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Ultrasound-assisted removal of malachite green from aqueous solution by dead pine needles

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Abstract

The dead needles of Aleppo pine (*Pinus halepensis*) were tested as a possible sorbent for the removal of malachite green from aqueous solutions in the absence and presence of ultrasound. Batch process was employed for sorption kinetic and equilibrium studies. Sorption experiments indicated that the sorption capacity was dependent of operating variables. Both the rate and the amount of malachite green sorption are markedly increased in the presence of the ultrasonic field. The dye removal with the assistance of ultrasound was enhanced with the increase of sorbate initial concentration and temperature, and with the decrease of sorbent dosage and ionic strength. The combination of stirring and ultrasound leads to an improvement of the removal of dye. The sorption kinetics was controlled by the intraparticle diffusion. The intraparticle diffusion coefficient increased 1.7 times in the presence of ultrasound and up to 3.6 times in the combined process. The sorption capacity, estimated according to the Freundlich model, indicates that ultrasound enhanced the sorption properties of the sorbent. The effect of ultrasound on the improvement of dye sorption is due to a variety of physical and mechanical effects as well as to thermal properties. The combination of ultrasound and stirring for the sorption process was shown to be of interest for the treatment of wastewaters contaminated with malachite green.

Keywords: Ultrasound; Sorption; Malachite green; Pine needles; Mass transfer

1. Introduction

Dyes are important pollutants, causing environmental and health problems to human being and aquatic animals. Malachite green (MG), a basic dye, is most widely used for coloring purpose, amongst all other dyes of its category [1]. This triarylmethane dye is widely used in the aquaculture industry worldwide as a biocide as well as in the silk, wool, cotton, leather, paper, and acrylic industries as a dye. Furthermore, it is also employed as therapeutic agent to treat parasites, fungal and bacterial infections in fish and fish eggs and as antiseptic, but only for external applications on the wounds and ulcers. Despite its extensive use, MG is a highly controversial compound due to its reported toxic properties which are known to cause carcinogenesis, mutagenesis, teratogenesis, and respiratory toxicity [2]. Its oral consumption is also hazardous and carcinogenic [2]. However, despite the large amount of data on its toxic effects, MG is still used in aquaculture and other industries. Therefore, the removal of MG from wastewater before discharging is necessary and very important.

The removal of color from dye bearing effluents is one of the major problems due to the difficulty in treating such wastewaters by conventional treatment methods. Sorption technique is proved to be an effective process for the removal of color from dye wastewaters, because of its efficiency, flexibility, and economic feasibility. Activated carbon is the most commonly used adsorbent for the removal of various pollutants from wastewaters. Therefore, finding alternative low-cost materials that have comparable capacity to activated carbon is highly desired. The purpose

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Nomenclature

C_e	the liquid-phase concentration at equilibrium (mg L^{-1})
D	the intraparticle diffusion coefficient based on the concentration in solids ($cm^2\ min^{-1}$)
d	the diameter of the sorbent (cm)
K_F	the Freundlich constant that is taken as an indicator of sorption capacity ($mg^{1-\frac{1}{n}}\ L^{\frac{1}{n}}\ g^{-1}$)
n	an empirical constant related to the magnitude of the sorption driving force
q	the sorbed amount at any time t (mg g^{-1})
q_e	the sorbed amount at equilibrium (mg g^{-1})

of this paper is to assess the ability of dead pine needles to sorb MG from aqueous solutions with and without the assistance of ultrasound. The use of dead pine needles as low-cost sorbent for the removal of dyes from aqueous phase, to our knowledge, has not been investigated.

The recent increase in the applications of ultrasound for benign environmental remediation has conducted many researchers to investigate the effects of ultrasound on sorption and desorption processes [3–12]. The process is based on the phenomenon of acoustic cavitation, involving the formation, growth, and sudden collapse of micro-bubbles in an irradiated liquid. Ultrasound causes the formation of cavitation bubbles leading to high localized temperatures and pressures. On the microscale, high bubble temperatures up to 5000 K and pressures up to 1000 atm have been estimated [13–16]. The most pertinent effects of ultrasound on liquid–solid systems are mechanical and are attributed to symmetric and asymmetric cavitation. In addition, shock waves are produced which have the potential of creating microscopic turbulence within interfacial films surrounding nearby solid particles, also referred to as micro-streaming [16]. Asymmetric collapse leads to the formation of micro-jets of solvent that impinge on the solid surface resulting in pitting and erosion. Acoustic streaming is the movement of the liquid induced by the sonic wave, which can be considered to be the conversion of sound to the kinetic energy, and is not a cavitation effect. These phenomena increase the rate of mass transfer near the surface as well as possibly thinning the film [16].

The aim of the present study was to investigate ultrasound-assisted sorption of MG from aqueous solutions and to compare this method to the sorption process in classical conditions (without ultrasound). The combination of ultrasound and stirring was investigated for the enhancement of the dye removal from water.

2. Materials and methods

2.1. Materials

The cationic basic dye (C.I. 42000; Basic Green 4), malachite green oxalate salt, (molecular formula $C_{52}H_{56}N_4O_{12}$, FW 929), was obtained from Merck and used without further purification. The structure of this dye is displayed in Fig. 1. Five hundred milligram per liter stock solution was prepared by dissolving the required amount of dye in distilled water. Working solutions of the desired concentrations were obtained by successive dilutions.

The dead pine needles used in the present study were collected from the Scientific Campus of the University of Annaba, Sidi-Amar, Annaba, Algeria. The collected needles were cut into small pieces (5 mm length) using scissors. The material was washed with distilled water several times to remove dirt particles and water soluble materials. The washing process was continued till the wash water did not contain any color. The washed material was then completely dried in an oven at 80 °C for 3 days and stored in a desiccator until use.

2.2. Experimental procedures

Batch sorption experiments were carried out in the experimental setup shown in Fig. 2. Experiments were performed in a 400 mL cylindrical jacketed glass vessel that was attached to an overhead mechanical stirrer. The agitator used was a 45° pitch four blades down pumping impeller (diameter 5 cm), which have a good suspension characteristics for the solid particles. The vessel was immersed in an ultrasonic cleaning bath (Fungilab, Spain) operating at a frequency of 40 kHz with an electrical nominal power of 125 W (indirect sonication). The ultrasonic power was determined by the calorimetric method and was 9 W.

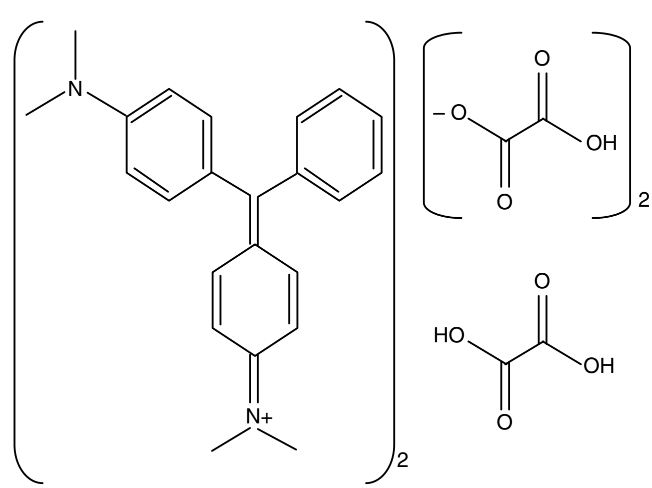

Fig. 1. Chemical structure of malachite green (oxalate salt).