ADSORPTIVE REMOVAL OF MALACHITE GREEN FROM AQUEOUS SOLUTION USING LIGNOCELLULOSIC WASTE MATERIAL

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Summary

The ability of poplar sawdust, a lignocellulosic waste material, for the adsorption of cationic dye malachite green from aqueous solution was studied. Batch experiments were carried out at 25 °C and contact time of 300 min. The effects of the initial dye concentration (15, 25, 35 and 50 mg/dm^3), adsorbent concentration (5, 10, 15 and 20 g/dm^3), temperature (25 and 35 °C) and solution pH (2.5, 4.4 and 6.4) on dye removal were investigated. Adsorption efficiency (dye removal) was higher than 90% in all runs. The percentage of dye removal increased with increase in adsorbent concentration and decrease in the initial dye concentration. This was the most obvious within the first 30 min of contact time. The temperature had no significant effect on the percentage removal, while the decrease in pH caused the reduction of percentage removal of malachite green during the first 90 min of contact time. After 150 min of contact time, the difference of percentage dye removal was insignificant for all the experiments. The results demonstrated that poplar sawdust could be considered as effective, low-cost, environmentally friendly adsorbent for malachite green removal.

Keywords: adsorption, malachite green, lignocellulosic waste, coloured wastewaters

Introduction

Synthetic dyes used in textile, paper, pharmaceutical, food, cosmetic and leather industries are the most common water pollutants. Over 100 000 different synthetic dyes are commercially available to date. The above-mentioned industries are generators of coloured wastewaters that often contain up to 10% of dye used during the production process (Yesilada et al., 2003). When discharged untreated to surface waters, coloured wastewaters are a matter of concern for both toxicological and aesthetical reasons (Rafatullah et al., 2010). They significantly reduce the quality of recipient (reduce oxygen concentration and

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light penetration), thus detrimentally affecting the aquatic ecosystems. Furthermore, they can endanger human health through the food chain. Synthetic dyes tend to bioaccumulate in the environment, because of their high chemical stability and recalcitrance towards biodegradation. As a result of low biodegradability of dyes, the efficiency of their removal by conventional biological wastewater treatment methods is low (Yesilada et al., 2003). Numerous physical, chemical and biological methods have been employed for dye removal from wastewater over the last 30 years, but only a few have been accepted and applied at industrial scale. Adsorption is one of the most often used, because of its simplicity, efficiency and versatility (Rafatullah, et al., 2010). However, the drawback of the adsorption is the cost of conventional adsorbents, such as the most widely used activated carbon. Many research studies have been conducted in order to develop low-cost, effective adsorbents that seek to solve the above-mentioned problem. By definition, the low-cost adsorbent is abundant in nature or is an industrial by-product or waste material that requires no or little processing (Rafatullah et al., 2010). Lignocellulosic waste materials from industry and agriculture represent a potentially economical alternative to conventional adsorbents. Different adsorbents derived from industrial or agricultural wastes have been used successfully for dye removal from aqueous solution such as apple pomace (Robinson et al., 2001; Velić et al., 2015), peanut hull (Gong et al., 2005), bagasse (Low et al., 2011; Velić et al., 2015), barley husk (Robinson et al., 2001), brewers' spent grain and wood sawdust (Velić et al., 2015), etc.

Malachite green (MG) is a cationic dye most commonly used for silk, wool, jute, leather and cotton dyeing. It is also used in microbiology and aquaculture as a bactericide, fungicide and ectoparasiticide (Roushdy and Abdel-Shakour, 2011). In mammals, MG induces damage in liver, spleen, kidney and heart and has a strong inhibitory effect on the reproductive system while direct contact with MG in humans causes allergies, dermatitis and skin irritation (Baek et al., 2010; Roushdy and Abdel-Shakour, 2011). Therefore, the removal of MG from wastewater is crucial for preservation of the human health.

The aim of this study was to explore the adsorptive capacity of lignocellulosic waste material (poplar sawdust) to remove cationic dye such MG, from aqueous solution.

Materials and methods

Biosorbents. Lignocellulosic waste material poplar sawdust (PS) (*Populus alba* L.) was used in the experiments. Poplar sawdust was kindly donated by ″Hrvatske šume″ d.o.o (Osijek, Croatia). Prior to adsorption experiments, biosorbent was dried (oven dried at 60 °C for 48 h) and milled using standard laboratory knife mill with 1 mm screen (MF10 basic, IKA Labortechnik, Germany) to ensure the particle size of adsorbent below 1 mm. No other chemical or physical treatments were applied prior to adsorption experiments.

Adsorbat. Malachite green (MG) used in this work was purchased from Kemika (Zagreb, Croatia). A stock solution of 1.5 g/dm^3 was used and prepared daily.

Adsorption experiments. Batch adsorption experiments were carried out by adding a fixed amount of adsorbent (5, 10, 15 and 20 g/dm^3) to 100 mL dye solution (5, 15, 25 and 50 mg/dm^3) taken in a 250 mL Erlenmeyer flask. The flasks were placed in the incubator (BD 53#04-63769, Binder, Tuttlingen, Germany) and kept at constant temperature of 25 °C (and 35 °C for temperature dependence experiments). Adsorbent was soaked in dye solutions for 300 min. The pH was not adjusted (except for pH dependence experiments), but it was monitored using pH-meter (SevenEasyTM pH, Mettler Toledo, Switzerland). Dye solution samples were collected at 30 min intervals and centrifuged at 10,000 rpm for 5 min (Heraeus, Multifuge 3L/3L-R, Kendro laboratory Products, London, UK). The dye concentrations in clarified supernatants were determined at 623 nm using spectrophotometer (UV-1700 PharmaSpec, Shimadzu, Japan). The percentage of dye removal was calculated by Eq. 1:

$$\% \text{ dye removal} = 100\ (\gamma_0 - \gamma) / \gamma_0 \qquad (1)$$

where γ_0 and γ are the initial dye concentration and dye concentration after certain contact time, respectively.
Duplicate batch adsorption experiments were run for comparison and samples were analysed in triplicates.

Results and discussion

In order to investigate the adsorptive capacity of PS for MG, a series of batch adsorption experiments were carried out at 25 °C and contact time of 300 min. The effects of the initial MG concentration (15, 25, 35 and 50 mg/dm^3), adsorbent concentration (5, 10, 15 and 20 g/dm^3), temperature (25 and 35 °C) and solution pH (2.5, 4.4 and 6.4) on dye removal were investigated. MG concentrations were selected based on the usual dye concentrations reported in actual textile effluents ranging from 10 to 50 mg/dm^3 (Nigam et al., 2000). The results are presented in Figs. 1 – 4.
In all conducted batch experiments the percentage of MG removal exceeded 90% after 300 min of contact time. The applicability of poplar sawdust as biosorbent is achieved through interactions of adsorbate with different functional groups present in the material (e.g. –OH and –COOH). Depending on the wood type, the chemical composition of wood is 40-45% cellulose, 30% hemicellulose, 20-30% lignin and 2-4% extractives (Sjostrom, 1993). High percentage of cellulose, hemicellulose and lignin provide variety of available functional groups.
The effects of contact time and initial MG concentration at 25 °C and adsorbent concentration of 10 g/dm^3 are given in Fig. 1.

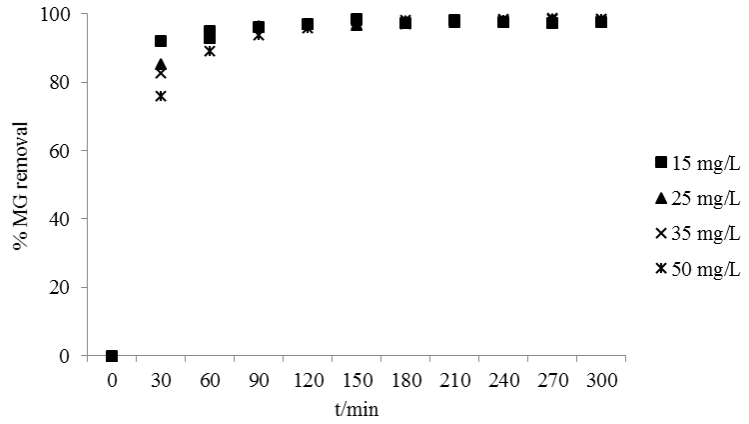

Fig. 1. Effect of initial MG concentration on the adsorption on PS (θ = 25 °C, V = 100 cm^3, $\gamma_{adsorbent}$ = 10 g/dm^3)

Within the first 60 min, the dye uptake was rapid (which can be seen from the steep slope on the graph), while in later stages it decreased until a point was reached when no more dye can be adsorbed onto the biosorbent. The percentage of MG removal decreased with an increase in the initial MG concentration. This is in agreement with other studies reporting that dye removal is highly concentration dependent (Khattri and Singh, 2009).
Fig. 2 shows the effect of adsorbent concentration on MG removal, which was the most evident within the first 60 min of the experiments and showed an increase in MG percentage removal due to the increase in adsorbent concentration. At later stages, the MG percentage removal was similar for all runs.

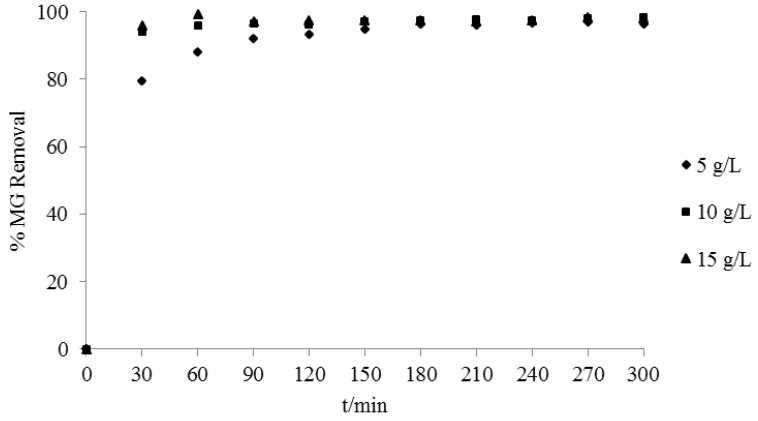

Fig. 2. Effect of biosorbent concentration on the MG adsorption on PS (θ = 25 °C, V = 100 mL, γ_{dye} = 15 mg/dm^3)

No considerable difference of MG percentage removal was observed at given temperatures (Fig. 3). On the other hand, pH of the solution significantly affected the adsorption of MG on PS. Decrease in pH caused reduction of MG percentage removal (Fig. 4). MG is basic cationic dye and acidic conditions result in the positively charged surface. The decrease in MG percentage removal at lower pH is probably due to competition between H^+ ions and dye cations (Hameed, 2009).

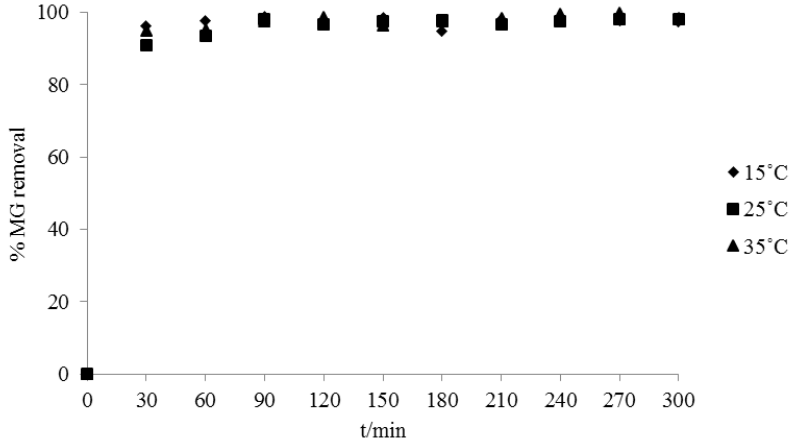

Fig. 3. Effect of temperature on the MG adsorption on PS
(V= 100 mL, γ_{dye} = 15 mg/dm^3, $\gamma_{adsorbent}$ = 10 g/dm^3)

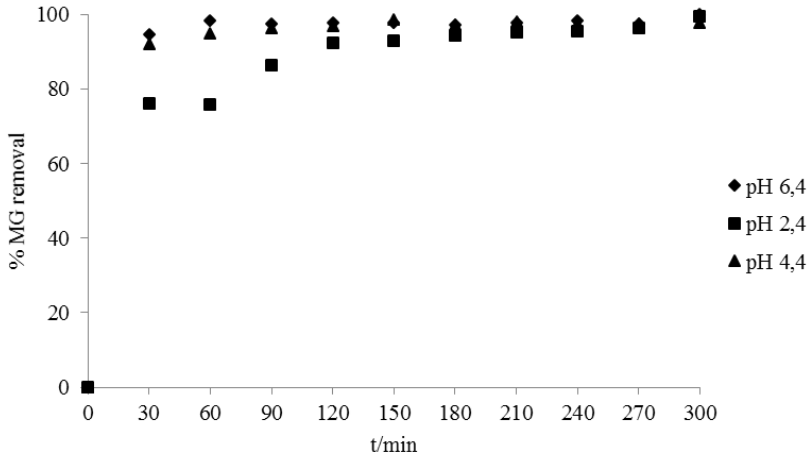

Fig. 4. Effect of pH on the MG adsorption on PS
(θ= 25 °C, V= 100 mL, γ_{dye} = 15 mg/dm^3, $\gamma_{adsorbent}$ = 10 g/dm^3)

Conclusions

The experimental results showed that waste lignocellulosic material poplar sawdust was suitable, highly efficient adsorbent for the removal of MG from aqueous solution. The adsorption of MG onto PS is influenced by contact time, the initial concentration of dye, the amount of adsorbent and pH value. Poplar sawdust could be considered for use as an alternative to conventional adsorbents used in wastewater treatment, because of its wide availability and high MG removal efficiency.

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