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Removal of malachite green dye from aqueous solutions using organically modified hydroxyapatite

Adel A. El-Zahhar[a,b,*], Nasser S. Awwad[a]

[a] *Chemistry Department, College of Science, King Khalid University, P.O. 9004, Abha 61321, Saudi Arabia*
[b] *Nucl Chem. Dept., Atomic Energy Authority, P.C. 13759 Cairo, Egypt*

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ABSTRACT

The removal of malachite green dye (MG) from aqueous solution was studied using organically modified hydroxyapatite. Hydroxyapatite (HAP) was organically modified with different concentrations of the organic surfactant ethylhexadecyldimethyl ammonium bromide (EHDAB). The modified apatite was characterized using FTIR, XRD and SEM. The modified apatite was studied for removal of MG from aqueous solution and the experimental parameters were studied. The effect of contact time, adsorbent dose, dye concentration and temperature was studied. The equilibrium uptake was increased with increasing the initial dye concentration in solution. The experimental isotherm data were analyzed using Langmuir adsorption isotherm model. The adsorbed amount of MG onto the modified apatite was found to increase with increasing the adsorbent concentration. The maximum monolayer adsorption capacity was found to be 188.18 mg/g at 30 °C.

1. Introduction

Malachite green (MG) is one of the synthetic dyes, which is widely used in different industrial fields and has the structure in Fig. 1. MG is used in textile coloring industry, paper industry, food industry and other biological fields [1,2]. As a synthetic dye, MG has a hazardous effect on the environment and aquatic system. The presence of MG in aquatic system has a harmful effect on the biological systems and reproductive organ and it also has carcinogenic, genotoxic, mutagenic effects. These hazardous effects were produced from high accumulation of MG, so a zero level of MG must be verified. Different authorities all over the world have applied restrictions for the usage of MG in food industries [3]. The discharge of MG containing waste in aqueous environmental systems results in water coloring and prevents sunlight from water penetration [3,4]. Therefore, the removal of MG from wastewater before discharging into the environment is an environmental requirement.

Different procedures were developed for removal of organic dyes from wastewater. These procedures include electrocoagulation, flotation, chemical oxidation, filtration, ion-exchange, ozonation, membrane separation and microbial degradation [5]. Adsorption techniques are also potentially used for removal of organic dyes with high efficiency and high removal percentage. Adsorption is an easy and simple procedure [6] for removal of hazardous species from aqueous streams. Adsorption process has economical impact [7] when applied in wastewater treatment technology. Materials used as adsorbents should be characterized by small size as huge surface area produce high adsorption efficiency. Particles with very small size would be hardly separated from water after loaded with hazardous materials. Different types of adsorbent materials were studied for removal organic dyes from aqueous waste streams.

Low coast and environmentally available agricultural waste was potentially studied either natural or carbonized in organic dye removal from aqueous solutions [8,9]. Activated carbon derived from agriculture waste was potentially studied as adsorbent for organic dyes; bamboo waste derived activated carbon was studied for removal azo dye [10]. The adsorption of acid yellow 17 dye was studied on activated carbon prepared from agriculture waste via microwave chemical activation procedure [11]. The removal of anionc dye (congo red) was studied by unmodified and chemically modified tea waste, which proved comparable adsorption capacity [12,13].

Apatite materials proved to be efficient adsorbent for removal of hazardous materials from waste solutions and found applications in biomedical fields [14]. Apatite materials were studied for rare earths and heavy metals separation [15–17]. The present work aims at studying the adsorption of MG from aqueous solutions

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* Corresponding author at: Chemistry Department, College of Science, King Khalid University, P.O. 9004, Abha 61321, Saudi Arabia.
E-mail address: adelelzahhar@yahoo.com (A.A. El-Zahhar).

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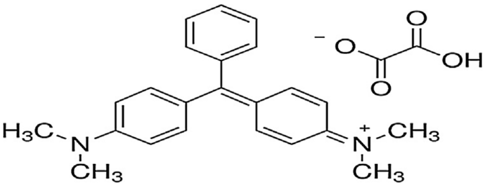

Fig. 1. Chemical structure of malachite green dye.

using the organically modified hydroxyapatite (HAP). The apatite sample was firstly modified using the organic surfactant ethylhexadecyldimethyl ammonium bromide (EHDAB), then characterized and used for adsorption of MG from aqueous solutions.

2. Experimental

2.1. Materials

The reagents used in the experimental work were of analytical grade and used without further purification. HAP was obtained from (Sigma–Aldrich) and the organic surfactant EHDAB was purchased from (Merck). MG was purchased from (Sigma–Aldrich). Different concentrations of MG were prepared from a stock of 1000 mg/L solution in distilled water, and the solution pH was adjusted to be neutral using NaOH and HNO_3 solutions.

2.2. Preparation and characterization of organically modified apatite (organo-apatite)

HAP was organically modified with EHDAB by applying a procedure based on cation exchange reaction of EHDAB with HAP. Briefly, appropriate amount of the HAP was dispersed in distilled water (6% w/w) with agitation (250 rpm) for 30 min followed by settling for 24 h. The quaternary ammonium salt was added to the suspension, then the mixture was stirred for further 30 min and left for settling period of 24-h. The organo-apatite was filtered out and dried at (60 ± 5) °C till constant weight. The above mentioned procedure was adapted from a previously used procedure [18]. The produced organo-apatite was characterized using Fourier transform infrared (FT-IR) of HAP and organo-apatite by KBr method on a NICOLET 6700 FTIR thermo scientific. The XRD patterns of both unmodified and modified samples were recorded on a XPert Philips X-ray diffractometer. All patterns were obtained using Cu/Kα1 radiation with a graphite monochromator at 0.02° min^{-1} scanning rate at King Khalid University. Scanning electron microscope (Philips XL 30 attached with EXD Unit) was used for assigning the surface morphology and surfaces characteristics of HAP the samples.

2.3. Adsorption experiment

MG solution was prepared by dissolving the dye in distilled water with the required concentrations. NaOH and HNO_3 solutions were used for adjusting the pH of the dye solutions. MG solution (25 mL) was mixed with 0.01 g of dry organo-apatite and shacked in a thermostat water bath shaker at 150 rpm. MG concentrations were measured before and after experiments using UV–vis spectrometer (model UV-1800, Japan) at wavelength of 618 nm after adjusting the pH 9. The adsorbed amount of dye onto the modified apatite (q mg/g) was calculated as:

$$q = (C_o - C_e) \times \frac{V}{m}(\mathrm{mg/g}) \tag{1}$$

where C_o and C is the initial and equilibrium dye concentration (mg/L), V is the solution volume (mL) and m is the weight of organo-apatite sample (g) while the distribution coefficient (K_d) were calculated as:

$$k_d = \frac{C_o - C_e}{C_e} \times \frac{V}{m}(\mathrm{ml/g}) \tag{2}$$

The chemical structure of malachite green dye MG is shown in Fig. 1.

3. Results and discussion

3.1. Characterization of HAP samples

XRD patterns of raw HAP and organo-apatite are given in Fig. 2. The data in these Figures revealed straight base lines and sharp peaks clarifying the crystalline nature of HAP, while the organo-apatite shows very slightly broadened peaks with nearly no shift in beak position produced in the pattern of organo-apatite due to the adsorption of the organic surfactant in the apatite lattice.

The FTIR spectra of the unmodified and modified HAP samples are presented in Fig. 3. The results in the spectra showed the

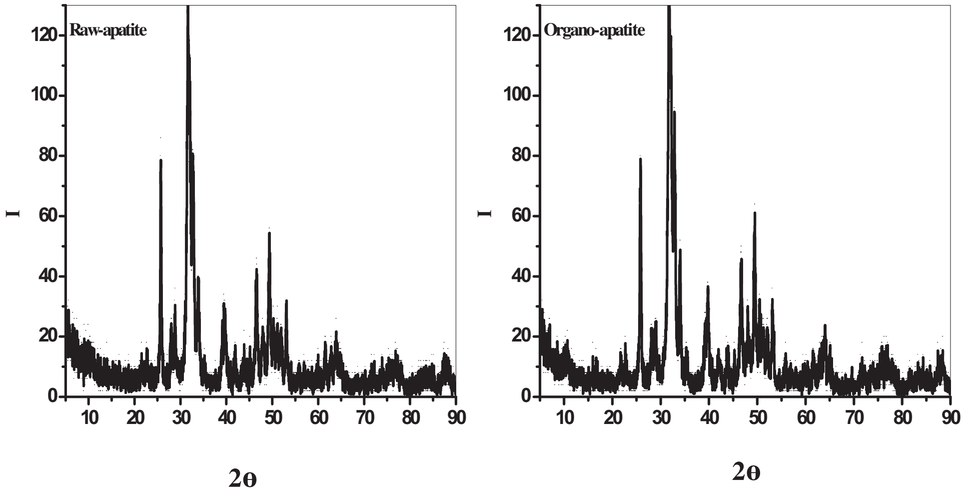

Fig. 2. XRD-patterns for raw and organo-apatite.