A brief review of "Eco-Friendly Approach to Textile Wastewater Treatment: Activated Date Palm Fibres as Bio-Adsorbents for Malachite Green."

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Abstract : The swift evolution of global society and the substantial population growth have led to increased human activities involving the processing and industrial production of dyes. These activities have resulted in severe environmental damage and pose significant risks to human health. Dyes are a principal pollutant from industries being discharged into water, and handling them has become a major issue. Industrial wastewater containing dyes presents considerable environmental hazards due to its potential carcinogenic, cytotoxic,mutagenic effects on ecological as well ashuman health.Current generation faces a significant challenge in removing non-biodegradable pollutants, prompting extensive research on adsorbing these contaminants from aquatic environments. The paper focuses on malachite green (MG), dye usually found in textile, printing, as well as paper industry effluents, along with other frequently used cationic dyes in industrial processes. Commercially available activated carbons (ACs) are neither cost-effective nor environmentally sustainable. Renewable and biodegradable materials are being explored as potential precursors for activated carbon synthesis, with date palm fiber residues garnering significant attention because of their high lignocellulosic content as well as low ash composition. The present research aims to thoroughly examine the efficacy of date palm and its derived activated carbons as adsorbents.Based on experimental results, a comprehensive analysis was conducted on various factors involving initial temperature, adsorbent dosage, dye concentration, pH, agitation, particle size, contact time, as well as stirring. Equilibrium data was examined using Freundlich and Langmuirisotherms.Kinetic analyses have been performed to identify most suitable method to characterizing the adsorption process.

Introduction

The primary challenge in decontaminating textile wastewaters is the elimination of dye coloration, as no single process currently provides sufficient treatment, primarily due to the complex nature of these effluents[1]. These toxic colorants impact aquatic ecosystems by hindering the photosynthetic capacity of aquatic plants through light obstruction and increased toxicity; furthermore, the most potent dyes can cause gene mutations, cancer, dermatitis, and allergies[2].

Malachite green (MG) isdye widely utilized in textile industry. The crystalline solid known as MG, or triarylmethane dye with the chemical formula $C_{23}H_{25}ClN_2$, is dark green in color. It possesses unique properties which is applicable in multiple domains. Since early times it has gathered widespread adoption in day to day lives, reflecting its versatility and importance. It serves as an important dye in textile industry, even its application extend to food industries.It exhibits toxic characteristics recognized for their potential to induce carcinogenesis, mutagenesis, teratogenesis, and respiratory toxicity[3]. MG was widely employed as topical fungicide[4]as well as ectoparasiticide in global aquaculture since

1936[5] .MG exhibits environmental persistence and acute toxicity to a diverse array of both marine and terrestrial fauna. It presents significant public health risks and may also lead to environmental issues. It reduces food consumption, growth, and reproductive rates, inflicts harm on liver, kidneys, spleen, heart, and induces lesions on bones lungs, eyes, skin[6].

The treatment of wastewater contaminated with dyes is challenging as well as costly task, as these compounds originate from intricate aromatic structures that exhibit resistance to microbial degradation, oxidative agents, water, heat, and light[7]. The elimination of effluents that contain intrinsically toxic dyes is currently being very seriously considered. A variety of dye removal models were investigated in order to reduce their adverse environmental effects[8]. There are numerous techniques to tackle this threat like oxidation[9, 10],chemical precipitation[11], photocatalytic degradation[12, 13], "membrane separation[14], electrochemical processes[15,16], electrocoagulation[17], ion-exchange[18], adsorption[19]. Adsorption ischeaper and superior approach among all other methods. Mostly, agricultural plant by-products and waste residues showed effective removal of dyes and heavy metals. These are cheaper, readily available, and can be degraded quickly. These include mango bark[20], orange peel[21], "hazelnut shell[22], lotus stalk[23]", pea shells[24], sugar beet pulp[25], etc.

Researchers proposed the use of AC due to its efficacy and cost-effectiveness in eliminating a wide array of pollutants[26]. Researchers also analyzed studies on the use of Air conditioning to purify waste streams. Their adsorption capacity is contingent upon their porous structure, and materials for AC have high carbon content[27]. Furthermore, it is essential to recognize that the properties of the carbon precursor and the methods used during its synthesis, including experimental criteria, significantly impact the final pore size distribution

of AC[28]. AC is a porous type of carbon-based on diverse carbonaceous raw materials, such as coconut shells, pinewood, coal, eucalyptus, sawdust, peat, and rice husks. It is made via the carbonization and activation of organic material. AC demonstrates remarkable adsorptive capacity in both granular and powdered forms, owing to its highly developed pore structure and vast internal surface area.

This study utilized an economical bio-waste material, namely Date Plant fibres activated with phosphoric acid, as effective adsorbent for extraction of MG Dye from wastewater in batch adsorption system. Fibers and date seeds have been sourced locally to function as an economical, environmentally sustainable bio-adsorbent material for mitigating environmental pollution.

This study utilized fibres and waste materials from date trees as a bio-adsorbent to remove MG dye from aqueous solutions via batch adsorption experiments, encompassing diverse experimental conditions based on their availability as a waste resource."Scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET), X-ray diffraction (XRD), and Fourier transform infrared (FTIR) spectroscopy"surface area analysis have been employed to examine adsorbents derived from date plant materials. The most suitable isotherm data was determined by analyzing Langmuir as well as Freundlich's adsorption isotherms. Kinetics of adsorption process have been also examined.

Materials and Methods

Date Palm pits utilized in production of AC were sourced from surrounding regions. Activation was done using procedures proposed by[29] as follows. The plant materials were thoroughly cleaned and then dried to eliminate any residual dust or peel. The materials were then sieved and ground, with the resulting powder filtered via standard 200-mesh sieve for activation.The resultant powder was combined

with 85% phosphoric acid in a 1:3 ratio. The activation and carbonization were achieved by heating for 5 hours in muffle furnace at 400°C. The carbon slurry had been thoroughly rinsed with distilled water unless a uniform pH was achieved. Thereafter, carbon products underwent drying for four hours at 100 °C in oven. The desiccated material was transformed into a fine powder as well as preserved under vacuum desiccators.

Analytical grade MG had been obtained from Merck Chemicals. The dye exhibited a purity of 99.8% and was of analytical grade. Stock solution (1000 mg per L) had been prepares simply mixing an accurately measured amount of dye in distilled water.

Adsorption Experiment

Adsorption studies are conducted in batch mode at temperatures of 30, 40, 50, and 60°C. An adsorbent of a specified mass is introduced to a solution of dye having a starting concentration varying from 50 - 250 mg/L. Contents are thoroughly mixed using a mechanical shaker at 150 rpm. The concentration of residual dye and the intervals were measured. Solution was subsequently filtered at the current time. Equilibrium adsorption, q_e (mol/g), had been calculated by utilizing given formula:

"$q_e = (C_o - C_e) V/m$" (1)

C_o as well as C_e (mol/L) represent initial and equilibrium concentrations of dye in liquid phase. Solution's volume is V, and dry adsorbent's mass is m. Equilibrium adsorption data have been examined using 2 isotherm models: Langmuir model as well as the Freundlich model. The removal % was calculated utilizing Equation 2:

Removal %=$[(C_o-C_e)/C_o] *100$ (2)

A kinetic studyhad been conducted at ambient temperature usingflask similar to employed in batch equilibrium experiments. The lask was persistently stirred to achieve equilibrium, and samples of aqueous solutions have been collected at specified time intervals, with dye concentrations quantified.

Effect of Adsorbent dosage

Varying quantities of the adsorbent have been taken, and dye solution was mixed with it. Resultant mixture was stirred in a mechanical shaker.

By keeping all other factors constant for distinct doses, the adsorption capacities have been determined.

Effect of dye Initial concentration

Experiments conducted with initial dye concentrations ranging from 50 to 250 mg per liter to determine adsorption rate while maintaining all other variables constant.

Contact time's effect

Effect of contact duration on dye removal by adsorbent has been examined while maintaining constant initial concentration, pH, dosage, as well as temperature.

Effect of pH

Adsorption tests were performed across a pH range of 2 to 10. Precise addition of dilute HCl and NaOH modulated the acidic and alkaline characteristics of the pH.
All other variables were held constant during the experiments. A pH meter was employed to ascertain pH levels.

Temperature's effect

Adsorption experiments have been conducted at 4 distinct temperatures: 30, 40, 50, 60°C, utilising a thermostat with a shaker.

Results and Discussion
Adsorption studies

Adsorption isotherms depict equilibrium distribution of adsorbates among both solid as well as liquid phases[30]. These isotherms are crucial for comprehending adsorbate-adsorbent interactions and estimating the adsorbent's capacity[31]. A maximum experimental adsorption capacity of (approximately 0.2136 molg[-1])[3]. Isotherm displays an S-type curve, as classified by[32], indicating that adsorption becomes

increasingly favorable with rising concentration[32]. The S-curve pattern signifies intense competition among adsorbed and solvent species for surface sites of adsorbent[32]. To determine a suitable model for design objectives, it is essential to assess isotherm data using multiple models[33]. "Langmuir isotherm Eq.(3), as well as Freundlich isotherm Eq.(4) models" of adsorption, have been employed so as to describesorption data. The importance of these equations was assessed using correlation coefficients (R_2) and maximum adsorption capacities. Langmuir equation is defined in following manner:

$$(1/q_e)=(1/Q_o)+(1/bQ_o)(1/C_o) \qquad ...(3)$$

In this equation, C_e signifies equilibrium concentration, q_e indicates the quantity of adsorbate adsorbed per unit mass of adsorbent (in mol per g), while b, Q_o are Langmuir constants representing adsorption rate as well as capacity. A graph of $1/C_e$ against $1/q_e$ in Langmuir model demonstrates a linear correlation, defined by slope of $(1/bQ_0)$ with an intercept of $(1/Q_0)$.

$$\text{"Log}q_e=\log K_f+(1/n)\log C\text{"}_e \qquad ...(4)$$

n and K_f were Freundlich constants denoting adsorption capacity as well as adsorption intensity. Variable n indicatesextent of nonlinearity among solution concentration as

well as adsorption: if n equals "1, adsorption is linear; if n exceeds 1, adsorption isphysical process; and if n is less than 1, adsorption is chemical process[34]".

According to R_2 values, both models accurately depict adsorption data; nonetheless, the Langmuir isotherm presents interpretative difficulties due to its negative q_e value.

Adsorption of dye MG onto adsorbent is precisely described through Freundlich model. Analysis revealed that n value in Freundlich equation is less than 1, indicating a cooperative process, as slope value of 1/n exceeds unity[3].

Effect of pH

Several papers Documented impact of pH on removal of MG dye utilizing date palm fiber within a (pH range of 4 to 10)[3]. The highest recorded removal is 95.725% at pH 10, and dye elimination augmentations with rising pH levels. The outcome is due to attractive forces between opposing charges; in alkaline conditions, the adsorbent's surface acquires a negative charge, leading to an attraction among positively charged dye molecules with negatively charged adsorbent. Under acidic conditions, surplus H+ ions competed alongside cationic dye for adsorption sites, thus hindering dye removal.

Fig1- removal of MG dye by date palm fibre at different pH[32]
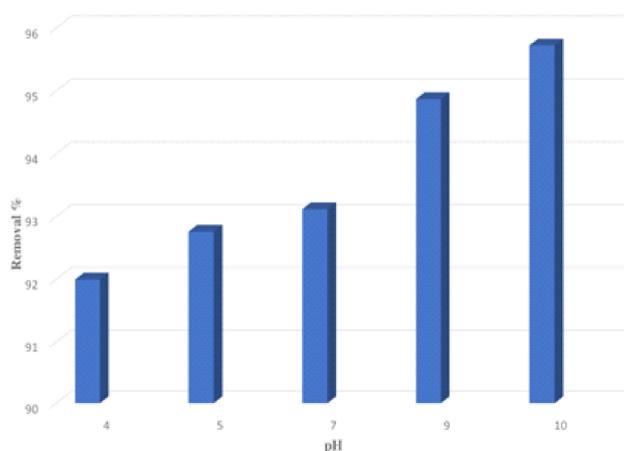
Effect of Temperature

Research papers documented a slight reduction in removal efficacy[3] as temperature rose from 25 to 45 °C, with a peak removal rate of 94.3% recorded at 25 °C. This pattern corresponds with the findings presented by[35] in their investigation of MB adsorption utilizing activated carbon derived from durian shells. They proposed that elevated temperatures weaken the physical interactions among organic compounds (such as dyes) as well as active sites of adsorbent. Moreover, elevated temperatures enhance dye solubility, thereby intensifying the solute-solvent interaction in comparison to the solute-adsorbent interaction. Consequently, this reduces the likelihood of solute adsorption. At 25°C, highest MG removal rate of 94.3 percent had been observed.

Kinetic study

The 2 models have been utilized to investigate adsorption kinetics of MG dye with date palm fibers at temperature of 25°C. Preliminary response exhibited pseudo-first-order kinetics, prompting application of Lagergren equation. Lagergren (1898) is referenced.

"$\ln(q_e - q_t) = \ln q_e - K_1 t$"   (5)

In this context, q_e signifies equilibrium adsorption capacity, q_t denotes adsorption capacity at time t, K_1 denotes constant rate. This model could not accurately define the adsorption capacity, as the correlation coefficient(R^2) is low as well as experimental q_e value didn't align with calculated value derived from equation.

The second model was formulated utilizing a linear pseudo-second-order equation. It is cited by "Ho and McKay (1998)".

"$(t/q_t) = 1/ (K_2 qe^2) + (1/q_e)t$"   …..(6)

Slope of resulting plot of t/qt versus t yields value of qe, while intercept can be examined to ascertain K_2. This graph generates a linear depiction[3]. Calculated value of qe is 0.080 mol per g that closely corresponds to experimental value at 25 °C.

Conclusion

This research investigated the adsorption of MG onto DPF surfaces from aqueous solutions across various MG concentrations. The adsorption data at equilibrium was evaluated utilizing Langmuir and Freundlich isotherms. pH as well as Temperature effects were examined by measuring the % of MG removed. Kinetic analyses demonstrated that pseudo-second-order model provided a better fit than pseudo-first-order model.

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