SAWDUST-BASED ACTIVATED CARBON FOR MALACHITE GREEN REMOVAL: KINETIC AND THERMODYNAMIC STUDY

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Abstract:  
Sawdust as a lignocellulosic solid waste, has been valorized and used as an adsorbent for the removal of Malachite green (MG) from aqueous solution. Impregnation in 20% KOH (SDK), and (NH4)2S2O8 (SDP) solutions then pyrolysis at 600°C for 3 hours were found to enhance the adsorption capacity of malachite green (MG) as a pollutant significantly relative to its inactivated state (SDU). The batch adsorption experiments resulted in a maximum adsorption capacity determined from Langmuir models of up to 434.78 mg/g, 238.10 and 200.0 for SDK, SDP and Merck respectively. Parameters influencing adsorption capacity such as contact time, adsorbent dosage, pH and temperature were studied. FT-IR analyses and iodine number determination were also performed to characterize the prepared adsorbents. Adsorption kinetics was found to comply with the pseudo second order with a good correlation factor ($R^2 = 0.99$) with intraparticle diffusion as the rate determining steps. Thermodynamic analysis and temperature effects of the process confirm that the adsorption reaction was spontaneous ($\Delta G^\circ < 0$) and endothermic ($\Delta H^\circ > 0$). This study showed that sawdust as a waste could prove to be a very useful in removing toxic substances from the environment.

Key words: sawdust; waste; activated carbon; adsorption; malachite green; kinetics.
INTRODUCTION

Commercial activated carbon is a remarkable, highly adsorbent material with a large number of applications in the remediation of contaminated groundwater such as colored effluents. Conventional methods for water purification are costly and sometimes not readily adapted to effluent treatment. The need to use other adsorbents as alternatives to the standard activated carbons is due to the rising production cost of the latter (Quek et al. 1998, Garg et al. 2003) and also to take advantage of available low-cost natural products. To minimize the cost, a variety of raw materials such as water hyacinth, tea leaves, tree barks, ground coffee, wool fibre, mucor rouxi etc., were used in activated carbon manufacture, making it plentiful, relatively inexpensive, and versatile, and have been the subject of intense interest for the removal of contaminants from water (Poots et al. 1997, Viraraghavan 2000, Marshall and Champagne 1995). Most dyestuffs are designed to be resistant to environmental conditions like light, effects of pH and microbial attack (Pagga and Taeger 1994).

Hence, their presence in wastewater is unwarranted, and it is desirable to remove coloring material from effluents, before their discharge in the environment. Malachite green removal by natural raw materials as adsorbents has been the subject of numerous studies not only because of its toxicity but its visibility as well (Garg et al. 2004, Garg et al. 2003). Among other methods used for color removal from industrial effluents, adsorption appears to have considerable potential (Khattri and Singh 1998).

In the present investigation, attention was focused on an adsorbents prepared from chemically treated sawdust species, an agro-industry waste, to remove Basic Green 4 (Malachite Green) from aqueous solution in a batch mode. Preliminary studies performed on the inactivated sawdust revealed interesting adsorptive properties of this dye.

MATERIALS AND METHODS

Stock solutions and adsorbents preparation

As shown in Fig. 1 Malachite green \((\text{C}_{52}\text{H}_{54}\text{N}_4\text{O}_{12})\) supplied by Merck was chosen as an adsorbate in this study because of its strong uptake onto solids. A1g/L stock solution of MG was prepared by dissolving the required amount of dye in a home made distilled water. Successive dilutions were used to prepare further solutions with desired concentrations.

A home made distilled water was used to prepare all the solutions from a 1g/L stock solution of MG by dissolving the required amount of dye.

The sawdust as a raw material was dried in sunlight before treating it in the laboratory, then ground using a jar mill to pass through a 0.071mm sieve. The amount of 50g of sawdust were mixed with 20% of KOH or \((\text{NH}_4)_2\text{S}_2\text{O}_8\) solutions during 24 hours. The obtained mixture was filtered, oven dried and then pyrolysed at 600°C for 3 hours. The obtained chemically activated carbon was washed with hot distilled water until constant pH is reached. The dried (110°C overnight) sawdust based activated carbon obtained was tested for iodine adsorption which give an indication of microporosity.

Adsorption studies

Malachite green adsorption

Adsorption tests of Malachite green (MG) onto prepared activated carbon were studied using batch process by placing 0.1g of adsorbent in a stoppered conical flask and 25ml of MG solution of a known concentration. The mixture was agitated magnetically until equilibrium is reached. Measurements were performed on the Malachite green solutions at 615nm using a UV–visible 2121 OPTIZEN spectrophotometer to determine the equilibrium concentration at ambient temperature against water as solvent reference. Solutions were diluted as required so that their absorbance remained with the calibration linear range of the calibrating curve established previously according to Beer-Lambert relationship. Experiments were carried out in triplicate at room temperature. The equilibrium adsorption capacities \((q_e)\) at different MG concentrations were determined according to the mass balance on the adsorbate (equation 1).

Iodine number determination

The activated carbon obtained was also characterid by measuring its iodine number (mg/g) which gives an indication of the adsorption capacity of activated carbon in micropores using 0.1N standardized iodine solutions. The titrant used was 0.1N sodium thiosulfate solution (Bestani et al. 2008).

RESULTS AND DISCUSSIONS

Effect of contact time

Preliminary tests were conducted to assess the contact time necessary for each adsorption system to come to equilibrium and, for experimental purposes, each system was given a contact time in excess of this
To determine the equilibrium, 25ml of solution of known concentration of MG were mixed successively with 0.2g of the prepared adsorbents and Merck activated carbon, and agitated during time intervals ranging from 60 to 300min at room temperature. The resulting supernatants were analyzed and the equilibrium concentrations were determined as shown in Fig. 1. Rapid equilibrium of 100min was attained using all adsorbents. As a consequence, subsequent adsorption tests were all performed for 120min which was assumed to be ample for all the experiments.

**pH effect**

Initial pH of the Malachite Green solution was varied from 2 to 10, by adding either 0.1N NaOH or 0.1N HCl solutions, to assess the effect of pH on the dye adsorption onto the SDK, SDP and Merck AC. The experiments were also performed at different initial dye concentrations with 8g/L adsorbents dose for a 120-min equilibrium time at room temperature. At low pH values, a decrease in the dye uptake was observed at lower pH values may be due to the protons competition with the dye molecules for the available adsorption sites (Vadivelan and Kumar 2005) whereas in the range 6–10, the uptake efficiency was maximum and slightly affected by pH. As the pH is increased, the surface charge density on the considered adsorbents changes by becoming negatively charged available sites resulting in an enhanced attraction between the positively charged dye molecule and the adsorbents surface. Similar results were found in literature reports (Batzias and Sidiras 2007).

**Adsorbent dose effect**

Among other parameters influencing the adsorption rate, the adsorbents dose is particularly important. It determines the rate of adsorption and the cost of activated carbon per unit of treated solution. 25mL of MG solutions of known concentrations were mixed and agitated at fixed pH with different adsorbent dosages (0.1, 0.2, 0.3 and 0.4mg) for 2 hours. After filtration, the supernatant was analyzed for final concentration determination. The study shows an increase of Malachite Green uptake with increasing dosage of the adsorbent because of the availability of sites until saturation is reached as shown in Fig. 2. Similar results were obtained by (Garg et al. 2004, Banat et al. 2003).

**Functional groups determination**

FT-IR spectra of the prepared adsorbents (PERKIN-ELMER Spectrometer) over the range 4000 – 400cm\(^{-1}\) using KBr pellets in order to determine the functional groups responsible for MG adsorption. Due to their complex structure, the materials used in this study show a number of adsorption peaks. In all cases, spectrum exhibits fine peaks in the frequency range 3500-3200cm\(^{-1}\) corresponding to the hydroxyl group (O-H) stretching vibrations. A intense peak at 2170cm\(^{-1}\) for SDK may be due to stretching vibrations of the (C-H) group. Another peak in the range of 1600cm\(^{-1}\) for both SDK and SDP due to the stretching vibration of carbonyl group CO, whereas in the case of Merck AC the peak in the range of 1640cm\(^{-1}\) was due to the presence of an amide group. A weak band at 1384cm\(^{-1}\) may indicate the presence of carboxylate ion COO\(^-\). A weak band appears at 1062cm\(^{-1}\), due to the vibration of the C-O group.

**Adsorption isotherms**

The equilibrium adsorption isotherms are of fundamental importance in the design of adsorption systems. In a batch system equilibrium is established between the liquid phase (free solution) and solid phase (adsorbent-attached solute) concentrations and can be described by adsorption isotherms determined at a fixed temperature. In most adsorption systems dye-adsorbents, Langmuir and Freundlich isotherms have been applied to describe the equilibrium between liquid-solid phases (Benderdouche et al. 2003, Batzias and Sidiras 2004, Malik 2003, Grag et al. 2003).

**Langmuir isotherm**

The linear plot of \(C_{eq}/q_{e}\) versus \(C_{eq}\) yields the Langmuir constants \(b\) and \(K\) (equation 2). The adsorption isotherms of Malachite Green studied on the inactivated and the chemically activated sawdust compared to Merck powdered activated carbon used as a reference are presented in Fig. 3a. Table 1 shows the results obtained from Langmuir fitting to the data obtained for the chemical activations and Merck AC systems. It can be seen that this model describes well the adsorptive properties of the SDK, SDP and Merck AC with correlation coefficients >0.98 for all considered adsorbents. In addition, the MG uptake was significantly improved (up to 434.78mg/g for SDK).

**Freundlich isotherm**

The Freundlich model has been widely used to characterize the adsorption experiments and the uptake of dyes occurs on a heterogeneous adsorbent surface. It is assumed that the stronger binding sites
are linearised first and that the binding strength decreases with the increasing degree of site occupation. The linearised form of Freundlich (equation3).

Where the parameters $k_f$ and $n$ can be obtained from the intercept and slope of the $\ln q_e$ versus $\ln C_{eq}$ plot. and are shown in Table 1. For MG adsorption, Freundlich fitted plots of the data for SDU and SDP presented in Fig. 3b show linear behaviour, with correlation coefficients of 0.98 and 0.96 for both types of adsorbent. As shown in Table 1, the chemically activated sawdust exhibits small iodine number compared to the commercial Merck AC. Usually adsorbents with a high iodine number have a high surface area and are suitable for adsorbing small compounds (Noszko 1984). In our case Malachite Green molecules are large and their adsorption is favored by mesoporous material instead of microporous one.

**Kinetics of adsorption of MG**

In this study, the applicability of the pseudo-second-order models and the intra-particle diffusion models were tested for the sorption of Malachite Green onto all prepared adsorbents in order to describe the mechanism of mass transfer (Duong 1998, Ho and McKay 2003, Ho and McKay 1999, Waranusantigul et al. 2003).

**The linearized form of pseudo-second-order model:**

Represented by (equation 4), where $k_2$ is the equilibrium rate constant of pseudo-second-order adsorption (g/(mg min)). The linear relationship of the plot $t/q_t$ versus $t$ (Figure not shown) and the higher correlation coefficients ($R^2=0.99$) shown in Table 2 indicate clearly that the adsorption of MG from aqueous solutions on all considered adsorbents obeys well pseudo second-order kinetics. This can be also confirmed by the experimental value of $q_{exp}$ and the calculated one $q_{cal}$ which are rather close as shown in Table 2. Similar phenomena were observed in the adsorption of acid dyes (El-Geundi 1991, Bulut and Aydin 2006).

**Intraparticle diffusion model**

Several intraparticle models can be used to describe factors controlling the sorption rate such as bulk diffusion (diffusion of the solute from the solution to the film surrounding the particle), external mass transfer resistance (diffusion from the film to the particle surface) and intra-particle mass transfer resistance (diffusion from the surface to the internal sites). When the intra-particle mass transfer resistance is the rate limiting step, then the sorption process is described as being particle diffusion controlled. The following equation is used to model the intra-particle diffusion employed to model sorption processes (McKay et al. 1980, Weber and Morris 1963, Wang et al. 2008). This is given by equation 5. Where $C$ is the intercept and $k_{int}$ is the intra-particle diffusion rate constant (mg (g min$^{-0.5}$)$^{-1}$) directly evaluated from the slope of the linear plot of $q_t$ versus $t^{1/2}$. This may present multilinearity indicating that two or more steps occur as seen by previous studies (Ahmad and Hameed 2007, Hameed 2009, Baysal 2009, Hameed and Ahmed 2009).

In Table 2 are shown the values of $K_{int}$ and $C$ parameters. These parameters increase with increasing initial concentration. We also notice that the increase of $C$ values corresponds to the increase of the thickness of the boundary layer.

**Thermodynamic parameters**

The study of temperature effect on adsorption process will give an idea about its spontaneity and heat change. Thermodynamic parameters such as enthalpy change ($\Delta H^o$), Gibbs free energy change ($\Delta G^o$) and entropy change ($\Delta S^o$) are very important and can be estimated by using equilibrium constants changing with temperature. These thermodynamic parameters can be estimated using equilibrium constants as a function of $T$ and related by equation 6 (Tan et al. 2008, Gupta et al. 2003). $K_c$ values obtained from the Langmuir model at different temperature can be used to compute the standard enthalpy and entropy changes (equation 7).

The slope and the intercept of plot between $\ln K_c$ and $1/T$ (Fig. 9) are used to evaluate $\Delta H^o$ and $\Delta S^o$ respectively. Values of all thermodynamic parameters are listed in Table 3. The positive value of $\Delta H^o$ indicates the endothermic nature of the process associated with physical link (Chen et al. 2007). Negative values of $\Delta G^o$ shown in Table 3 confirms the spontaneity of the adsorption process of Malachite Green by all three adsorbents and, also that the interface is more efficient with increasing temperature. Moreover, the positive values of $\Delta S^0$ indicate the existing affinity of all considered adsorbents toward Malachite Green ions in aqueous solutions by the increase of the degrees of freedom at the solid-liquid interface during adsorption (Al Rub 2007).

**List bullet:**
- Lignocellulosic waste type as an alternative for dye removal.
- Simultaneous actions of sawdust improve its adsorptive capacity.
- Powdered species are suitable for adsorbing fairly large compounds such as dyes.
**Fig. 1**
Contact time effect of MG adsorption Example 1

**Fig. 1**
Dose effect of MG adsorption.
**Fig. 2**
*Linearized adsorption isotherm of MG (pH=6, dose = 8g/L, t = 2h)*
a - by Langmuir; b - by Freundlich.

**Fig. 4**
*Plot of ln $K_c$ vs 1/T for thermodynamic parameters estimation.*

### Table 1
*Isotherm constants and iodine number for Malachite green adsorption on Sawdust based carbons and Merck AC*

<table>
<thead>
<tr>
<th>Isotherm type</th>
<th>Adsorbents</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SDU</td>
<td>SDK</td>
</tr>
<tr>
<td>Langmuir</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$b$ (mg g$^{-1}$)</td>
<td>68,965</td>
<td>434,783</td>
</tr>
<tr>
<td>$K$ (L g$^{-1}$)</td>
<td>0,015</td>
<td>0,328</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0,993</td>
<td>0,998</td>
</tr>
<tr>
<td>Freundlich</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_f$ (L g$^{-1}$)</td>
<td>21,010</td>
<td>190,57</td>
</tr>
<tr>
<td>$n$</td>
<td>5,435</td>
<td>4,785</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0,980</td>
<td>0,855</td>
</tr>
<tr>
<td>Iodine number (mg/g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>491</td>
<td>437</td>
</tr>
</tbody>
</table>
### Table 2

**Table description – Kinetic parameters of MG adsorption by various activated carbons**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
<th>Intraparticular diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_{exp}$ (mg/g)</td>
<td>$q_{cal}$ (mg/g)</td>
<td>$K_1$ (min$^{-1}$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SDK</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_0=1800$ mg/L</td>
<td>224.95</td>
<td>3.19</td>
<td>0.047</td>
</tr>
<tr>
<td>$C_0=2000$ mg/L</td>
<td>265.78</td>
<td>139.63</td>
<td>0.095</td>
</tr>
<tr>
<td>SDP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_0=400$ mg/L</td>
<td>49.91</td>
<td>1.76</td>
<td>0.028</td>
</tr>
<tr>
<td>$C_0=500$ mg/L</td>
<td>56.65</td>
<td>11.46</td>
<td>0.030</td>
</tr>
<tr>
<td>Merck AC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_0=1400$ mg/L</td>
<td>174.90</td>
<td>5.29</td>
<td>0.037</td>
</tr>
<tr>
<td>$C_0=1600$ mg/L</td>
<td>199.47</td>
<td>23.95</td>
<td>0.031</td>
</tr>
</tbody>
</table>

### Table 3

**Thermodynamic parameters of MG adsorption by various activated carbons**

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>$\Delta G$ (kJ mol$^{-1}$)</th>
<th>$\Delta H$ (kJ mol$^{-1}$)</th>
<th>$\Delta S$ (kJ mol$^{-1}$K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298 K</td>
<td>303 K</td>
<td>313 K</td>
</tr>
<tr>
<td>SDK</td>
<td>15.89</td>
<td>16.29</td>
<td>16.80</td>
</tr>
<tr>
<td>SDP</td>
<td>13.48</td>
<td>14.47</td>
<td>15.31</td>
</tr>
<tr>
<td>Merck AC</td>
<td>20.07</td>
<td>19.99</td>
<td>22.66</td>
</tr>
</tbody>
</table>

\[
q_e = \frac{(C_0 - C_{eq})}{1000 m} V \text{ [mg/g]} \tag{1}
\]

\[
\frac{C_{eq}}{q_e} = \frac{1}{K b} + \frac{1}{b} C_{eq} \tag{2}
\]

\[
\log q_e = \log k_f + \frac{1}{n} \log C_e \tag{3}
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_{e,2}^2} + \frac{1}{q_e} t \tag{4}
\]

$q_t$ and $q_e$ are the adsorption capacities at time $t$ and at equilibrium (mg g$^{-1}$) respectively.
$k_2$ is the pseudo-second order rate constant (mg g$^{-1}$ min$^{-1}$). $k_2 q_{2o}^2$ can be assumed as the initial adsorption rate as $t$ goes to zero.

$$q_t = k_{int} t^{0.5} + C \quad \text{(5)}$$

$K_{in}$ (mg·g$^{-1}$·min$^{-1/2}$) is the intra-particle diffusion rate constant and $C$ (mg·g$^{-1}$) is the intercept. The value of $C$ gives an idea about the thickness of the boundary layer.

$$\Delta G^\circ = T \Delta S^\circ - \Delta H = -RT \ln K_c \quad \text{(6)}$$

$R$ - universal gas constant = 8.314, in J·mol$^{-1}$·K$^{-1}$

$T$ - absolute temperature, in K

$K_c = (C_{Ae}/C_{eq})$ a constant related to the affinity of the binding sites

$C_{Ae}$ - amount of dye adsorbed on the material at equilibrium, in mg/L

$C_e$ - equilibrium concentration, in mg/L

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \text{(7)}$$

CONCLUSION

This investigation shows that adsorbents prepared from low cost material sawdust chemically activated have an effective adsorption capacity with regard to the removal of Malachite Green from aqueous solution. The chemically activated sawdust by KOH has better adsorption capacity compared to the commercially Merck activated carbon. The uptake of Malachite Green is strongly affected by some parameters such as contact time, adsorbent dose and pH. The experimental data were well fitted by the Langmuir isotherm model. The results showed that the adsorption kinetics obeys the pseudo-second order.

The positive value of $\Delta H^\circ$ indicates the endothermic nature of the process is associated with physical link. Negative values of $\Delta G^\circ$ confirm the spontaneity of the adsorption process of Malachite Green by all considered adsorbents and, also the interface is more efficient with increasing temperature. Moreover, the positive values of $\Delta S^\circ$ indicate the existing affinity of all considered adsorbents toward Malachite Green ions in aqueous solutions. Finally, the significant Malachite Green adsorption also showed that the remarkable prepared adsorbents are suitable for adsorbing large compounds such as dyes, which may make them successful adsorbents in the treatment of textile industry effluents.

REFERENCES


