



REMOVAL OF METHYLENE BLUE FROM AQUEOUS SOLUTIONS USING DATE PITS

By

Nada Mohamed Ahmed Aboeleneen

A Thesis Submitted to the
Faculty of Engineering at Cairo University
in Partial Fulfillment of the
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Nomenclature

Abbreviations

AC	Activated Carbon
ADP	Activated Date Pits
BET	Brunauer, Emmett And Teller
CDS	Crushed Date Seeds
CI	Color Index
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
DP	Date Pits
DSAC	Date Stones Activated Carbon
DSO	Date Seed Oil
FTIR	Fourier Transform Infrared Spectrometer
GAC	Granular Activated Carbon
GAE	Gallic Acid Equivalent
MB	Methylene Blue Dye
NCI	National Cancer Institute
PAC	Powdered Activated Carbon
RDP	Raw Date Pits
R-K	Dubinin and Radushkevich Isotherm
SEM	Scanning Electron Microscope.
UV	Ultra Violet

Symbols

ΔG	Free energy change (kJ/mole).
ΔH	Change in enthalpy (kJ/mole).
ΔS	Change in entropy (kJ/mole.k).
c_e	dye concentration at equilibrium (mg/l)
c_i	initial dye concentration (mg/l)
c_t	Concentrations of adsorbate at time t mg/l
D	constant related to the energy of transfer
ε	Polanyi potential
k_1	Pseudo first order rate constant (1/min).
k_2	Pseudo second order rate constant (g/mg min).
k_f	Freundlich constant represent adsorption capacity(mg/g)
k_l	langmuir affinity constant (l/mg)
k_t	Timken constant (l/g)
n	Freundlich constant be related to the adsorption intensity
q_e	Concentration of adsorbate in solid phase at equilibrium (mg/g).
q_m	maximum adsorption capacity (mg/g)
q_t	Concentration of adsorbate in solid phase at any time (mg/g).
R	ideal gas constant (kJ/mol .k)
t	Time (min)
v	volume of solution (ml)
w	Mass of dry adsorbent (g)

Abstract

Dyes have become one of the main sources of severe water pollution as a result of the rapid development of industries. The adsorption processes have been preferred to remove colors from waste effluents because of their low initial costs, simplicity of design and ease of operation. In Egypt, date pits is produced annually as a waste of date palm. The retention profile of methylene blue from aqueous solutions onto the solid sorbent date pits has been investigated in a batch system.

The characterization and adsorption efficiency for methylene blue was evaluated using date pits. Fourier Transform Infrared Spectrometer (FTIR) was assigned to particular vibration of groups or bonds, scanning electron microscope (SEM) has been a primary tool for characterizing the surface morphology, Brunauer-Emmett-Teller (BET) analysis have been investigated using N₂ adsorption/desorption measurements at 77 K were performed to determine the characteristics of the material.

The effect of contact time, initial dye concentration, adsorbent dosage, temperature, and solution pH were investigated. The adsorption was found to increase with increasing time, decreasing temperature and increasing dosage up to equilibrium values which was 20 minute, 25°C, and 0.1 gram adsorbent respectively. The adsorption was favorable at pH=7.

The adsorption equilibrium data were best fitted by Freundlich isotherm. The adsorption kinetics was found to follow the pseudo second order kinetic model. Thermodynamic parameters such as free energy, enthalpy, and entropy were calculated and found to be -4.6kJ/mole, -7.9kJ/mole, and -11.8 J/mole.K respectively. The thermodynamic parameters of the uptake of methylene blue onto the date pits indicated that, the process is exothermic and proceeds spontaneously at low temperature.

A single stage batch adsorber was designed for adsorption of methylene blue by Date Pits based on optimum isotherm. Finally, the results in this research confirmed that the date pits was useful as low cost, readily available and suitable adsorbents for the removal of cationic dye from aqueous solutions.

Chapter 1: Introduction

Water is the origin of life on Earth, essential component of this universe and plays an important role in the proper functioning of the Earth's ecosystems. Nowadays, from the main problems is the degradation in water quality and the high increase in water needs for different purposes (domestic, agricultural, and industrial). More than seven hundred organic and inorganic pollutants have been reported in water which are dangerous because of their highly toxic and carcinogenic nature [1].

One of the important classes of these pollutants is dyes and dying materials. Dyes have bad effects on the water bodies because of its direct and indirect effects. The direct effects are its toxicity and inhibitory effects on the microorganisms which make self-purification of the water body. The indirect effects lies in the penetration of light energy necessary for photosynthesis process that producing oxygen required for adjusting the dissolved oxygen in water bodies [2].

To remove dyes from industrial wastewater various treatment methods can be used such as coagulation using alum, chemical oxidation using chlorine, membrane process [3] physical and chemical degradation [4,5], Fenton's oxidation, electrocoagulation [6], and ozonization [7,8]. Many of these methods do not operate at low dye concentration so, adsorption must be used [9].

Adsorption is the most economical treatment technique which does not add undesirable by-products to water and have simple design and operation. It is a physico-chemical wastewater treatment method, which has gained popularity in the wastewater treatment because of the high-quality treated effluents it produces. In many cases, these treated effluents can be re-used in a range of processes as good quality water [10].

Activated carbon is a highly adsorbent material with a large number of applications in the industrial wastes such as colored effluents. However, activated carbon is an expensive adsorbent because of its high costs of manufacturing [11]. For the purpose of removing pollutants from water at a low cost, there are several reports on the removal of dyestuffs by agricultural wastes and industrial waste products such as sawdust [12], hardwood [13], bagasse pith [14], banana pith [15], rice husk [16], and maize cob [17].

The present work aims to study an economical method for removal of methylene blue from aqueous solutions using adsorption on date pits. Batch studies were carried out involving process parameters such as pH, contact time, temperature, dosage of adsorbent, and initial dye concentration. Equilibrium, kinetic, thermodynamic Studies and single stage adsorber design were performed.