | 20 | 451 | 0,000369 | -0,7918 | 2,76 |
| **4** | 240 | 50 | 165 | 20 | 15 | 20 | 451 | 0,000369 | -0,7918 | 2,76 |
| **8** | 180 | 0 | 165 | 20 | 15 | 20 | 4715 | 0,000212 | -0,9565 | 28,92 |
| **8** | 180 | 50 | 165 | 20 | 15 | 20 | 7089 | 0,000351 | -0,9211 | 30,16 |
| **8** | 180 | 50 | 165 | 20 | 15 | 20 | 5695 | 0,000259 | -0,9799 | 20,96 |

*2.4 Continuous fixed-bed column studies*

The column can be filled with random dumped packing (creating a 'random packed column') or with structured packing sections, which are arranged or stacked (creating a ‘stacked packed column’). In the column, liquids tend to wet the surface of the packing and the vapors pass across this wetted surface, where mass transfer takes place [1-2]. Packing material can be used instead of trays to improve separation in distillation columns. Packing offers the advantage of a lower pressure drop across the column (when compared to plates or trays), which is beneficial while operating under vacuum. Differently shaped packing materials have different surface areas and void space between the packing. Both of these factors affect packing performance [2].

Packed columns are most frequently used to remove contaminants from a gas stream (adsorption). However, packed columns can also be used to remove volatile components from a liquid stream by contacting it with an inert gas (stripping). They are also used in distillation applications where the separation is particularly difficult due to close boiling components.

*2.5 Instrumental Analysis*

The concentration of output solution was measurement at *λ=*664 nm and using HACH DR4000U UV-vis spectrophotometer. Finally, pH measurements were made using a digital pH meter, MultiLab model 540.

## Results and Discussion

*3.1 Continuous fixed-bed-column adsorption models*

Bohart and Adams (1920) came up with the Bohart-Adams (B-A) model when they proceeded with their work of analyzing the typical chlorine charcoal transmission curve [15]. A widely used continuous fixed-bed-column model was established by Bohart and Adams [15], who assumed that the rate of adsorption is controlled by the surface binding (through chemical reaction or physical interaction) between adsorbate and unused capacity of the solid, i.e., adsorption rate *= K.C.Cu*, where *K* is the adsorption rate coefficient, *C* is the adsorbate concentration at the solid phase at distance *x*, and *Cu* is the unused surface adsorptive capacity at time *t*, expressed as mass per volume of bed. The material balance for adsorbate is given by the partial differential equation

 (1)

while the corresponding partial differential equation for the *Cu* decrease is

 (2)

where *u* is the superficial liquid velocity. These equations are obtained neglecting diffusion and accumulation terms, assumptions that are valid in chemical engineering practice, provided that strict scale up specifications are kept in the design stage and successful operation conditions are kept in the industrial operation stage.

The differential equations can be integrated over the total length *x* of the bed to give:

 (3)

Where *N* (mg L-1) is the initial or total adsorption capacity coefficient, also quoted as *Cu,*0 [15]; *C*=effluent concentration (mg L-1); *Ci*=influent concentration (mg L-1); *K*=adsorption rate coefficient (); *x*=bed depth (cm); *u*=linear velocity (cm*.*min-1); and *t*=time (min). Since is usually much greater than unity, this equation can be simplified to:

 (4)

Which is commonly used by researchers, because of its convenience in estimating the values of parameters *K* and *N* through linear regression either of ln[(*C*0 */ Ci*)– 1] vs *t* or *t* vs *x* when the following rearrangement is adopted:

 (5)

In this rearrangement, *t* is the time to breakthrough, i.e., the time period required for concentration to reach a predetermined value. For using the last expression as a linear regression model, wastewater is passed through beds of varying depths, keeping constant *Ci* and *u*, preferably at values similar to those expected to prevail under real conditions at full scale. Alternatively, it can be performed by the aid of at least three columns arranged in series. In such a case, sampling takes place at the bottom of each column and measured for adsorbate concentration, making more frequent measurements when approaching the breakthrough concentration *C*. Finally, the time at which the effluent reaches this concentration is used as the dependent variable while *x* plans the role of the independent one. Evidently, the use of such a regression model implies the additional error of measuring the independent variable with less precision in comparison with the dependent. The common error in both models comes from the estimation of concentration from measuring adsorbance although the reference relation/curve has been structured/drawn in the inverse mode, i.e., for predetermined concentrations the corresponding adsorbances have been measured.

In the present work, the model of eq. (4) has been used for parameter values estimation through linear regression to obtain numerical results comparable with corresponding data found for other fixed bed adsorption studies in literature. The non-linear form of this model is:

 (6)

where*; *. The model of eq. (6) has been used for parameter values estimation through NLRA to obtain more reliable numerical results, i.e., with a lower total standard error of estimate (SEE). In the last curve, the regression model is written under the form for parameter identification through *Ci* value estimation (a) endogenously and (b) exogenously.

On the other hand, Clark [16] has advanced the Bohart and Adams model [15] by incorporating the parameter *n* of the Freundlich adsorption isotherm:

 (7)

Where *n* = inverse of the slope of the Freundlich isotherm [18]. Finally, the Bohart and Adams model [15] can be reduced for *n=*2 from Clark model [16].

*3.2. Continuous fixed-bed-column results*

In this study continuous fixed-bed-column systems were investigated. The column systems were filed with spruce at various initial dye concentrations, flow rates and bed-depths.

Table 1: Fixed Bed Column Systems for spruce

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Ci** | **Q (mL/min)** | **x (cm)** | **m (g)** | **N** | **K** | **R** | **qo (mg/g)** |
| 160 | 20 | 15 | 12 | 6683 | 0.000318 | -0.9506 | 40.99 |
| 160 | 20 | 15 | 12 | 7400 | 0.000100 | -0.9367 | 45.38 |
| 160 | 20 | 15 | 13 | 6507 | 0.000356 | -0.9992 | 36.84 |
| 160 | 20 | 15 | 13 | 6387 | 0.000518 | -0.9539 | 36.16 |
| 160 | 20 | 15 | 13 | 6387 | 0.000518 | -0.9539 | 36.16 |
| 160 | 20 | 15 | 15 | 5329 | 0.000416 | -0.9153 | 26.14 |
| 160 | 20 | 15 | 19 | 5274 | 0.000415 | -0.9457 | 20.16 |
| 160 | 20 | 15 | 19 | 5274 | 0.000415 | -0.9457 | 20.16 |
| 160 | 20 | 15 | 20 | 9248 | 0.000110 | -0.9530 | 19.19 |
| 160 | 20 | 15 | 20 | 8738 | 0.000216 | -0.9765 | 32.15 |
| 160 | 40 | 15 | 20 | 4459 | 0.000515 | -0.9903 | 16.41 |
| 160 | 40 | 25 | 34 | 5320 | 0.000347 | -0.9892 | 19.19 |
| 160 | 20 | 25 | 34 | 6154 | 0.000243 | -0.9870 | 22.20 |
| 80 | 40 | 25 | 34 | 4480 | 0.000689 | -0.9911 | 16.16 |

Table 2: Fixed Bed Column Systems for spruce modified by autohydrolysis (x=15cm)

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **T (oC)** | **t (min)** | **Ci** | **Q (mL/min)** | **m (g)** | **N** | **K** | **R** | **qo (mg/g)** |
|  |  |  |  |  |  |  |  |  |
| 160 | 0 | 160 | 20 | 16.5 | 9643 | 0.000146 | -0.9313 | 43.01 |
| 160 | 0 | 160 | 20 | 16.5 | 6492 | 0.000541 | -0.9651 | 28.96 |
| 160 | 20 | 160 | 20 | 16.5 | 6362 | 0.000449 | -0.9573 | 28.38 |
| 160 | 30 | 160 | 20 | 16.5 | 7176 | 0.000381 | -0.9325 | 32.01 |
| 160 | 40 | 160 | 20 | 16.5 | 6092 | 0.000596 | -0.9779 | 27.17 |
| 160 | 50 | 160 | 20 | 16.5 | 10412 | 0.000193 | -0.8966 | 46.44 |
| 180 | 10 | 160 | 20 | 16.5 | 6926 | 0.000371 | -0.9740 | 30.89 |
| 240 | 30 | 160 | 20 | 13.81 | 7355 | 0.000229 | -0.9551 | 41.06 |
| 240 | 50 | 160 | 20 | 14.16 | 5389 | 0.000275 | -0.9813 | 28.38 |

Table 3: Fixed Bed Column Systems for spruce modified by brine treatment

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Concen****trated X Times** | **T (oC)** | **t (min)** | **Ci** | **Q (mL/min)** | **x (cm)** | **m (g)** | **N** | **K** | **R** | **qo (mg/g)** |
| 1 | 180 | 50 | 165 | 20 | 15 | 20 | 4948 | 0.000353 | -0.9481 | 18.21 |
| 2 | 180 | 50 | 165 | 20 | 15 | 20 | 6975 | 0.000242 | -0.9683 | 25.67 |
| 4 | 140 | 0 | 165 | 20 | 15 | 12.11 | 8461 | 0.000153 | -0.9616 | 51.42 |
| 4 | 160 | 0 | 165 | 20 | 15 | 11.7 | 4304 | 0.000694 | -0.9946 | 27.07 |
| 4 | 160 | 50 | 165 | 20 | 15 | 20 | 5834 | 0.000300 | -0.9662 | 21.47 |
| 4 | 180 | 0 | 165 | 20 | 15 | 11.6 | 6054 | 0.000257 | -0.9744 | 38.41 |
| 4 | 180 | 50 | 165 | 20 | 15 | 20 | 5666 | 0.000444 | -0.9479 | 20.85 |
| 4 | 200 | 0 | 165 | 20 | 15 | 12.3 | 4682 | 0.000866 | -0.9667 | 28.01 |
| 4 | 200 | 50 | 165 | 20 | 15 | 14.6 | 9259 | 0.000132 | -0.9390 | 46.67 |
| 4 | 200 | 50 | 165 | 20 | 15 | 20 | 7713 | 0.000157 | -0.9232 | 28.38 |
| 4 | 220 | 50 | 165 | 20 | 15 | 12 | 5840 | 0.000235 | -0.9863 | 35.82 |
| 4 | 200 | 50 | 165 | 20 | 15 | 20 | 9233 | 0.000181 | -0.9466 | 33.97 |
| 4 | 240 | 50 | 165 | 20 | 15 | 13 | 1358 | 0.000899 | -0.9237 | 7.69 |
| 4 | 240 | 50 | 165 | 20 | 15 | 12 | 451 | 0.000369 | -0.7918 | 2.76 |
| 4 | 240 | 50 | 165 | 20 | 15 | 12 | 451 | 0.000369 | -0.7918 | 2.76 |
| 8 | 180 | 0 | 165 | 20 | 15 | 12 | 4715 | 0.000212 | -0.9565 | 28.92 |
| 8 | 180 | 50 | 165 | 20 | 15 | 17.3 | 7089 | 0.000351 | -0.9211 | 30.16 |
| 8 | 180 | 50 | 165 | 20 | 15 | 20 | 5695 | 0.000259 | -0.9799 | 20.96 |

Table 4: Adsorption by untreated spruce

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Ci** | **Q (mL/min)** | **x (cm)** | **m (g)** | **N** | **K** | **R** | **qo (mg/g)** |
| **165** | 20 | 15 | 12 | 6683 | 0,000318 | -0,9506 | 40,99 |
| **165** | 20 | 15 | 12 | 7400 | 0,000100 | -0,9367 | 45,38 |
| **165** | 20 | 15 | 13 | 6507 | 0,000356 | -0,9992 | 36,84 |
| **165** | 20 | 15 | 13 | 6387 | 0,000518 | -0,9539 | 36,16 |
| **165** | 20 | 15 | 13 | 6387 | 0,000518 | -0,9539 | 36,16 |
| **165** | 20 | 15 | 15 | 5329 | 0,000416 | -0,9153 | 26,14 |
| **165** | 20 | 15 | 19 | 5274 | 0,000415 | -0,9457 | 20,16 |
| **165** | 20 | 15 | 19 | 5274 | 0,000415 | -0,9457 | 20,16 |
| **165** | 20 | 15 | 20 | 9248 | 0,000110 | -0,9530 | 19,19 |
| **165** | 20 | 15 | 20 | 8738 | 0,000216 | -0,9765 | 32,15 |
| **165** | 40 | 15 | 20 | 4459 | 0,000515 | -0,9903 | 16,41 |
| **165** | 40 | 25 | 34 | 5320 | 0,000347 | -0,9892 | 19,19 |
| **165** | 20 | 25 | 34 | 6154 | 0,000243 | -0,9870 | 22,20 |
| **80** | 40 | 25 | 34 | 4480 | 0,000689 | -0,9911 | 16,16 |
| **165** | 2 | 72 | 4470 | 6110 | 6,66E-05 | -0,9435 | 0,02 |
| **165** | 2 | 20 | 4470 | 3576 | 0,000287 | -0,9195 | 0,02 |
| **165** | 2 | 40 | 4470 | 3644 | 0,000277 | -0,9255 | 0,02 |
| **165** | 2 | 56 | 4470 | 4347 | 0,000468 | -0,9681 | 0,02 |
| **80** | 1 | 20 | 4470 | 8669 | 9,6E-05 | -0,9625 | 0,02 |
| **165** | 2 | 72 | 4470 | 9087 | 8,29E-05 | -0,9423 | 0,03 |
| **165** | 2 | 20 | 4470 | 5852 | 0,000171 | -0,9228 | 0,03 |
| **165** | 2 | 40 | 4470 | 6013 | 0,000197 | -0,9261 | 0,03 |
| **165** | 2 | 56 | 4470 | 6584 | 0,000197 | -0,8918 | 0,03 |
| **80** | 1 | 40 | 4470 | 7620 | 6,36E-05 | -0,9612 | 0,03 |
| **330** | 1 | 72 | 4470 | 6894 | 8,89E-05 | -0,9282 | 0,02 |
| **330** | 1 | 20 | 4470 | 3079 | 0,000229 | -0,9549 | 0,02 |
| **330** | 1 | 40 | 4470 | 4409 | 0,00026 | -0,9669 | 0,02 |
| **330** | 1 | 56 | 4470 | 6547 | 0,000131 | -0,8401 | 0,02 |
| **80** | 1 | 56 | 4470 | 6727 | 0,000162 | -0,9798 | 0,02 |
| **165** | 1 | 72 | 4470 | 8178 | 0,000111 | -0,9541 | 0,02 |
| **165** | 1 | 20 | 4470 | 3367 | 0,000142 | -0,9386 | 0,02 |
| **165** | 1 | 40 | 4470 | 4480 | 0,000181 | -0,9214 | 0,02 |
| **165** | 1 | 56 | 4470 | 6270 | 0,000204 | -0,9606 | 0,02 |
| **80** | 1 | 72 | 4470 | 6650 | 0,000259 | -0,9228 | 0,03 |
| **165** | 1 | 20 | 4470 | 3367 | 0,000142 | -0,9386 | 0,03 |
| **165** | 2 | 40 | 4470 | 3644 | 0,000277 | -0,9255 | 0,03 |
| **165** | 2 | 56 | 4470 | 6584 | 0,000197 | -0,8918 | 0,03 |
| **165** | 1 | 72 | 4470 | 8178 | 0,000111 | -0,9541 | 0,04 |
| **165** | 2 | 20 | 4470 | 3576 | 0,000287 | -0,9195 | 0,04 |
| **165** | 2 | 40 | 4470 | 6013 | 0,000197 | -0,9261 | 0,04 |
| **165** | 2 | 72 | 4470 | 6110 | 6,66E-05 | -0,9435 | 0,04 |
| **165** | 2 | 20 | 4470 | 5852 | 0,000171 | -0,9228 | 0,04 |
| **165** | 1 | 56 | 4470 | 6270 | 0,000204 | -0,9606 | 0,02 |
| **165** | 2 | 72 | 4470 | 9087 | 8,29E-05 | -0,9423 | 0,02 |
| **165** | 1 | 40 | 4470 | 4480 | 0,000181 | -0,9214 | 0,02 |
| **165** | 2 | 56 | 4470 | 4347 | 0,000468 | -0,9681 | 0,02 |
| **165** | 2 | 27 | 8691,25 | 7916 | 0,000131 | -0,9575 | 0,02 |
| **165** | 1 | 107 | 8691,25 | 4496 | 7,59E-05 | -0,9625 | 0,02 |
| **165** | 1 | 137 | 8691,25 | 3743 | 6,74E-05 | -0,9760 | 0,02 |
| **165** | 1 | 27 | 8691,25 | 10041 | 3,08E-05 | -0,9818 | 0,01 |
| **165** | 1 | 67 | 8691,25 | 5410 | 3,13E-05 | -0,9809 | 0,01 |
| **80** | 1 | 72 | 4470 | 7398 | 6,08E-05 | -0,7585 | 0,02 |
| **165** | 1 | 72 | 4470 | 8178 | 0,000111 | -0,9541 | 0,04 |
| **165** | 1 | 20 | 4470 | 3367 | 0,000142 | -0,9386 | 0,04 |
| **165** | 1 | 40 | 4470 | 4480 | 0,000181 | -0,9214 | 0,04 |
| **165** | 1 | 56 | 4470 | 6270 | 0,000204 | -0,9606 | 0,02 |
| **165** | 2 | 72 | 4470 | 6110 | 6,66E-05 | -0,9435 | 0,02 |
| **165** | 2 | 20 | 4470 | 3576 | 0,000287 | -0,9195 | 0,02 |
| **165** | 2 | 40 | 4470 | 3644 | 0,000277 | -0,9255 | 0,02 |
| **165** | 2 | 56 | 4470 | 4347 | 0,000468 | -0,9681 | 0,02 |
| **165** | 2 | 72 | 4470 | 9087 | 8,29E-05 | -0,9423 | 0,02 |
| **165** | 2 | 20 | 4470 | 5852 | 0,000171 | -0,9228 | 0,02 |
| **165** | 2 | 40 | 4470 | 6013 | 0,000197 | -0,9261 | 0,02 |
| **165** | 2 | 56 | 4470 | 6584 | 0,000197 | -0,8918 | 0,02 |

Table 5: Adsorption by untreated spruce

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Ci** | **Q (mL/min)** | **x (cm)** | **m (g)** | **N** | **K** | **R** | **qo (mg/g)** |
| **165** | 20 | 15 | 12 | 6683 | 0,000318 | -0,9506 | 40,99 |
| **165** | 20 | 15 | 12 | 7400 | 0,000100 | -0,9367 | 45,38 |
| **165** | 20 | 15 | 13 | 6507 | 0,000356 | -0,9992 | 36,84 |
| **165** | 20 | 15 | 13 | 6387 | 0,000518 | -0,9539 | 36,16 |
| **165** | 20 | 15 | 13 | 6387 | 0,000518 | -0,9539 | 36,16 |
| **165** | 20 | 15 | 15 | 5329 | 0,000416 | -0,9153 | 26,14 |
| **165** | 20 | 15 | 19 | 5274 | 0,000415 | -0,9457 | 20,16 |
| **165** | 20 | 15 | 19 | 5274 | 0,000415 | -0,9457 | 20,16 |
| **165** | 20 | 15 | 20 | 9248 | 0,000110 | -0,9530 | 19,19 |
| **165** | 20 | 15 | 20 | 8738 | 0,000216 | -0,9765 | 32,15 |
| **165** | 40 | 15 | 20 | 4459 | 0,000515 | -0,9903 | 16,41 |
| **165** | 40 | 25 | 34 | 5320 | 0,000347 | -0,9892 | 19,19 |
| **165** | 20 | 25 | 34 | 6154 | 0,000243 | -0,9870 | 22,20 |
| **80** | 40 | 25 | 34 | 4480 | 0,000689 | -0,9911 | 16,16 |

*3.5. Discussion*

Our study is aresearch on theadsorption capacityof thespruceandits application toindustrial scale. There is objectforfurtherresearch to determinethe sprucequantityby region distribution and correspondingexploitationby industrial scale unit.

The Methylene Blue adsorption capacity for various lignocellulosic materials found in the literature was compared to the spruce adsorption capacity estimated in the present work. The adsorption capacity of the spruce was better than the adsorption capacity of other waste biomass such as peanut husk [21], *turbinaria turbinate*alga [18], and wheat straw [19].

The present study is a part of continues involvement of our Research Group in the study of wastewater treatment using original and modified (pretreated) lignocellulosic biomass as potential adsorbents. Consequently, spruce is of high interest for industrial scale application, especially in wood producing countries. The use of spruce could be an answer, given its abundance as a common waste in industry and rural environment. It is therefore a challenge to find a solution to the problem of wastewater cleaning.

The search for a low cost and easily available adsorbent has led to the investigation of materials of agricultural and biological origin, along with industrial by-products, as adsorbents. When biomass is immobilized the number of binding sites easily accessible to pollutant in solution is greatly reduced since the majority of sites will lie within the bead.

So a good support material used for immobilization should be rigid, chemically inert and cheap, should bind cells firmly, should have high loading capacity and should have a loose structure for overcoming diffusion limitations. For continuous operation with immobilized biomass, the most convenient configuration is that of a packed column, much like that used for ion exchange. A packed bed column is an effective process for cyclic sorption/desorption, as it makes the best use of the concentration difference known to be a driving force for adsorption and allows more efficient utilization of the sorbent capacity and results in a better quality of the effluent.

## 4. Conclusions

Fixed-bed or column adsorption is the most popular option in practical application of adsorption process, and due to the complexity of a column adsorption system and lack of solid theory, its mathematical modeling is obviously more difficult thanbatch adsorption.To choose or develop a suitable model, accuracy and convenience should be considered simultaneously.

Fixed bed columns systems with continuous flow allow the regenerating cycles operation. Using an appropriate effluent solution, the sorbent can be regenerate. The regeneration process liberates small volumes of concentrated metal solutions, which

is more appropriate for conventional recovery processes.

Calculated breakthrough curves of the model were in approximate agreement with the experimental ones. It was established that the column behavior of this biosorbent was not entirely predictable on the basis of the simplistic Bohart and Adams model. A more detailed analysis using mass transfer models will be the subject of futurecommunications.

The process allows treatmentof a given volume of effluent by using a minimal mass ofadsorbent which concentrates maximal content of dye.The adsorptionbreakthrough curves obtained at different flow rates indicate that an increase in flow rate decreases the volume treated until the breakthrough point and therefore decreases the service time of the bed.Lower removal capacities were observed, probably due to the fact that contact timeswas insufficient for the adsorption equilibrium to develop between the spruce and the dye.

However, from the literature reviewed, the sorbent used in this study was compared in term of cost with those that stand out for high absorbency such as activated carbon, fungi biomass, ion-exchange resins, marine algae. Although, improved sorption capacity may compensate the cost of additional processing it was noticed that the spruce presented a better option with a completereusability, lower purchase price, biodegradable, by-product and easy handling.

**References**

[1] S. Chakraborty, S. Chowdhury, P.D. Saha, Adsorption of Crystal violet from aqueous solution onto NaOH-modified rice husk, Carbohydr. Polym., 86 (2011) 1533–1541.

[2] R.Ahmad, Studies on adsorption of crystal violet dye from aqueous solution onto Coniferous. Pinus Bark Powder (CPBP),J. Hazard.Mater., 171(2009) 767–773.

[3] P.Senthilkumar, S.Ramalingam, C.Senthamarai, M.Niranjanaa, M.Vijayalakshmi, M.Sivanesan, Adsorption of dye from aqueous solution by cashew nut shell: studies on equilibrium isotherm, kinetics and thermodynamics of interactions, Desalination 261(2010) 52–60.

[4] A.Saeed, M.Sharif, M.Iqbal, Adsorption potential of grape fruit peel as dye sorbent: kinetics, equilibrium and mechanism of Crystal violet adsorption, J. Hazard.Mater., 179(2010) 564–572.

[5] S.Chowdhury, P.D.Saha, Artificial neural network (ANN) modeling of adsorption of methylene blue by NaOH–modified rice husk in a fixed-bed column, Environ Sci.Pollut. Res.,20(2013) 1050–1058.

[6] C.H.Weng, Y.T.Lin, T.W.Tzeng, Removal of methylene blue from aqueous solution by adsorption onto pineapple leaf powder, J. Hazard.Mater., 170(2009) 417–424.

[7] U.Farooq, J.A.Kozinski, M.A.Khan, M.Athar,Biosorption of heavy metal ions using wheat based bio-adsorbents, Bioresour. Technol., 101(2010) 5043–5053.

[8] O.Tunc,H.Tanaci, Z. Aksu, Potential use of cotton plant wastes for the removal of Remazol Black B reactive dye, J. Hazard.Mater.,163(2009) 187–198.

[9] K.Upendra, B.Manas, Fixed bed column study for Cd (II) removal from wastewater using treated rice husk, J. Hazard.Mater.,B 129(2006) 253–259.

[10] S.H.Hasan,D.Ranjana, M.Talat, Agro-industrial waste wheat bran for the biosorptive remediation of selenium through continuous up-flow fixed-bed column, J. Hazard.Mater.,181(2010) 1134–1142.

[11] K.S.Low,C.K. Lee, Cadmium uptake by the Moss, Calymperesdelesserti,Besch. Bioresour Technol., 38(1991) 1–6.

[12] B.Cheknane,M. Badu,J.P.Basly, O.Bouras, F.Zermane, Modeling of basic green 4 dynamic sorption onto granularorgano–inorgano pillared clays (GOICs) in column reactor, Chem. Eng. J., 209(2012)7–12.

[13] S.T. Akar, A.Gorgulu, T.Akar, S.Celik,Decolorization of reactive blue 49 contaminated solution by Capsicum annuum seeds: batch and continuous mode biosorption applications, Chem. Eng. J. 168 (2011) 125–133.

[14] F.A. Batzias, D.K. Sidiras, Dye adsorption by calcium chloride treated beech sawdust in batch and fixed-bed systems, J. Hazard.Mater. B 114 (2004) 167–174.

[15] M. Malekbala, S. Hosseini, S.K. Yazdi, S. MasoudiSoltani, The study of the potential capability of sugar beet pulp on the removal efficiency of two cationic dyes, Chem. Eng. Res. Des. 90 (2012) 704–712.

[16] S.K. Theydan, M.J. Ahmed, Adsorption of methylene blue onto biomass-based activated carbon by FeCl3 activation: Equilibrium, kinetics, and thermodynamic studies, J. Anal. Appl. Pyrol. 97 (2012) 116–122.

[17] M.J. Ahmed, S.K. Dhedanb, Equilibrium isotherms and kinetics modeling of methylene blue adsorption on agricultural wastes-based activated carbons, Fluid Phase Equilibr. 317 (2012) 9–14.

[18] W.E. Oliveira, A.S. Franca, L.S. Oliveira, S.D. Rocha,Untreated coffee husks as biosorbents for the removal of heavy metals from aqueous solutions, J. Hazard. Mater.152 (2008) 1073–1081.