REMOVAL OF ANIONIC AND CATIONIC DYES BY RAW SAWDUST FROM AQUEOUS SOLUTION

By

YOSRA MOHAMED MAHMOUD MAROUF

A Thesis Submitted to the
Faculty of Engineering at Cairo University
In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE
In
CHEMICAL ENGINEERING

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Title of Thesis:
Removal of anionic and cationic dyes by raw sawdust from aqueous solution.

Key Words:
Sawdust; Acid red57; Basic fuchsin; Adsorption; Dyes.

Summary:
The aim of the present work is the use of low cost available adsorbent, sawdust for the removal of anionic dye acid red57 (AR57) and cationic dye basic fuchsin (BF) from aqueous solution. The effect of parameters such as contact time, pH, adsorbent dosage, initial dye concentrations and temperature were performed for AR57 and BF dyes by batch adsorption studies. The optimum operating conditions of adsorption of AR57 were obtained as contact time 50min, adsorbent dose of 0.1g and pH ranging from 3 to 4 whereas for BF the optimum operating conditions at contact time 50min, adsorbent dose of 0.2g and pH ranging from 6 to 7. Fitting equilibrium data to Langmuir, Freundlich and Temkin isotherms showed that Freundlich model was more suitable to describe AR57 and BF. The kinetic studies showed that the adsorption of AR57 and BF followed pseudo-second-order model. Thermodynamic parameters for AR57 and BF were calculated. The surface characteristics, pore structure, bonding behavior of the samples are characterized by nitrogen adsorption/desorption (BET), scanning electron microscope (SEM) and Fourier transform infrared spectrometer (FTIR). A single stage batch adsorber was designed for adsorption of AR57 and BF by SD based on the optimum isotherm.

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List of Abbreviations

AR57:	Acid red57
BET:	Brunauer-Emmett-Teller
BF:	Basic fuchsin
C_e:	Equilibrium concentration
C_f:	Final concentrations
C_i:	Initial concentration
$C_{o:}$	Initial concentration
C_t:	The concentrations at time t
FTIR:	Fourier transform infrared
ΔG:	The free energy change
ΔH:	The change in enthalpy
K:	Equilibrium constant
K_1:	Pseudo first order rate constant
K_2:	Pseudo second order rate constant
K_F:	Freundlich constant
K_L:	Langmuir constant
K_T:	Temkin constant
M:	The mass of dry adsorbent
n:	Heterogeneity factor
q_e:	Adsorption capacity at equilibrium
q_m:	Maximum adsorption capacity
q_t:	Adsorption capacity at time t
R:	Universal gas constant
ΔS:	The change in entropy
SD:	Sawdust
SEM:	Scanning electron microscope
T:	The absolute temperature
V:	Volume of solution

Abstract

The aim of the present work is the use of low cost available adsorbent, sawdust for the removal of anionic dye acid red57 (AR57) and cationic dye basic fuchsin (BF) from aqueous solution. Adsorption studies of AR57 and BF from aqueous solution onto sawdust were performed by the batch equilibrium technique. The effect of parameters such as contact time, pH, adsorbent dosage and temperature were performed with different concentrations of AR57 and BF dyes to determine the optimum conditions for dye removal.

The adsorption of AR57 and BF on SD was increased with an increase in contact time and adsorbent dosage, while decreased with increase in temperature and initial dye concentration. The increases in pH decrease the adsorption of AR57 and increase the adsorption of BF. The optimum operating conditions of adsorption of AR57 were obtained as contact time 50 min, adsorbent dose of 0.1 g and pH ranging from 3 to 4 whereas for BF the optimum operating conditions at contact time 50 min, adsorbent dose of 0.2 g and pH ranging from 6 to 7.

Fitting equilibrium data to Langmuir, Freundlich and Temkin isotherms showed that Freundlich model was more suitable to describe AR57 and BF. The kinetic studies showed that the adsorption of AR57 and BF followed pseudo-second-order model. Thermodynamic parameters calculated from the adsorption of AR57 and BF were spontaneous and exothermic with negative values of ΔG and ΔH. The negative values of ΔS showed that the randomness decrease during the adsorption process.

The surface characteristics, pore structure, bonding behavior of the samples are characterized by nitrogen adsorption/desorption (BET), scanning electron microscope (SEM) and Fourier transform infrared spectrometer (FTIR). A single stage batch adsorber was designed for adsorption of AR57 and BF by SD based on the optimum isotherm. Experimental results indicate that SD is an effective and cheap adsorbent for the removal of anionic and cationic dye molecules from aqueous solutions.

Chapter 1: Introduction

The annual worldwide dyes production is approximately 8 x 10^5 tonnes which used in different industries and these industries discharging highly colored waste water. Dyes are widely used in several industries such as textile, paper production, plastic, rubber, carpets, petroleum, cosmetics, leather tanning, ceramics and paint [1, 2]. Depending on the dyeing processes about (10 – 50%) of dyes are released as industrial waste water into water bodies [3].

Dyes are important class of organic pollutants and having hazardous effects on both environment and human even at low concentrations (less than 1 ppm) [4]. The harmful effects of dyes on environment are retardation in photosynthetic activity by inhibiting the penetration of light into water which cause reduction in the dissolved oxygen (DO) level and destroy aquatic life [5]. Many dyes are carcinogenic, toxic and mutagenic to both human and animals due to presence of aromatic ring in their structure [6].

Dyes are divided into non-ionic, anionic and cationic dyes. Acid Red57 (AR57) is well known anionic dye for leather, nylon fabric, wool and silk. Basic fuchsin (BF) is atypically cationic dying material which has been extensively applied in paints, artificial fiber, leather, paper, inks and cotton [7]. Acid red57 and basic fuchsin are toxic and mutagenic synthetic dyes [8, 9]. Acid red57 can cause serious health problems and toxicological problems to the aquatic environment agriculture lands [8, 10]. Basic fuchsin may cause irritation to skin or gastrointestinal or respiratory tract by the inhalation, ingestion or direct contact with it [11]. Thus it is necessary to remove these dyes from waste water before their final disposal.

For the removal of dyes from industrial effluents before discharged to environment various methods have been investigated in order to control negative impact of dyes. Effluent treatment methods can be divided into physical, chemical and biological processes [12]. Techniques such as reverse osmosis [13], ion exchange [14], coagulation [15], flocculation [16], membrane filtration [17], chemical oxidation [18], electrochemical reduction [19] and microbiological decomposition [20] are widely applied for dye removal. Each techniques often has disadvantages like low efficiency in dye removal, high cost of treatment, intensive energy requirement, incapable of treating large volumes of effluent and harmful byproduct, so that adsorption has preferred for dye removal [21].

Adsorption technique was widely used and proven to be efficient and favorable method for removal a wide range of pollutants from wastewater, especially organic pollutant [22]. Adsorption has the advantages of simplicity in design and operation, low energy requirement, high removal efficiency even from dilute solutions and low processing cost [23].

The effective adsorption process was widely employed by using solid materials as adsorbents for industrial waste water [24]. Activated carbon has shown a good performance in adsorption a wide range of pollutants as dyes. However, activated

carbon has some constraints such as high cost for manufacturing and operating, it become undesirable for water treatment [25]. Thus several alternative low cost adsorbents has been reported for various dyes removal including rice husk [26], orange peels [27], sugar beet pulp [28], bean [29], sawdust [30] and banana fiber [31].

Sawdust is low cost, locally available material and solid residue, can be used as efficient adsorbent in adsorption process. It can easily traps contaminants such as dyes and heavy metals from wastewater due to lignocellulosic composition [32]. Some studies have been performed for removal dyes with sawdust such as methylene blue [33], acid red7, basic red29 [34] and basic crystal violet [35].

The aim of the present work is the use of sawdust as low cost adsorbent for the removal of anionic dye (acid red57) and cationic dye (basic fuchsin) from aqueous solution. The effect of parameters such as contact time, pH, adsorbent dosage, initial dye concentration and temperature were performed in batch experiments. Thermodynamic, kinetics and isotherms studies and single stage adsorber design were carried out.

Chapter 2: Literature Review

2.1. Overview on dyes

For thousands of years, dyes (colorants) have been used and the earliest known use of it is believed to be by Neanderthal man around 1,80,000 years ago. Blue indigo is the first known organic colourant from ancient time (nearly 4000 years ago) which was found in wrappings of mummies in Egyptian tombs [36]. Insects, mollusks, plants, trees, and minerals were used as sources of natural dyes until the first synthetic dye, mauveine was discovered by an English Chemist (Sir William Henry Perkin) in 1856 [37, 38]. By the end of 19^{th} century, dyes were manufacturing synthetically on large scale and replaced the natural dyes due to that synthetic dyes improved the properties of the dyed materials, less expensive and offered wide range of new colors [39].

Synthetic dyes are widely used in many fields e.g., textile, paper, plastic, rubber, carpets, petroleum, cosmetics, leather tanning, ceramics and paints. Due to extensive application and large scale production, dyes can cause considerable environmental pollution such as reduction in the dissolved oxygen (DO) level, retardation in photosynthetic activity and inhibition the growth of aquatic biota. Dyes have serious hazard to human and animals due to its carcinogenicity and toxicity. Figure 2.1 presents a typical example of dyes production and wastes which producing from it [40].

Dye is a colored substance used for addition or changing the color of various materials and composed of two essential kinds of parts: chromophore (responsible for color production) and auxochrome is acts as supplier for chromophore and enhanced the affinity toward the fibers [41]. It can attach to materials by mechanical retention, formation of metal-complex or salt, by formation of covalent chemical bonds or by physical adsorption. Dyes are classified on different bases, their application to the fiber type and the chemical composition [42].