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Removal of congo red dye from aqueous system using *Phoenix dactylifera* seeds

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ABSTRACT

In this study, *Phoenix dactylifera* seeds (PDS) was used as a biosorbent for the removal of congo red (CR) dye from aqueous system. Biosorbent was characterized by some instrumental techniques such as Fourier transform infrared spectroscopy (FTIR), X-ray diffractometer (XRD), transmission electron microscopy (TEM). The effect of various adsorption parameters such as initial dye concentration, sorbent dosage, contact time, pH, electrolyte, surfactants and temperature was optimized for maximum sorption of dye. Langmuir, Freundlich and Tempkin isotherms were applied for the interpretation of experimental data. Langmuir model was found to be best fitted with maximum adsorption capacity equal to 61.72 mg g^{-1}. The kinetic study showed that the adsorption process was described by pseudo-second order kinetics. The thermodynamic parameters such as energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were found to be −3.51 kJ/mol, 22.89 kJ/mol and 87.130 J/mol/K, respectively. Recycling efficiency of PDS was investigated for the sorption of CR and after 5 cycles, the adsorption efficiency of PDS was reduced to 53.90% from 76.12%.The results indicated that *Phoenix dactylifera* seeds were used as a suitable sorbent for the adsorption of CR dye from aqueous solution in a feasible, spontaneous and endothermic way.

1. Introduction

Biomass has been broadly used for the removal of pollutants such as dyes, heavy metals, phenols and chlorophenols found in the effluents of the textile, leather, food processing, dyeing, cosmetics, paper and dye manufacturing industries [1–2]. It was observed that 10–15% of dyes were released into the environment during their manufacturing and usage [3]. Dyes and pigments present in wastewater of industries leads to the generation of hazardous affects to the animal and human health [4–5]. Dyes have complex aromatic molecular structures and stable towards heat and oxidizing agent. In addition, most of dyes are toxic and harmful to some microorganisms [6]. Colored dyes are esthetic, carcinogenic and obstruct the light penetration into aquatic system. Several dyes are toxic to flora and fauna and therefore, caused health hazard [7].

Congo red is a direct diazo dye and causes allergic reaction. It is a recalcitrant and metabolized to benzidine which is a human carcinogen. Congo red is very difficult to remove because it possesses the thermal, physico-chemical and optical stability due to their aromatic structure [8].Thus the removal of dyes remains an important issue for researchers and environmentalists. Many conventional methods such as chemical precipitation, ion exchange, electro-dialysis, ultra-filtration membrane separation, photo-degradation, electrochemical oxidation etc. have been widely used for the treatment of dyes bearing wastewater [9–13]. However, due to various disadvantages associated with conventional methods, adsorption process has been explored by many researchers [14–18]. Adsorption is a well-known separation technique in terms of initial cost, simplicity of design, ease of operation, insensitive to toxic substances and ability to treat dyes in more concentrated form, besides it provides sludge free cleaning operations [19–20].

Activated carbon has been used as a standard adsorbent for the removal of colour and other effluents from water system. But the use of activated carbon is limited on large scale, mainly due to its high cost and connected hardship to regenerate [21–25].

Recently, attention has been paid on the development and use of highly effective and low cost adsorbents [26–28]. Thus renewable biosorbents have been explored due to their low cost, easy availability, good modifiability and low toxicity. Various renewable materials, such as rice husk [29], castor seed shell [30], banana peel [31], wheat shell [32], sugarcane bagasse [33], soy meal hull [34], orange peel [35], saw dust [36–37], waste wood-shaving bottom ash [38], *Trichoderma harzianum* mycelial waste [39], *Ficus carica* [40], luffa cylindrical fiber [41] etc. have been used for the removal of organic pollutants from aqueous solution. These natural materials are available in large quantity and can be discarded without expensive regeneration. Despite the availability of large number of absorbents, newer adsorbent materials are being investigated for wastewater treatment.

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Phoenix dactylifera seeds (PDS) a readily available agro-based material, may be used as an alternative for the removal of organic pollutants from wastewater. *Phoenix dactylifera*, commonly known as dates is cultivated as an edible sweet-fruit and widely distributed in many tropical and subtropical regions [42]. *Phoenix dactylifera* seeds are the by-product of date stoning and used for the production of pitted dates or date paste. These are traditionally used for animal feed. It can be used as a source of oil which has antioxidant properties valuable in cosmetics or as a coffee substitute.

In this paper, *Phoenix dactylifera* seeds (PDS) has been explored as novel biosorbent for the removal of congo red in waste water treatment. The biosorbent was characterized by Fourier transform infra-red spectroscopy (FTIR), X-ray diffractometer (XRD), transmission electron microscopy (TEM).The effect of some parameters such as initial dye concentration, contact time, temperature, adsorbent dosage, pH, electrolyte concentration and surfactants on the adsorption efficiency has been investigated. The adsorption isotherms, kinetics and thermodynamic study have been carried out to determine the mechanism of adsorption process. The inputs obtained from this research have been useful for designing low-cost, easily available adsorbents based on agro-material for the removal of dye-containing effluents.

2. Materials and methods

2.1. Reagents

All chemicals such as congo red ($C_{32}H_{22}N_6Na_2O_6S_2$), hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium chloride (NaCl), cetyltrimethyl ammonium bromide (CTAB), sodium dodecylbenzenesulfonate (SDS), polyoxyethyleneglycol t-octylphenyl ether (Triton X-100) used in this research work were of analytical grade reagents. All dilutions and washing were carried out using double distilled water.

2.2. Instrumentation

A double beam UV–visible spectrophotometer (Shimadzu UV-1601) was used for the determination of dye concentration. The pH measurements were made using a pH meter (ELICO model LI-127, India). Characterization of biosorbent was done using a Fourier transform infrared spectrophotometer (Perkin Elmer Spectrum-BX USA), transmission electron microscope (FEI Tecnai F 20) and X-ray diffraction (Philips1830 diffractometer).

2.3. Preparation of biosorbent

The *Phoenix dactylifera* seeds (PDS) were collected from farmland located in Saudi Arabia. The PDS were repeatedly washed with double distilled water until the water became colorless. Then biomaterial were filtered and dried in oven at 60 °C for 24 h. The dried biomaterial smashed into mesh size of 0.1 mm to 0.4 mm. The smashed particles were stored in a desiccator for further study.

2.4. Characterization

2.4.1. Fourier transforms infrared absorption spectra (FTIR)

FTIR spectra of PDS were recorded by Fourier transform infrared absorption spectrophotometer using KBr disc method. The bio-substance was thoroughly mixed with KBr, powdered and disc was formed by applying the pressure. The absorption spectra were recorded in the range from 4000 to 400 cm^{-1}.

2.4.2. Transmission electron microscopy (TEM) studies

TEM micrographs of PDS was determined by preparing the suspension of bio-substance in ethanol onto carbon copper grid and analyzed.

2.4.3. X-ray diffraction (XRD) studies

X-ray analysis was carried out by X-ray diffractometer (Philips 1830 diffractometer) equipped with the graphite monochromator using Cu Kα radiation. It was operated at 45 kV and 40 mA. The rotation occurs between 10° to 90° at 2θ scales.

2.5. Adsorption experiment

The adsorption of dye onto PDS was performed using batch adsorption experiments. The batch adsorption experiments were conducted in 100 mL Erlenmeyer flasks containing required amount of adsorbent and 50 mL of CR solution with various initial concentrations. The pH of each solution was adjusted with 0.1 N HCl and 0.1 N NaOH solutions. The mixtures were agitated in an incubator shaker at 140 rpm and 30 °C until the equilibrium reached. The resultant mixture was centrifuged at 2500 rpm for 10 min. The equilibrium concentrations of dye in the solution were measured at 498 nm using UV–visible spectrophotometer (Shimadzu UV-1601). The experiments have been conducted in duplicate and the negative controls (without sorbent) were simultaneously carried out. No filter paper was used in the solid–liquid separation because the surface acidic functional groups of filter paper have the potential to adsorb dye molecules. The amount of dye sorbed (q_e mg g^{-1}) and percentage removal of CR were calculated using Eqs. (1) and (2) as:

$$q_e = (C_o - C_e)\frac{V}{M} \tag{1}$$

$$\%\text{Removal} = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

where C_0 and C_e is the initial and equilibrium concentration of CR (mg/L), V is the volume of solution (L), M is the mass of biosorbent (g).The experimental conditions have been optimized at different dye concentrations (20–120 mg/L), adsorbent dosage (20–120 mg), pH (2 − 12), temperature (30–55 °C) and contact time (20–140 min). The effect of electrolyte and surfactants has been investigated onto sorption process.

2.6. Desorption and regeneration

The dye loaded biosorbent was desorbed with 50 mL of 0.05 M NaOH solution. It was stirred in an incubator shaker at 120 rpm for 1 h. Then it was centrifuged at 2500 rpm for 10 min and biosorbent was washed with double distilled water and regenerated. Subsequently, it was used in five sequential cycles of desorption-adsorption.

2.7. Equilibrium isotherms

The adsorption isotherms indicate the amount of dye adsorbed onto adsorbent and equilibrium concentration of the dye in solution at a given temperature. The relationship between the concentration and dye uptake was determined by Langmuir, Freundlich and Tempkin isotherms.

2.7.1. Langmuir isotherm

The Langmuir isotherm presumed that adsorption was observed at homogenous surface containing a finite number of biosorption sites within uniform distribution of energy level and no transmigration of adsorbate on the surface takes place. The linear form of Langmuir model is given as follows [43]:

$$\frac{C_e}{q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \tag{3}$$

where q_e (mg g^{-1}) is the amount of dye adsorbed per unit weight of adsorbent, C_e (mg/L) is the unadsorbed dye concentration at equilibrium, b is the equilibrium constant or Langmuir constant related to the affinity of binding sites (L/mg) and Q_m represents the particle limiting adsorption