Adsorption of Hexavalent Chromium in various water sources using modified wheat straw

Dimitrios Sidiras, Dorothea Politi

Abstract—The aim of this study was to develop a promising and competitive biosorbent with abundant source, low price and environmentally friendly characteristics to remove heavy metals from wastewater. The wheat straw modified by autohydrolysis was prepared, characterized and used to remove hexavalent chromium, Cr(VI), from aqueous solution. What makes this study unique is that a simulation of cleaning of water sampled by various actual locations, by Cr(VI) was performed. The four locations that we chose to perform our research belong to Athens industrial zone, namely two ports for seawater (Skaramaga Port and Piraeus Port), one lake (Koumoundourou Lake), and one stream (Pikrodafnis Stream). The (a) isotherm and (b) kinetic experimental batch adsorption system data were simulated using (a) Freundlich and Langmuir isotherm models and (b) first order, second order and intraparticle diffusion kinetic models, respectively. The results show that (i) the autohydrolysis pretreatment increased the adsorption capacity of wheat straw and (ii) the Lake Koumoundourou results were better compared to the other three areas results.

Keywords—lignocellulosic biomass, hexavalent chromium, biosorption, wastewater.

I. INTRODUCTION

With the advancement in industrialization, the natural habitat frequently experiences inconvenient impacts of industrial contamination. In light of the seriousness of substantial metal tainting in water environment and potential adverse health impact on the individuals, huge endeavors have been made to sanitize waters containing heavy metals [1].

Hexavalent chromium (Cr (VI)) is an heavy metal that is known to be cancer-causing and mutagenic, and is broadly found in wastewater created from the leather tanning, mining, textile dyeing, steel fabrication, wood preservation and electroplating industries [2]. Because of the toxicity of Cr (VI) contamination, it has brought about numerous issues influencing both human and oceanic biological systems [3].

Various physical techniques, for example, ultrafiltration [4], electrodialysis [5], reverse osmosis [6] and chemical methods such as electroflotation [7] and electrochemical oxidation [8] have been used by analysts for chromium expulsion from aqueous solutions.

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In any case, these treatment approaches are not observed to be financially savvy and furthermore a portion of these treatment systems include utilization of over the top synthetic chemicals which likewise create extra ecological concerns. These restrictions might be overcome by the method of adsorption [9].

Activated carbon is the most efficient and famous adsorbent and has been utilized widely for the disposal of heavy metals. Be that as it may, because of its high recovery cost and misfortunes in the application forms, it can't be utilized on an industrial scale [10].

Biomass offers a modest and inexhaustible wellspring of adsorbents and can be utilized in their unique structure, modified or transformed to activated carbon. These waste materials have next to zero monetary worth and frequently present a disposal problem. In this manner, there is a need to valorize these low-cost by-products. Researchers look at different low-cost adsorbents from agricultural by-products and their capacity to remove Cr (VI) from aqueous solutions. These incorporate rise straw [11], sawdust [12], walnut shells [13] and Magnolia leaf [14].

In this work, various water sources (tap water, seawater, stream water and lake water) were used to study the removal of Cr (VI) by wheat straw modified by autohydrolysis pretreatment, using untreated wheat straw as control. The adsorption isotherms and the adsorption kinetics of Cr(VI) were used to estimate and compare the adsorption capacity of the untreated and pretreated wheat straw as well as in which water source has the better adsorption results in comparison.

II. MATERIALS AND METHODS

A. Material

The wheat straw used in this work was obtained from the Kapareli village, close to the Thiva city at the Kopaida area in central Greece, as a suitable source for full-scale industrial applications. The moisture content of the material when received was 8.8% w/w; after screening, the fraction with particle sizes between 10 and 20 mm was isolated. The content of the raw material is shown in Table I.

B. Water sources locations

Within the current study, samples of surface water were obtained by four different areas in Athens in collaboration with Hellenic Centre for Marine Research on the same day of month April. Specifically, samples of four water zones of...
Table I: Composition of wheat straw.

<table>
<thead>
<tr>
<th>Component</th>
<th>Wheat straw % w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>32.7</td>
</tr>
<tr>
<td>Hemicelluloses</td>
<td></td>
</tr>
<tr>
<td>Xylose</td>
<td>19.3</td>
</tr>
<tr>
<td>Arabinose</td>
<td>2.7</td>
</tr>
<tr>
<td>Acetyl groups</td>
<td>2.5</td>
</tr>
<tr>
<td>Klason lignin</td>
<td>16.8</td>
</tr>
<tr>
<td>(acid insoluble)</td>
<td></td>
</tr>
<tr>
<td>Ash</td>
<td>4.7</td>
</tr>
<tr>
<td>Extractives</td>
<td>6.2</td>
</tr>
<tr>
<td>Other components</td>
<td>15.1</td>
</tr>
</tbody>
</table>

Attica are taken and those areas are presented in Figure 1. Precisely, the areas ΑΣ = Skaramaga Port, ΑΠ = Piraeus Port, ΑΚ = Koumoundourou Lake and P6 = Pikrodafnis Stream.

During sample collection, the physicochemical parameters of water where measured on spot using a portable multiparametric instrument, which consist of: temperature, pH, electrical conductivity, diluted oxygen, saltiness and turbidity. The samples of surface water and groundwater were stored in special canisters, within which 1ml of mercury chloride (Hg2Cl2) was inserted per 500 ml of sample. Lastly, the samples were transferred to laboratory to perform chemical analysis.

C. Material modification
The autohydrolysis pretreatment was executed in a 3.75-L batch reactor PARR 4843. The isothermal hydrolysis times was 10min (not including the non-isothermal preheating and the cooling time-periods); the liquid-to-solid ratio was 20:1; the liquid phase volume was 2000 mL and the solid material dose was 100 g; stirring speed=150 rpm. The temperature value was 200°C, reached after 47min preheating period value, respectively.

D. Adsorption isotherms studies
Isotherms were attained from batch experiments. After the batch process, accurately weighed quantities of tissue were transferred to 0.8-L bottles, where V = 0.5 L adsorbate solution was added. The adsorbent weight was 0.5 g, the temperature was T = 23°C, the initial Cr(VI) concentration varied from 15 mg L⁻¹ to 70 mg L⁻¹; K₂Cr₂O₇ was used as Cr(VI) source. The pH of the solutions was adjusted to 2.0 using dilute H₂SO₄. The bottles were sealed and mechanically filled for a period of 7 days. This time period was chosen after pilot studies (the time varies from 4 hours to 14 days) to ensure that nearly equilibrium conditions are achieved. The resulting solution had determined concentrations and balance data from each bottle represented one point on the adsorption isotherm plots.

E. Kinetic adsorption studies
Adsorption rate batch experiments were conducted in a 2-L glass totally mixed reactor equipped with a twisted blade agitator type, operating at 600 rpm, for maintaining the lignocellulosic material in suspension. The reactor, containing V = 1 L aqueous solution of Cr (VI) was placed in a water bath to maintain constant temperature at the desired level. The adsorbent mass was m = 1 g, the temperature was 23oC, the initial concentration of Cr (VI) was C₀ = 7.0 mg L⁻¹. The pH of the solutions was adjusted to 2.0 using dilute H₂SO₄.

III. DISCUSSION
A. Water sources locations
Piraeus port is characterized by a large traffic load. The operation of both the passenger and freight ports and their connection to the rest of Greece with Kifissos Avenue - National Road Athens - Thessaloniki and Athens - Corinth Highway. The area has tanneries, approximately 140 paint production plants, metallurgists, 350 shipbuilding units and oil storage companies.

Pikrodaφnι stream mainly operates handicrafts and furniture, but also clothing, ironworks, aluminum constructions, car repair shops, florists, etc., a significant number of which operate illegally. Quarrying activity is observed in the upstream part of the basin of Pikrodaφnι stream in Ymittos. The road network of the area, the main feature of which is the existence of large roads (Poseidonos, Vouliagmeni, Amfithea, Eleftheria, Agios Dimitrios and Agios Varvara avenues).

Koumoundourou Lake - Skaramagka port host numerous industries and crafts (Aspropyrgos Refineries of Hellenic...
Table II: Physicochemical measurements. Water: tap water, seawater (two Ports), stream water and lake water.

<table>
<thead>
<tr>
<th>Region</th>
<th>Koumoundourou Lake</th>
<th>Pitrodaños Stream</th>
<th>Piraeus Port</th>
<th>Skaramaga Port</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
<td>23.2</td>
<td>20.9</td>
<td>17.0</td>
<td>18.6</td>
</tr>
<tr>
<td>pH</td>
<td>7.74</td>
<td>7.74</td>
<td>7.62</td>
<td>8.10</td>
</tr>
<tr>
<td>Conductivity</td>
<td>18030</td>
<td>1142</td>
<td>64050</td>
<td>34240</td>
</tr>
<tr>
<td>DO (mg L⁻¹)</td>
<td>9.66</td>
<td>9.50</td>
<td>10.70</td>
<td>9.58</td>
</tr>
<tr>
<td>Salinity (ppm)</td>
<td>8.98</td>
<td>0.26</td>
<td>31.79</td>
<td>16.87</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>5.3</td>
<td>9.1</td>
<td>2.4</td>
<td>25.6</td>
</tr>
</tbody>
</table>

Petroleum SA, Cement Industry ET BETON · HALYHH, POLYECO SA, ELLENIC PLASTIC SA) and tanneries which burden the area, as their waste, in some percentage, end up in tanks or streams in the area and eventually, another percentage will filter into the groundwater body, which communicates with Lake Koumoundourou and the Gulf of Elefsina. There is a particularly dense and busy road network, while south of the lake passes the National Road, which connects Athens with the Peloponnese and north the Attica Road.

Table II presents the physicochemical measurements taken in the 4 regions for sampling in April.

The value of pH in most natural waters ranges from 6 to 9, whereas the influx of acidic or alkaline waste may cause the value to change. It is observed from Table II that the value of pH ranges from 7.62 to 8.10.

It is observed that Diluted Oxygen values range from 9.06 to 10.70. The quality of all waters based on their Diluted Oxygen content is rated high as all values exceed 7 mg L⁻¹.

Regarding salinity, it is shown that the type of water (sweet, brackish, salty) is distinguished by the minimum salinity value of Pitrodaños Stream and the maximum of the two harbors.

Notably, Skaramaga Port has the highest turbidity value indicating that there are high values of floating solids.

B. Kinetics of adsorption

Kinetic models’ equations: The kinetics of adsorption of Cr(VI) on untreated and autohydrolysis wheat straw has been extensively studied using four kinetic equations. The widely used Lagergren equation [15] is shown below:

\[ q - q_i = q_s \cdot e^{-k \cdot t} \]  

(1)

where \( q \) and \( q_s \) are the amounts of Cr(VI) adsorbed per unit mass of the adsorbent (in mg g⁻¹) at equilibrium time \( t \to \infty \) and adsorption time \( t \), respectively, while \( k \) is the pseudo-first order rate constant for the adsorption process (in min⁻¹). Furthermore,

\[ q = (C_0 - C_e)V / m \quad \text{and} \quad q_t = (C_0 - C)V / m \]  

(2)

where \( C, C_0, C_e \) are the concentrations of Cr(VI) in the bulk solution at time \( t \), 0, and \( \infty \), respectively, while \( m \) is the weight of the adsorbent used (in g), and \( V \) is the solution volume (in mL). Further modification of eq. (2) in logarithmic form gives:

\[ \ln(q - q_i) = \ln q - k \cdot t \]  

(3)

The commonly used second-order kinetic model [16] is as follows:

\[ q_i = q - \left[q^{-1} + k_2 t\right]^{-1} \]  

(4)

or

\[ q_i = q - \frac{1}{\frac{1}{q} + k_2 t} \]  

(5)

The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model [17]:

\[ q_i = c + k_p \cdot \sqrt{t} \]  

(6)

where \( q_i \) is the amount of Cr(VI) adsorbed at time \( t \), \( c \) is a constant (mg g⁻¹) and \( k_p \) is the intra-particle diffusion rate constant in mg g⁻¹ min⁻⁰·⁵.
Fig. 2: Lagergren kinetics for Cr(VI) adsorption on untreated and pretreated (autohydrolysis 200°C, 10 min isothermal time) straw. Water from (a) Pirkodafnis Stream, (b) Koumoundourou Lake, (c) Skaramanga Port and (d) Piraeus Port.

Table III: Parameters of pseudo-second-order kinetic model of Cr(VI) adsorption on untreated and pretreated barley straw. Water: tap water, seawater (two Ports), stream water and lake water.

<table>
<thead>
<tr>
<th>Locations</th>
<th>$k_2$ (g mg⁻¹ min⁻¹)</th>
<th>$q_e$ (mg g⁻¹)</th>
<th>SEE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tap water</td>
<td>0.0002</td>
<td>3.96</td>
<td>0.02</td>
</tr>
<tr>
<td>Koumoundourou</td>
<td>0.019</td>
<td>0.88</td>
<td>0.11</td>
</tr>
<tr>
<td>Lake</td>
<td>0.013</td>
<td>1.04</td>
<td>0.14</td>
</tr>
<tr>
<td>Pirkodafnis Stream</td>
<td>0.0025</td>
<td>1.57</td>
<td>0.07</td>
</tr>
<tr>
<td>Skaramanga Port</td>
<td>0.0058</td>
<td>1.28</td>
<td>0.07</td>
</tr>
<tr>
<td>Pretreated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tap water</td>
<td>0.0020</td>
<td>4.21</td>
<td>0.28</td>
</tr>
<tr>
<td>Koumoundourou</td>
<td>0.0014</td>
<td>4.14</td>
<td>0.12</td>
</tr>
<tr>
<td>Lake</td>
<td>0.0004</td>
<td>5.33</td>
<td>0.15</td>
</tr>
<tr>
<td>Pirkodafnis Stream</td>
<td>0.0056</td>
<td>1.64</td>
<td>0.12</td>
</tr>
<tr>
<td>Piraeus Port</td>
<td>0.0003</td>
<td>7.72</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Table IV: Parameters of intra-particle kinetic models of Cr(VI) adsorption untreated and pretreated barley straw. Water: tap water, seawater (two Ports), stream water and lake water.

<table>
<thead>
<tr>
<th>Locations</th>
<th>$k_a$ (mg g⁻¹ min⁻¹)</th>
<th>$c$ (mg g⁻¹)</th>
<th>SEE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tap water</td>
<td>0.038</td>
<td>-0.12</td>
<td>0.04</td>
</tr>
<tr>
<td>Koumoundourou</td>
<td>0.047</td>
<td>0.06</td>
<td>0.09</td>
</tr>
<tr>
<td>Lake</td>
<td>0.051</td>
<td>0.02</td>
<td>0.13</td>
</tr>
<tr>
<td>Pirkodafnis Stream</td>
<td>0.054</td>
<td>-0.09</td>
<td>0.08</td>
</tr>
<tr>
<td>Skaramanga Port</td>
<td>0.090</td>
<td>-0.23</td>
<td>0.21</td>
</tr>
<tr>
<td>Pretreated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tap water</td>
<td>0.202</td>
<td>-0.15</td>
<td>0.26</td>
</tr>
<tr>
<td>Koumoundourou</td>
<td>0.170</td>
<td>-0.19</td>
<td>0.13</td>
</tr>
<tr>
<td>Lake</td>
<td>0.13</td>
<td>-0.30</td>
<td>0.18</td>
</tr>
<tr>
<td>Pirkodafnis Stream</td>
<td>0.076</td>
<td>0.001</td>
<td>0.10</td>
</tr>
<tr>
<td>Skaramanga Port</td>
<td>0.177</td>
<td>-0.44</td>
<td>0.24</td>
</tr>
</tbody>
</table>

The water adsorption on untreated and pretreated wheat straw is presented in Fig. 2, on stream water, lake water and seawater (Skaramanga Port and Piraeus Port). The modified wheat straw adsorption capacity has improved in comparison to the untreated. The water absorptivity of the pretreated material is significantly enhanced.

In Table III all the parameters of the second-order kinetic model and in Table IV the parameters of intra-particle diffusion model are presented.
C. Adsorption Isotherms

The comparison of the adsorption capacity of the seaweed samples was based on the Freundlich [18] and Langmuir [19] isotherm models.

The Freundlich [18] isotherm is given by the following equation:

\[ q = K_F \cdot (C_e)^n \]

where \( q \) is the amount adsorbed per unit mass of the adsorbent (mg g\(^{-1}\)), \( C_e \) is the equilibrium concentration of the adsorbate (mg L\(^{-1}\)) and \( K_F \) [(mg g\(^{-1}\))(L mg\(^{-1}\))\(^{1/n}\)], \( n \) are the Freundlich constants related to adsorption capacity and intensity, respectively. The \( K_F \) and \( n \) values were estimated by non-linear regression analysis (NLRA) from the experimental adsorption data obtained at 23 °C for Cr(VI).

The Langmuir isotherm equation [19] is based on the following ‘pseudo-monolayer’ adsorption model.

\[ q = \frac{K_L q_m C_e}{1 + K_L C_e} \]

or \[ \frac{1}{q} = \left( \frac{1}{q_m} \right) + \left( \frac{1}{K_L q_m} \right) \left( \frac{1}{C_e} \right) \]

where \( K_L \) is the Langmuir constant related to the energy of adsorption (L mg\(^{-1}\)) and \( q_m \) the amount of Cr(VI) adsorbed (mg g\(^{-1}\)) when saturation is attained. In cases where the isotherm experimental data approximates the Langmuir equation, the parameters \( K_L \) and \( q_m \) can be estimated either by plotting \( 1/q \) versus \( 1/C_e \) either by NLRA. In Fig. 3 the Langmuir isotherm-parameters \( q_m \) estimated using NLRA are presented.

Table V: Parameters of the Langmuir isotherms for Cr(VI) adsorption on untreated and pretreated wheat straw. Water: tap water, seawater (two Ports), stream water and lake water.

<table>
<thead>
<tr>
<th>Locations</th>
<th>Untreated</th>
<th>Pretreated</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q_m ) (mg g(^{-1}))</td>
<td>21.81</td>
<td>54.98</td>
</tr>
<tr>
<td>( K_L )</td>
<td>0.02</td>
<td>0.09</td>
</tr>
<tr>
<td>SEE</td>
<td>3.14</td>
<td>4.40</td>
</tr>
<tr>
<td></td>
<td>24.41</td>
<td>57.87</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>2.49</td>
<td>5.84</td>
</tr>
<tr>
<td></td>
<td>33.18</td>
<td>45.52</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>4.08</td>
<td>2.62</td>
</tr>
<tr>
<td></td>
<td>22.87</td>
<td>35.27</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>5.48</td>
<td>7.46</td>
</tr>
<tr>
<td></td>
<td>19.93</td>
<td>36.99</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td>1.57</td>
<td>5.81</td>
</tr>
</tbody>
</table>

The standard error of estimate (SEE) was calculated in each case by the following expression

\[ SEE = \sqrt{\sum_{i=1}^{n'} (y_i - y_{i,theor})^2 / (n' - p')} \]

where: \( y_i \) is the experimental value of the depended variable, \( y_{i,theor} \) is the theoretical or estimated value of the depended variable, \( n' \) is the number of the experimental measurements and \( p' \) is the number of parameters (the
The importance of this particular study lies with the fact that Cr(VI) removal simulation was conducted on samples of various water sources using modified wheat straw as the absorbent material. Wheat straw is a low cost efficient absorbent for the removal of Cr(VI) from aqueous solutions. Also, the autohydrolysis pretreatment on wheat straw is a low cost process. The adsorption capacity for Cr(VI), using the Langmuir isotherm model on wheat straw, was 58 mg g⁻¹ for autohydrolyzed wheat straw, compared to 24 mg g⁻¹ for untreated wheat straw.

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REFERENCES


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Post-Doc Researcher, Dr. Dorothea Politi holds a 5-year diploma (2008) in Environmental Management from the University of Patra and a PhD (2016) at the Department of Industrial Management and Technology of the School of Maritime and Industrial Studies of the University. Her research interests include: biomass, adsorption materials, biofuels, renewable energy sources with emphasis on biomass for energy and materials production.