PVA supported Microporous adsorbents for the remediation of dye house wastewater

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Received: 15 February 2012; revised: 07 August 2012; accepted: 12 December 2012

Microporous activated carbons with high surface area are of great interest for the remediation of textile wastewater in a sustainable manner. An activated carbon prepared from *Euphorbia antiquorum L.* (EAC) was impregnated with Polyvinyl alcohol solution to provide mechanical stability and increase the abrasion resistance. The surface area of EAC and PVAC were 918 and 713.8 m²/g respectively. An adsorption characteristic of the Polyvinyl Alcohol Supported Activated Carbon (PVAC) was analyzed with the help of pseudo first order and second order kinetic models. Both the adsorbents show maximum adsorption at a pH of 8. The pseudo second order model describes the kinetics with very high correlation coefficient of > 0.995. The Langmuir monolayer adsorption capacity was 49.42 and 50.45 mg/g for EAC and PVAC, respectively; further it increases with increase of temperature. Characteristics of PVAC and dye adsorption studies prove that PVA supported EAC is a promising adsorbent for the removal of colour from wastewater.

**Keywords:** Activated carbon, Surface Area, Polyvinyl Alcohol, Adsorption and Wastewater.

**Introduction**

Everyday the science and technology is rapidly growing. Majority of these developments make more comfort for human being but creates lot of stress on the environment. Dyes have been used in many industries such as textiles, printing and publication, pulp mills, leather, food, plastics, etc. The effluent from these industries normally contains some residual dyes. An estimated 10,000 different commercial dyes, pigments exist and more than 7×10^5 tons are produced per year world-wide¹. It has been found that about 10-15% of these dyes is released to the environment after dyeing process². Removal of synthetic dyes are of great concern, because some dyes and their degradation products are carcinogenic and more toxic³. Owing to this toxic and carcinogenic nature these pose a serious hazard to aquatic living the wastewater containing dyes are very difficult to treat, since the dyes are recalcitrant organic molecules, resistance to aerobic digestion and are stable to light, heat and oxidizing agents⁵. The dye removal process has got a considerable attention over the past few decades⁶. Many dyes removal techniques like coagulation, chemical oxidation, membrane separation, electrochemical process, biological treatment⁷, nanofiltration, reverse osmosis, and adsorption using various kind of adsorbents⁸-¹⁰ are being practiced. The adsorption technique has been proven to be an effective process for the removal of various pollutants from its aqueous solutions because adsorption techniques can remove pollutant in wide range of concentrations¹¹-¹².

To improve the efficiency of the adsorption processes, it is essential to develop the more effective and cheaper adsorbents with higher adsorption capacities¹³-¹⁴. Cheap and effective adsorbents have been developed from various waste materials such peat¹⁵, rice husk¹⁶, tea waste¹⁷, saw dust¹⁸, pinus pinaster bark¹⁹, eucalyptus bark²⁰, agricultural wastes²¹, oil palm waste²², easy growing wood species²³, tamarind kernel powder²⁴, palm shell²⁵, tropical wood²⁶, babool wood²⁷ etc. Adsorbents developed from these materials have many advantages, since they are renewable sources of raw materials and have negligible cost when compared to commercial activated carbon. Exploration of good low cost adsorbent may contribute to the sustainability of the environment and also offer promising benefits for commercial purpose in future.
One of the typical approaches in sorption science is the production of adsorbent containing pre-existing insoluble matrix which will allow the adsorbent to comfortably interact with the pollutants present in the wastewater. These type of adsorbents embedded in a polymer matrix are of great interest because they have many advantages. The matrix gives high mechanical strength and imparts essential physical and chemical properties like surface area and porosity. The adsorbents embedded in a polymer matrix may have the following characteristics (i) controlling and improving the affinity of the material for the pollutant; (ii) changing the selectivity series for sorption; (iii) enhancing sorption kinetics; (iv) improving the stability of the material.

The purpose of the present work is to evaluate the sorption of Methylene Blue from its aqueous solution using *Euphorbia antiquorum* *L* wood activated carbon (EAC) and Polyvinyl alcohol supported *Euphorbia antiquorum* *L* wood activated carbon (PVAC). The activated carbon was prepared by H$_3$PO$_4$ impregnation method. About the precursor, it is widespread throughout peninsular India; it can be found growing in the regions of an altitude of 800 m. One of the largest armed tree in Euphorbias with an average height of 5-7 meter, the vernacular name of the plant is “Triangular Spurge”.

**Materials and methods**

**Adsorbent**

The *Euphorbia antiquorum* *L* wood cut into pieces of 2 to 3 cm size, dried in sunlight for 10 days. The dried material soaked in a boiling solution of 10 % H$_3$PO$_4$ for one hour and kept at room temperature for 24 hours. After 24 hours the wood material separated, air dried and carbonised in muffle furnace at 400°C. The carbonised material was powdered and activated in a muffle furnace at 800°C for a period of 10 minutes and labeled as EAC. Then the activated carbon is mixed with 1% solution of Polyvinyl Alcohol (i.e the ratio of carbon & PVA is 1:1), oven dried at 105°C until the complete removal of water, powdered and it is labeled as PVAC. The characteristics of the EAC & PVAC were analysed as per the standard procedures$^{28-29}$ and few important parameters are given in Table 1.

**Adsorbate**

All the chemicals used are reagent grade. Methylene Blue (MB) having molecular formula C$_{16}$H$_{18}$ClN$_3$S (Mol Wt: 319.85), (E. Merck, India) was chosen as the adsorbate. The structure of MB is given in Figure 1. A stock solution containing 1000 mg of the dye per litre was prepared by dissolving the dye in double distilled water and was used to prepare the adsorbate solutions by appropriate dilution as required (the percentage purity is also taken into consideration while preparing the stock solution).

**Adsorption studies**

The adsorption experiments were carried out by agitation 100 mg of adsorbent with 200 ml of dye solution at 200 rpm in a temperature controlled orbital shaker (REMI make). The mixture was withdrawn at specified interval, centrifuged using electrical centrifuge (Universal make) at 5000 rpm for 10 minutes and the unadsorbed supernatant liquid was analyzed for the residual dye concentration using Elico make Bio-UV visible spectrometer (BL-198) at 664 nm. All the experiments conducted in duplicate and mean of the two values is taken for calculation.

**Kinetics of adsorption**

Many kinetic models have been proposed to elucidate the mechanism of solute adsorption. The rate and mechanism of adsorption is controlled by various factors like physical and/or chemical properties of adsorbent as well as mass transfer process. These kinetic models are

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**Table 1—Important Physico Chemical Properties of EAC & PVAC**

<table>
<thead>
<tr>
<th>S.No</th>
<th>Properties</th>
<th>EAC</th>
<th>PVAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pH</td>
<td>6.90</td>
<td>6.72</td>
</tr>
<tr>
<td>2</td>
<td>Conductivity, mS/cm</td>
<td>0.181</td>
<td>0.436</td>
</tr>
<tr>
<td>3</td>
<td>Moisture content, %</td>
<td>7.56</td>
<td>7.63</td>
</tr>
<tr>
<td>4</td>
<td>Ash, %</td>
<td>13.4</td>
<td>18.9</td>
</tr>
<tr>
<td>5</td>
<td>Volatile matter, %</td>
<td>21.1</td>
<td>12.1</td>
</tr>
<tr>
<td>6</td>
<td>Matter soluble in water, %</td>
<td>0.40</td>
<td>0.40</td>
</tr>
<tr>
<td>7</td>
<td>Matter soluble in 0.25 M HCl, %</td>
<td>1.22</td>
<td>1.44</td>
</tr>
<tr>
<td>8</td>
<td>Bulk density, g/mL</td>
<td>0.42</td>
<td>0.45</td>
</tr>
<tr>
<td>9</td>
<td>Specific Gravity</td>
<td>0.94</td>
<td>0.85</td>
</tr>
<tr>
<td>10</td>
<td>Porosity, %</td>
<td>55.32</td>
<td>47.06</td>
</tr>
<tr>
<td>11</td>
<td>Surface area, m$^2$/g</td>
<td>918</td>
<td>773.8</td>
</tr>
<tr>
<td>12</td>
<td>Methylene Blue Value, mg/g</td>
<td>375</td>
<td>318</td>
</tr>
</tbody>
</table>
useful for the design and optimization of effluent treatment process. In order to investigate the mechanism of MB adsorption by EAC & PVAC the following kinetic models were considered.

**Pseudo first order kinetic model**

The pseudo first order kinetic model suggested by Lagergren\textsuperscript{10}. It is used for this analysis.

**Pseudo second order kinetics**

The adsorption may also be described by pseudo second order kinetic model\textsuperscript{31} if the adsorption does not follow the first order kinetics.

**Isotherm Studies**

**Langmuir model**

The Langmuir model\textsuperscript{32-44} was originally developed to describe the adsorption of gas on to solid surface. It suggests the formation of monolayer adsorption and also the surface is energetically homogeneous.

**Results and discussions**

The Table 1 gives the comparative physico-chemical characteristics of EAC and PVAC. The low conductivity values indicate that only a few replaceable ions present on the surface of the activated carbon. The amount of matter soluble in water and acid is very less in both the adsorbents, which will give good quality water (lesser contaminants released from the adsorbent) after the adsorptive removal of solutes from water. Even though the surface area of PVAC is marginally lower than EAC, in view of higher abrasion resistance and good mechanical stability this reduction can be compromised. Moderate methylene blue number indicates that the adsorbent can be conveniently employed for the removal of organic pollutants present in wastewater. There is no much difference noticed with respect to the properties, in order to improve the abrasion resistance, the carbon is impregnated with PVA matrix. The carbon embedded in PVA matrix can with stand more number of cycles when it is used for continuous column mode operations with proper regeneration.

**Effect of pH on MB uptake**

The effect of initial pH on the removal of MB was investigated at an initial concentration of 50 mg/L and room temperature. The initial pH values of dye solution exerts the chemistry of a dye molecule presumably due its influence on the surface properties of the adsorbent and ionization/dissociation of the adsorbate molecule. Figure 2 shows the variation in the removal of dye from aqueous solution at various pH. From the Figure, it is evident that the maximum removal of MB is observed at pH 8 for both EAC and PVAC. This type of high adsorption at higher pH indicates that the surface morphology of surface functional are not altered very much due to the incorporation of EAC in PVA matrix.

**Effect of temperature for the adsorption of MB onto EAC and PVAC**

The equilibrium sorption capacity of MB onto EAC & PVAC increases for both the adsorbents while increasing the temperature from 30 to 50°C. The increase in uptake with increase in temperature indicates that the sorption of MB onto EAC & PVAC is an endothermic process. The enhancement in adsorption is due to the decrease in the thickness of the boundary layer surrounding the sorbent with temperature, so that the mass transfer resistance of adsorbate in the boundary layer decreases. This may have caused as a result of increase in the mobility of the dye (due to increase of kinetic energy) with the raise of temperature. If adsorption is governed only by physical phenomena, an increase in temperature will be followed by a decrease in adsorption capacity. Temperature could influence the desorption and consequently the reversibility of the adsorption equilibrium also.

**Kinetics of Dye Adsorption**

The adsorption data is analysed with the help of first order and pseudo second order kinetic models. The
calculated \( q_e \) values obtained from pseudo first order model plot (Figure 3) are in good agreement with the experimental \( q_e \) values. The correlation coefficients \( r^2 \) were relatively low. This plot proves that initial adsorption follows first order. Even though \( q_e \) (cal), and \( q_e \) (exp) values are closer, the \( r^2 \) values suggest that the adsorption data fitted poor to pseudo first- order kinetics. Hence the adsorption of MB onto EAC and PVAC is not diffusion controlled. The data for the adsorption of MB on to EAC and PVAC applied to pseudo second order kinetic model as shown in Figure 4 and the results are presented in table 2. From the results, it is clear that equilibrium sorption capacity \( q_e \) increases with increase in temperature. The correlation coefficients for the second order kinetic model are greater than 0.9992, which led to belief that the pseudo second order kinetic model provided good correlation for the adsorption of MB onto EAC and PVAC. The results indicate that the adsorption of MB onto both EAC and PVAC follows only pseudo second order kinetics.

Analysis of the Langmuir monolayer adsorption capacity obtained for the adsorption of MB onto PVAC agrees well with the other adsorbents reported by the past researchers. The comparative data gives an indication that PVAC has great potential as a sorbent for the adsorption of MB from the effluent

**Conclusion**

An activated carbon conveniently and economically prepared from *Euphorbia antiquorum L* (EAC) was impregnated with Polyvinyl alcohol solution to provide mechanical stability and increase the abrasion resistance. The physico-chemical properties of PVAC are comparable with EAC. Adsorption characteristics of the EAC and Polyvinyl Alcohol Supported Activated Carbon (PVAC) were analyzed with the help of pseudo first order, second order kinetic models and Langmuir adsorption isotherm. The comparative data gives an indication that EAC and PVAC are good sorbents for
the removal of solutes from waste water. Also PVAC has great potential as a sorbent for the adsorption of MB from the effluent with more number of recycles due to its high mechanical strength and abrasion resistance.

References


