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Ultrasonic modified corn pith for the sequestration of dye from aqueous solution

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ABSTRACT

In this research, the ultrasonic waves were used to prepare the novel material from corn pith for the removal of malachite green (MG) dye from aqueous solution. The prepared material was characterized by BET, FTIR, SEM, TGA and XRD analyses. Adsorption system followed Freundlich and pseudo-first order kinetic models. Langmuir monolayer capacity of the adsorbent was calculated as 488.3 mg g^{-1} which was higher as compared with other local materials. Adsorption thermodynamics was found to be exothermic and spontaneous. The adsorber was designed using Freundlich model. The novel material showed good adsorption capacity for sequestration of MG dye from wastewater.

Introduction

For the last few decades, the dye pollution has been one of the most serious threats to our environment. Large amount of synthetic dye effluents from different industries such as paper production, hair coloring, textile, leather, silk, wool, cotton and food industries that are directly released into the water streams [1–9]. Effluents from the dye finishing industries are perilous pollutants due to their high toxicity, scant degradability, complex structure and high solubility in water. The presence of dye in wastewater, even less than 1 mg L^{-1}, is adverse, highly discernible and recalcitrant [10,11]. These dye effluents cause a major change in the physical and chemical properties of water which affects human health, increases the micro toxicity in aquatic life, reduction in light penetration and gas solubility in water, slows down photosynthetic activity and reduces the growth of living organisms in water streams [12–14]. Among the common synthetic dyes in use, malachite green dye is most commonly used as a coloring agent for many fibers such as leather, silk, jute, wool, cotton and paper. MG dye, a dark green N-methylated diamino triphenylmetane dye, is highly effectual for the treatment of fungal and bacterial infections and it was widely used as medical disinfectant and food coloring agent. However, MG dye has become one of the most perilous and toxic dyes to humans, aquatic and terrestrial animals, due to its carcinogenic, teratogenic, chromosomal fracturing, respiratory toxic and mutagenic properties [13,15–17]. MG dye has many adverse effects on human health such as skin allergies, anemia, liver toxicity, damage to the immune system, reproductive system, gastrointestinal tract and kidneys, thyroid abnormalities and cancer [18–20]. Therefore, in response to the health threat, the removal of MG dye from aqueous solution is very essential. Several conventional technologies such as membrane separation, coagulation, electrodialysis, ultra filtration, micro filtration, nano filtration, reverse osmosis, flotation, ion exchange, electrochemical treatment and chemical precipitation have been used for the removal of toxic dyes from the aqueous solution [21–25]. Amongst these, adsorption process is the most promising technology for the removal of organic and inorganic pollutants from the aqueous solution due to its low cost in application, superior potential for the removal of toxic dyes and metal ions at low concentration, sludge reuse, easy availability and provision of large surface area. Different adsorbents have already

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been used by many researchers such as activated carbon: sawdust activated carbon [26], ground nut shell activated carbon [12], etc., and microbial adsorbent: *Ganoderma lucidum* [27], *Poria cocos* [23], *Cosmarium sp* [28], etc., algae biomass: *Caulerpa racemosa* [29], etc., and different agricultural byproducts [30,31]. But still, there is a requirement to develop an effective adsorbent material for the separation of toxic dyes from wastewater. Recently, a surface modified agricultural biomass has been focused as an effective adsorbent due to its large surface area, high thermal stability and large volume of micropores and mesopores in its structure. In this present research, a novel effective surface modified agricultural biomass: ultrasonic assisted corn pith (UACP) has been utilized as an effective adsorbent material, in order to attain the rapid and high removal of dyes from the aqueous solution. Corn pith consists of polysaccharide (hemicelluloses) that plays an imperative role for the adsorption of MG dye from wastewater effluent. Hemicellulose consists of simple sugars such as glucose, xylose, mannose, galactose and arabinose. Generally, the high value of arabinose and xylose is represented as arabinoxylan. Arabinoxylan is the important content in the hemicellulose [32]. The surface morphology and the composition of the synthesized adsorbent material was characterized by various techniques such as Brunaner–Emmett–Teller (BET), Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM), Thermogravimetric analyses (TGA) and X-ray diffraction (XRD). The adsorption of MG dye was evaluated under several experimental conditions such as solution pH, adsorbent dosage, initial dye concentration, contact time and temperature in detail by batch adsorption experiments. The adsorption isotherm, kinetics and thermodynamic parameters were also evaluated and discussed. A single stage batch adsorber was designed by using the best fitted adsorption isotherm model.

Experimental

Preparation of Malachite green dye solutions and analysis

MG dye (molecular weight: 364.911; λ_{max} = 618.32 nm; molecular formula: $C_{23}H_{25}ClN_2$), a green crystalline powder was purchased from E. Merck, Mumbai, India. Stock solution of malachite green dye (1000 mg L^{-1}) was prepared by dissolving the required amount of MG dye crystalline powder in 1000 mL of distilled water. The prepared stock solution was diluted by using deionized water to attain the working solution of different desired concentrations (50–500 mg L^{-1}). The concentration of MG dye in the solution before and after adsorption was examined by using UV–vis spectrometer (JASCO, USA). The pH of the solution was calculated with Hanna pH meter (HI 98107, Hanna equipments private limited, Mumbai, India) using a combined glass electrode. The solution pH was adjusted to the appropriate value by adding 0.1 *N* NaOH or 0.1 *N* HCl.

Preparation and characterization of UACP

Corn pith was collected from the agricultural field (Kanchipuram district, Tamil Nadu, India) during the process of removing kernels. This agricultural waste biomass was used as a precursor for the preparation of an effective adsorbent material. This raw material was rinsed thoroughly with water to remove the impurities and dust particles. After that, the washed adsorbent material was allowed to dry in sunlight and then the dried material was grounded to fine powder by using a still mill. The dried powdered corn pith was treated with concentrated sulphuric acid in the ratio of 1:2 and the mixture was kept for about 24 h. The excess acid present in the dehydrated corn pith powder was removed by washing with deionized water until the pH of supernatant reaches the constant pH value of 7.0. Then the material was dried at 80 °C in hot air oven for about 3 h. The dried material was sieved at a particle size of 0.354 mm. Further, about 4.0 g of sulphuric acid treated corn pith was mixed with 50 mL of deionized water. This mixture was allowed to undergo the sonication process [33,34] with an ultrasonicator (Sonics Materials Inc., Newtown, USA) at a working frequency of 24 kHz and mechanical agitation of 500 rpm for about 1 h. After the sonication, the solution mixture was filtered by using the Whatman 42 filter paper and then dried at 40 °C for about 24 h. The resulting material was called as ultrasonic assisted corn pith (UACP) and it was effectively used as an adsorbent material for the removal of MG dye from the wastewater. The adsorbent material (UACP) was characterized by different techniques such as BET, FT-IR, SEM, TGA and XRD.

Brunaner–Emmett–Teller (BET)

A BET surface analyzer (Micromeritics ASAP 2020 Surface Area and Porosity Analyzer V3.00 H, USA) was used for the determination of surface properties of adsorbent materials. The samples were degassed via helium purging at 150 °C for about 12 h. The BET experiments were carried out to examine the UACP properties such as pore volume, micro pore area and surface area by using the adsorption isotherm of nitrogen was measured at 77 K.

Fourier transform infrared spectroscopy (FTIR)

The FT-IR (Agilent Cary 630 FTIR Spectrometer, USA) spectrum was performed with the solid samples to find the nature of interaction between the adsorbent material and the MG dye. The FT-IR spectra was analyzed by attenuated total reflectance within the range of 400–4000 cm^{-1}. The peak values from the IR studies showed the different functional groups were present in the adsorbent material (UACP) and which helps to determine the role of the particular functional groups in the adsorption process.

Scanning electron microscopy (SEM)

Scanning electron microscopy (Hitachi S-3400 Model, Tokyo, Japan) can be used for the determination of surface morphology of the adsorbent material (UACP). In this system, the samples were rising on an aluminum proprietor with aluminum conductive tape. After that, the sputtering mark Denton Vacuum Model Desk II was used for covering the samples with 150 Å thickness of gold layer. The SEM images were attained with a backscattered electron detector.

Thermogravimetric analysis (TGA)

A TGA analysis (SDT Q600 V8.0 Build 95 Model, TA Instruments, USA) was performed by placing the samples in the furnace and gradually raising the temperature of the sample at a heating rate of 10 °C min^{-1} with the temperature ranging from room temperature to 80 °C. In TGA, mass loss is observed if a thermal event involves loss of a volatile component. The thermal transition of the material can be determined by plotting the curve between the weight of the sample and temperature.

X-ray diffraction (XRD)

An X-ray diffraction (PANalytical XPERT-PRO, Powder X-ray Diffractometer, The Netherlands) analysis was performed by placing the samples in the cathode ray tube. The X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The diffracted ray was attained between 2° and 100° by the interaction of the incident rays with the sample at 40 kV and 2 Theta steps of 0.4°–0.5° for about 60 min.