



Malachite green dye behaviors in the presence of biosorbents from maize (*Zea mays* L.), their Fe-Cu nanoparticles composites and Fe-Cu nanoparticles.



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ABSTRACT

The sorption behaviors of biosorbent based on maize (*Zea mays*, ZM) cane (bagasse and stalk), their composites (ZM/Fe-Cu nanoparticles) and Fe-Cu nanoparticles for malachite green from aqueous solutions were investigated in this work. Adsorbents were characterized using BET, infrared spectroscopy, X-ray diffraction, SEM-EDS, and Fe-Cu nanoparticles were characterized by TEM. The study of the sorption kinetics indicates that the adsorption on malachite green by stalk and their composite follows second-order kinetics and nanoparticles and bagasse and their composite follow the pseudo-second order model. The malachite green adsorption by ZM/Fe-Cu composites were faster than natural materials and only showed two phases in the intraparticle diffusion model, probably due to the minor internal diffusion resistance. The adsorption isotherms experimental data were analyzed by the Langmuir, Freundlich and Langmuir–Freundlich models and the equilibrium data was well described by the Langmuir–Freundlich isotherm model. The adsorption was more favorable at basic pH. The OH-groups were proportional to dye adsorption capacities. Results showed that composites (ZM/Fe-Cu nanoparticles) and Fe-Cu nanoparticles possessed good adsorption abilities to malachite green.

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1. Introduction

Industrial dyeing and finishing processes generate large amounts of colored wastewater, which are discharged into natural streams with undesirable consequences to the environment and human health [1]. Malachite green (MG) dye is most commonly used for dyeing cotton, silk, paper, leather and also in manufacturing of paints and printing inks. Malachite green is widely used in distilleries and also considered as an antiseptic for external applications on wounds and ulcers, however, its oral consumption is toxic, hazardous and carcinogenic [2]. Malachite green when discharged into streams affects aquatic life and causes detrimental effects in liver, gill, kidney, intestine, gonads and pituitary gonadotropic cells. Therefore, it would be desirable to remove it from wastewaters before they are discharged [3].

The conventional treatments of dyed wastewater include chemical coagulation, biological, ozonation, advanced oxidation processes; filtration, ion exchange and adsorption by activated

carbon, each of these methods have inherent limitations. Yagub, et al. reported the advantages and disadvantages of different dye removal methods [4]. Adsorption has been shown to be the most promising process for all non-biodegradable organics for the removal from aqueous streams, activated carbons is the most common adsorbent for this purpose due to its effectiveness and versatility, but it is an expensive sorbent.

Low-cost adsorbents are materials that generally require little processing and are abundant in nature, or are by-products or waste materials from other processes [5]. Agricultural by-products are available in large quantities and constitute one of the most abundant renewable resources in the world [6]. The lignin cellulosic biomasses behave as good effective adsorbents; however they have low sorption efficiencies, therefore structural modifications onto the biosorbents have been performed in order to enhance their binding capacities, selectivity and environmental stability in terms of their reusability [7,8]. Many researchers have reported the feasibility of using various low cost adsorbents and non-conventional sorbentes to remove malachite green from aqueous solutions, such as bivalve shell-treated *Zea mays* L. (maize) husk leaf [9], pine wood [10], clay [11], carbon from spent tea

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leaves [12], walnut shell [13], sodium alginate-coated Fe_3O_4 nanoparticles [14].

Maize particularly is a widely cropped annual cereal that grows rapidly, produces extensive fibrous root system, withstands adverse conditions, and produces abundant seeds. Various investigators have modified the nature biopolymers with specific functional groups to remove specific pollutants and to improve their adsorption abilities and efficiencies, such as modifications with carboxyl groups [15].

Recently, it has been found that Fe/Cu bimetallic particles prepared by deposition of Cu^0 on the surface of Fe^0 and chemical reduction method, can enhance rates of pollutants reduction remarkably due to the high potential difference (0.78 V) between Cu and Fe [16]. Some studies suggested that Fe/Cu bimetallic particles could be proposed as a cost-effective pretreatment materials for the toxic organic wastewater. The mechanism for organic compounds removal using Fe/Cu bimetallic particles in absence of dissolved oxygen (DO) is that the Cu located on the iron surface can accelerate the corrosion of Fe and the generation of $[\text{H}^+]$. In contrast, under oxic conditions, DO can enhance the generation of hydroxyl ions and improve the formation of iron hydroxides. It has been found that iron hydroxide can easily adsorb organic molecules containing electron-donating groups, so plenty of newborn organic compounds in the aqueous solution was adsorbed and co-precipitated with iron hydroxides. Several studies have indicated that Fe corrosion in the presence of air can generate hydrogen peroxide onto aqueous system. The hydrogen peroxide can react with Fe^{2+} (Fenton-like reaction) and produce strong oxidants such as hydroxyl radical OH^\bullet , the presence of Cu could enhance the corrosion of Fe to generate ferrous iron so that the oxidation could be improved [17].

In this work, the components of maize cane (bagasse and stalk) were modified with nanoparticles Fe-Cu for the removal of malachite green from aqueous solutions. The adsorption performance parameters (i.e., contact time, concentration, temperature, pH and mass effect) and the mechanism of the adsorption process were determined.

2. Materials and methods

2.1. Materials

Malachite green (Basic Green 4, C.I.: 42,000, molecular formula: $\text{C}_{23}\text{H}_{25}\text{N}_2\text{Cl}$, molecular wt.: 365 g/mol, λ_{max} : 620 nm), was purchased from Hycl, Mexico, and its chemical structure is shown in Fig. 1. Dye solution was prepared by dissolving an appropriate amount of dye in distilled water. The concentrations of the samples were determined by using a standard calibration plot that showed a linear variation up to 100 mg/L concentration.

The maize (*Zea mays*, ZM) stalk from Tenancingo, Mexico was dried. Bagasse material was separated from the maize stalk before being ground; the particle size of both materials used in this work

was between 0.84 mm and 0.42 mm. Materials were washed with distilled water several times to remove the dust and finally dried in an oven for 3 days at 30 °C. The adsorbent materials were soaked for 24 h in a 0.2% formaldehyde solution and they were washed with distilled water and dried at 60 °C for 24 h. The synthesis of Fe-Cu nanoparticles and ZM/Fe-Cu nanoparticles composite was carried out following the method previously reported in the literature [18].

2.2. Characterization

2.2.1. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM)

For scanning electron microscopy (SEM) observations, the biosorbents, Fe-Cu nanoparticles and ZM/Fe-Cu nanoparticles composites samples, before and after malachite green adsorption, were mounted directly on the holders and then observed at 20 kV in a JEOL JSM-5900-LD electron microscope. The microanalysis was done with an EDS (Energy X-ray Dispersive Spectroscopy) system. Transmission electron microscopy (TEM) observations of Fe/Cu nanoparticles were carried out at 200 kV using a JEM-2010F FASTEM microscope.

2.2.2. X-ray diffraction (XRD)

XRD analysis was carried out on a Siemens D500 X-ray diffractometer operated with an accelerating voltage of 40 kV, with Bragg-Bretano chamber, X-ray source Cu $\text{K}\alpha$, $\lambda = 1.5406 \text{ \AA}$, and current emission of 30 mA. The conventional diffractograms were used to identify the material structures of biosorbents, Fe-Cu nanoparticles and ZM/Fe-Cu composites.

2.2.3. IR spectroscopy

The IR spectra in the $4000\text{--}400 \text{ cm}^{-1}$ range were recorded for all adsorbents at room temperature using a Nicolet Magna IRTM 550 FTIR. The samples were prepared using the standard KBr pellet method.

2.2.4. Specific surface areas

Specific surface areas were determined by the N_2 Brunauer-Emmett-Teller (BET) nitrogen adsorption method in a Micromeritics® Gemini 2360 surface area analyzer. The dry and degassed samples were then analyzed using a multipoint N_2 adsorption-desorption method at room temperature.

2.2.5. Zero charge point and concentrations of the acid-base groups

The experiments were carried out with all materials and 0.01 M NaCl solutions, whose pH values were previously adjusted between 2 and 8, with intervals of 2 units by adding 0.1 M HCl or NaOH solutions. After 24 h of contact, the samples were centrifuged, decanted, and pH was analyzed in the final liquid phases with a Hanna Instruments HI 2550 pH meter.

Determination of acid-base groups concentrations was performed as follows: samples of 20 mg of each adsorbent were put in contact with 25 mL of a 0.025 M HCl solution, using dark glass bottles, and shaken for 24 h at 120 rpm and 25 °C. After that, the samples were decanted and the excess acid was titrated with 0.025 M NaOH to determine superficial basicity. The superficial acidity was obtained by a similar procedure, a 0.025 M NaOH solution was put in contact with each adsorbent and the solutions were titrated using a 0.025 M HCl solution. The experiments were done in duplicate.

2.3. Adsorption kinetics

Kinetic removal of malachite green (MG) by biosorbents, Fe-Cu nanoparticles or ZM/Fe-Cu composites, was performed as follows:

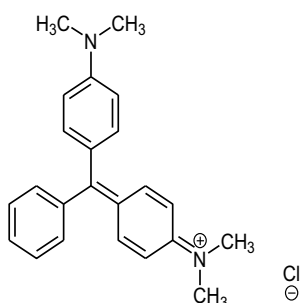


Fig. 1. Structure of malachite green dye.

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