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Removal of Malachite Green, a hazardous dye from aqueous solutions using *Avena sativa* (oat) hull as a potential adsorbent

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ABSTRACT

Adsorptive potential of an agricultural waste, oat hull for the removal of a dye, Malachite Green from aqueous solutions was investigated. The adsorbent was characterized by FTIR, XRD, SEM, and BET. Batch adsorption experiments were conducted to examine the sorption behavior of MG at different adsorbent particle sizes, solution pH, initial dye concentration, contact time and temperature. Optimum conditions were investigated as adsorbent particle size ~150 μm; initial pH, 8.0, contact time, 80 min and at 313 K. The study of sorption kinetics was found to be more consistent with pseudo second-order model and film diffusion mechanism was interpreted as rate limiting step. The adsorbate–adsorbent interaction as a function of temperature was assessed and the data fitted better in Freundlich model. The adsorption capacity increases with increasing temperature and maximum Langmuir's adsorption capacity was found to be 83 mg/g at 313 K. Thermodynamic studies indicated that the process of removal of MG was spontaneous in nature. The efficacy of the batch sorption process was further investigated by column experiments. Factors like effect of flow rate and bed depth were examined in column mode. The column sorption data was mathematically treated with bed depth service time (BDST) and Thomas models. The above findings recommend that oat hulls can be successfully used for the decoloration of MG contaminated wastewater.

1. Introduction

Rising economy contributes to unprecedented growth of industries that result in large scale consumption of dyes during various industrial processes [1–3]. Dyes are mainly consumed in textile, printing, leather and paint industries and the large volume of effluents released from these industries were discharged directly into surface and subsurface water bodies [4]. The colored effluents pose adverse effect on aquatic ecology and severely deteriorate the esthetic value of the water bodies. Moreover, the industrial discharges also cause severe health hazards to human beings as most of the dyes are either carcinogenic and/or mutagenic in nature [5]. Thus, removal of the colored contaminants from waste streams is of great environmental relevance. Efforts have been made by researchers in search for suitable water treatment technique that ensures high removal efficacy and economic viability as well. Various methods like chemical oxidation, biodegradation, photo degradation, electro-coagulation, membrane separation and reverse osmosis [6] have been developed to remove dyes from wastewaters. Each of these techniques suffered from various setbacks and merits and demerits of these techniques have been documented [6–8]. Among these methods, adsorption technique dictated the research interest owing to its simplicity of design, easy operation, high efficiency and economic feasibility [4,6–8]. Researchers have focused on optimizing adsorption process for removal of dyes from aqueous solutions by using economically viable and non-conventional alternative materials as adsorbents instead of traditional sorbents [9]. Due to their abundance, biodegradable and non-toxic nature, low commercial value and high cost-effectiveness, lignocellulosic enriched natural biomaterials have found place as adsorbents. Moreover, as the wastes are unexploited resources and can cause serious disposal problems, their application is of concern. Recently, numerous agricultural materials such as pomegranate seed powder, swede rape straw, cocoa pod husk, peanut hulls, and cempedak durian peel, mahogany fruit shell, cashew nut shell and wheat husk [9–16] have been successfully employed as adsorbent materials.

Avena sativa (oat) has been considered as an important cereal crop globally. Oat ranked sixth in the world's cereal production statistics. The annual global production of oats is nearly 22.5 million tons [17]. Thus, each year large amount of oat hull is produced during processing. Oat hull is structurally composed of cellulose, hemicellulose, lignin and

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protein [18]. This agricultural by-product is produced in such a large quantity that its management is a challenge. The direct disposal of oat hull biomass in the soil or in natural aqua resource results in abrupt contamination of environment by increasing the biological oxygen demand of the natural water and also reported to cause putrefaction of the biomass that released various chemical compounds and microorganisms which deteriorate the soil quality as well. However, the waste hull biomass has been increasingly used as a fuel, packing material and as animal feed, but nevertheless, the generation of waste biomass is far greater than its utilization. Thus, efforts are directed towards its innovative and environment friendly application which contributes to best possible use of waste biomass. The use of biological material in wastewater treatment offers an efficient and effective approach for waste management. Oat hulls, chemically composed of several metabolites such as phenols, ketones, aldehydes and carboxylate render it suitable for binding with dye ions by either donating or exchanging their pair of electrons [19].

Malachite Green (MG), a basic dye belonging to triphenylmethane family, has been extensively used in dyeing of leather, silk, paper, wool and also in distilleries. It is also broadly used as a bactericide, fungicide and parasiticide in several aquaculture industries worldwide. However, due to its genotoxic and carcinogenic effects, it is reported to be highly toxic to aquatic fauna, flora and human beings [20] and its removal from the effluent streams is highly desirable.

To the best of our knowledge, the potential of oat hulls as an adsorbent material remains unexplored till date. Therefore, the objective of the present investigation is utilization of oat hulls in removal of Malachite Green from aqueous solutions. The optimization of various process variables was conducted in batch mode. Studies on adsorption kinetics as well as isotherm equilibrium were also carried out. In an attempt to make the sorption process more feasible and reliable at industrial level, column study was also conducted.

2. Materials and methods

2.1. Oat hulls as adsorbent

Oat hulls were collected from a farm house located near Naini, Uttar Pradesh, India. The collected material was washed liberally with distilled water several times to remove the surface adhered particles and water soluble materials. Later, it was dried in sunlight for 2 days. The completely dried and crusty material was grinded to powder and was washed again with double distilled water. The resultant material was finally dried in a hot air oven (Gupta Scientific Industries, Ambala, India) at 110 °C for 24 h. After drying, the oat hull powder was sieved to obtain various size fractions of 625–250 μm, 250–150 μm and <150 μm using 25, 60 and 100 BSS standard sieves, respectively and was stored in desiccator for further application. The adsorbent material was used directly for experiments without any further treatment.

2.2. Preparation of adsorbate solutions

Malachite Green (MG) used in this study was procured from E. Merck (Mumbai, India) having 99.0% purity was used for the preparation of dye solution without any prior purification. Dye stock solution (1000 mg L^{-1}) was prepared by dissolving 1.0 g of MG in 1000 mL of double distilled water. The dye solutions of different concentrations (25–200 mg/L) were prepared by diluting the stock solution with suitable volume of double distilled water.

2.3. Adsorbent characterization

The determination of functional groups on the adsorbent surface and their participation in dye adsorption are supported by Fourier Transform Infrared (FTIR) spectroscopic analysis. FTIR spectra of the raw and dye loaded adsorbent were taken using FTIR spectrophotometer (Simadzu, Japan/8400S). Prior to analysis, pellets of the sample were made using KBr powder. The nature and surface characteristics of the adsorbent were ascertained by its X-ray diffraction (XRD) analysis by X-ray diffractometer (Rigaku Powder Diffractometer, Japan). The surface morphology of the adsorbent was investigated through Scanning Electron Microscope (Zeiss, Germany) at an electron acceleration voltage of 20.0 kV. The surface area and pore volume of the adsorbent were determined through N_2 adsorption–desorption isotherm at 77 K using BET (Brunauer, Emmett and Teller) surface area analyzer (Micromeritics ASAP 2020). The pH_{ZPC} of the adsorbent was determined by solid addition method [21]. Initial pH of 0.01 M NaCl was adjusted from 2.0 to 12.0 by adding either 0.1 N HCl or NaOH. 50 mL of 0.01 M NaCl was taken in 250 mL Erlenmeyer flasks and 0.20 g of adsorbent was added to each solution and flasks were left for 48 h and the final pH of the solutions was measured. A plot was obtained between "pH_{final} vs $pH_{initial}$". The point of intersection (pH_{final} vs $pH_{initial}$) has been defined as pH_{ZPC} of the adsorbent.

2.4. Batch experiments

The batch tests were carried out in 250 mL glass-stoppered flasks with 100 mL of working volume, with a concentration of 25 mg/L. A weighed amount (0.25 g) of adsorbent was added to the solution. The flasks were agitated at a constant speed of 200 rpm for 120 min in a thermostatic water bath shaker to reach equilibrium at 303 K. The pH of the experimental solutions was adjusted by adding 0.1 M HCl or NaOH solutions. After equilibration, the supernatant liquids were filtered and residual dye concentration was determined. The influence of particle size (600–150 μm), pH (1.0–10.0), initial dye concentration (25–200 mg/L), and temperature (303, 313 and 323 K) were investigated using optimized adsorbent dose of 2.5 g/L for all experiments. Samples were collected from the flasks at predetermined time intervals for analyzing the residual dye concentration in the solution. After adsorption, the residual dye concentration in each flask was investigated using UV/vis spectrophotometer (Systronics-2203, Ahmedabad, India) at maximum wavelength of MG (λ_{max} = 618 nm). The amount of dye adsorbed was calculated using following expression:

$$q_e = \frac{C_i\text{-}C_e}{W} * V \tag{1}$$

where q_e is the amount adsorbed on per unit mass of the adsorbent (mg/g), C_i and C_e are the initial and equilibrium concentrations of MG, respectively (mg/L), W is the mass of adsorbent(g) and V (L) is the volume of solution.

2.5. Column adsorption studies

Fixed bed column studies were performed using six separate glass columns with internal diameter of 3.0 cm and length 50.0 cm. The adsorbent was supported on a glass wool and the same was also used to cover the top of the adsorbent bed. Prior to experiments, a definite volume of distilled water was run through the column in order to get rid of air bubbles and to ensure appropriate distribution of fluid within the column. In this study, adsorbate solution of known concentration (25 mg/L) was made to pass through the column in an up flow direction by peristaltic pump (Peripro-4L-220, USA). The experiments were performed to investigate the effect of flow rate (2.0–10.0 mL/min) and bed thickness (1.0–10.0 cm). The residual dye concentration collected after each column operation was determined spectrophotometrically. The column was operated till the collected effluent concentration matched with the concentration of the loaded dye.