Demonstration of Efficient Separation, Surface Investigation and Thermodynamics Study of Sodium4-[(4-dimethylamino) phenyldiazenyl) Benzene Sulphonate Dye from Aqueous Solution onto Acid Activated Modified Purple Knight

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Summary: The organic dye pollution has become increasingly serious in recent years and removal of organic dyes from the water samples has received intense attention. In present work the acid modified purple knight (*Alternanthera dentata*) leaves powder (MALP) is used as an adsorbent in order to remove sodium 4-[(4-dimethylaamino) phenyldiazenyl) benzene sulphonate (methyl orange dye) from an aqueous solution. The absence of stretching vibrations (1008cm^{-1} , 1400cm^{-1},1600cm^{-1} and 3184cm^{-1}) of characteristic functional groups of modified purple knight plant in FTIR-analysis, as well as a significant decrease in the lambda max value from 600 to 420 in the electronic study, indicate that the texture of the purple knight (*Alternanthera dentata*) leaf is changed. The influences of pH and contact time on adsorption is also investigated at the actual experimental conditions as pH range of 2-4.5, a methyl orange concentration of 0.1M, and contact time of 5-60 minutes at 26 ^oC. Elovich and intraparticle diffusion models accurately described the kinetics experimental data for various solutions. The kinetic results indicate that adsorption process occurs in two or more steps. The adsorption models such as Langmuir, Freundlich, Temkin, Brunauer-Emmett-Teller(BET)and Dubinin –Radusshkevich (D-R) are used to explain adsorption process at different temperatures ranging from 26 to 60 ^oC . In comparison to others adsorption models, equilibrium data at 26^oC provide clear information about the regression coefficient, adsorption capacity, (RL= 0 to 1) and Freundlich constant (1/n <1). These values indicate Langmuir, and Freundlich models fit very well, while other fit at >26 ^oC. Values for the free energy change, enthalpy change, and entropy change indicate that the adsorption process is spontaneous and endothermic. The negative value of ΔG^o at different temperatures indicate that at low temperatures, physical adsorption occurs, whereas at higher temperatures, its value become more negative and chemisorption occurs, revealing the orbital interaction between adsorbate and adsorbent molecules.

Key words: Purple Knight, Modified *Alternanthera dentata* leaf powder, Sodium 4-[(4-dimethylaamino) phenyldiazenyl) benzene sulphonate, Adsorption Analysis, Kinetics Study, Thermodynamic Study.

Introduction

Water pollution is a highly contentious issue on a global scale, as it has continuing toxic consequences for living creatures [1]. Additional to one-third of the world's sustainable freshwater is spent for industrial, native, and irrigation, and the majority of these accomplishments pollute water with a variety of synthetic complexes such as insecticides, color importing materials, manures, heavy metals, radioactive elements, and so on [2-14]. Water adulteration initiated by numerous accomplishments has already become a major municipal problem around the globe. Water contamination produced by dyes is one of the most concerning of these pollutants because it alters usual appearance of water at minute l absorptions. [15, 16]. These industries use a large number of dyes that are eventually released unswervingly into the environment, and poses serious environmental complications due to the toxic and unpleasant nature of dye [17, 18]. Dyes create issues, reducing the photosynthetic activity of marine plants, [19], produce cancerous effluents, causes lung diseases, contact dermatitis, skin irritation, and mucous membrane agitation.

Overall world Governments have established environmental protection laws on the quality of colored effluents, requiring dye-using businesses to decolorize their effluents before discharging them. The wastewater treatment methodologies are divided into several phases, including initial, secondary and tertiary process. Initial water supply is then subjected to removal of frothy inorganic and inorganic material by scanning, flotation, sedimentation, microbial degradation and dissolved organic matter, which stabilizes waste components. Organic and inorganic pollutant separation from the

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water has been a challenging worldwide problem. Dye containing water is treated in a similar manner; however, there is no single ordinary handling procedure for all types of dye -wastes. Table -1 listed the drawbacks of some methods for treating dye contaminated water. Each treatment method has a number of challenging issues, such as lower capacity, higher investment or operation cost, unnecessary sludge and the cost of, preservation, that make them inappropriate for financial usage [20, 21].

Nevertheless, the adsorption process is the most popular for its cheap cost, convenience, lower power consumption, simple setup, inattentiveness to toxic pollutants, capacity to eliminate all categories of dyes and outstanding performance [22, 23]. Moreover, no toxic material is formed as a result of this technique. It is a surface phenomenon that occurs when adsorbate (adsorptive molecules) binds to adsorbent (a solid surface) from its gaseous or liquid environment [24, 25]. Because of the difficulties adsorbate can interrelate with the atoms and molecules of the adsorbent, a variety of concepts are possible during the adsorption mechanism that is likely to occur. Physisorption and chemisorption can be distinguished based on the energy and interaction mechanism of adsorbed species with adsorbent. Physisorption is characteristically revocable, nonselective, with lower enthalpy changes of 5-40KJ/mol and have adsorbent –adsorbate weak interactions (Van der Waals, dipole-dipole, and hydrogen bonding). On the other hand, chemisorption is thought to be irrevocable, selective, escorted by a sophisticated heat change, typically 40-125KJ/mol, and provides a strong bond, primarily ionic or covalent interactions. [26, 27] Adsorption is currently a well-known and useful process that is regarded as a reliable, low-cost, adoptable, easy to operate, previously stated, adaptable and simple to operate and design, resulting in high-quality for wastewater treatment. [29].

Chemically modifying the adsorbent can increase its adsorption capacity. Despite the fact that adsorption is widely used to remove a wide range of water-soluble dyes. Moreover, the adsorbent cost renders the process economically unviable. Biomass, particularly agricultural waste, has received significant attention in recent decades in order to make this process economically viable. Some of the reported bio-adsorbents and their adsorption capacities are listed in Table -2. In the current manuscript, acid activated *Alternanthera dentata* leaf powder was used to remove dye from an aqueous methyl orange solution (MO). *Alternanthera dentata* is also known as Purple Knight. It's a tropical plant with dark purple leaves that grows quickly and is widely available and distributed around the world. It is distinguished by its purple-colored leaves and purple stems, and it is widely used for decorative, pharmaceutical, and antiseptic purposes. Purple Knight is used in this study to remove methyl orange dye from aqueous solution via adsorption under various conditions due to its evaluated low-cost adsorbent, easy availability, and remarkable antimicrobial activity. [29]

Table-1: Disadvantages of Wastewater Handling Techniques.

Techniques	Demerits	Reference
Process of advanced oxidation	The cost of maintenance and operation is high. Method is rigid	[29]
Precipitation by Chemical means.	This technology necessitates the use of numerous chemicals as well as the creation of useless dirt.	[30]
The Exchange of ions Technology	Pricey to recharge ,produce a lot of effluents, is extremely sensitive ,and does not work all dyes.	[31]
Electrochemical Techniques	Repair costs, electricity costs and effluents formation are all high.	[28]
Chemical Oxidation	The cost of p^H maintenance is high and an overpriced catalyst is required for effective treatment.	[32]
Ozonation	Complex and costly strategies with a short half-life, the production of noxious intermediates and by-products, and the need for constant pH monitoring of the run-off.	[33]
Hydrogen peroxide	Low reaction speed, significantly larger storage space and higher price is required for this process	[28]
Coagulation and flocculation	Water -soluble dyes are not suitable, toxic mud is produced, environmentally unsustainable techniques and chemical recycling process is expensive	[29]

Table-2: Adsorption capacitates of adsorbates on several natural Adsorbents.

Adsorbate	Adsorbent	Reference
Congo red	*NPL	[34]
Methyl Orange	*NPL	[34]
Methyl Red	*NPL	[35]
K2Cr2O7	*NPL	[35]
Malachilte green	*NPL	[36]
Methylene Blue	*NPL	[37]
Cadmium	*NPL	[38]
lead	*NPL	[38]
Chromium (VI)	*NPL	[39]

*NPL (*Azadirachta indica leave* powder), *ABDAC (Animal bone derived activated charcoal), *CSDAC (Coconut Shells derived Activated Carbon), *CDAC (Corncob Derived Activated carbon), *MPL (*Mangnifera indica* leave Powder)

Experimental studies

Material and Methods.

Analytical grade, Methanol, Ethanol, sulphoric acid, hydrochloric acid, Sodium 4-[(4-dimethylaamino) phenyldiazenyl) benzene sulphonate, were used without further purification. The *Alternanthera dentata leave* before and after modification were analyzed using the Fourier Transform Infrared Spectrum (Model Shimadzu8400) in the range of 4000-400cm^{1-} , electronic study was recorded using double beam UV-Visible spectrometer (Model Shimadzu-1800). The pH measurement were recorded with a pH meter (Model APX175E/C,).

Preparation of Modified Alternanthera dentata Leave Powder (MALP).

The *Alternanthera dentata* leave were collected from the local garden of Government college university Faisalabad, Sahiwal campus Sahiwal, District Sahiwal, Pakistan. The leaves were splashed with distilled water desiccated at 60 to 80ºC in an oven. Dehydrated leaves were crumpled and boiled in distilled water for 5 hours to eliminate color. Afterward the scum was saturated with concentrated sulphoric acid for 6 hours and dried at 110 ºC for 8 hours. The desiccated solid was grounded mechanically for 1-2 weeks and kept in air close-fitting container.

Batch Adsorption study of sodium 4-[(4-dimethylaamino) phenyldiazenyl) benzene sulphonate (MO) solution onto Alternanthera dentata Leave Powder (MALP).

By diluting the stock solution with distilled water, the dye solutions of desired concentration were prepared, and the p^H was adjusted with 0.1N HCl solution. The equilibrium adsorption study of MO was carried out by shaking o.068g of MALP of various solution for different intervals at 26-60ºC in water bath-cum-mechanical shaker. Approximately 1-6 ml solutions were withdrawn after time interval and centrifuged and equilibrium concentrations of different solutions were determined. For adsorption isotherm and kinetic studies, the experiments were performed using 0.068g of adsorbent with 50ml of different solution and shaken on equilibrium contact time at 26-60ºC.

Result and Discussion:

Characterization of the adsorbent Modified Alternanthera dentata Leave Powder (MALP).

UV-Visible studies of modified leaves without color pigments (MALP) and original purple Knight plant purple color leaves (OPL) were conducted in the 200-800 nm range using 1.10^{-3}M/MeOH. The decrease in the λ-maximum value from 600-420 nm in the electronic spectrum (Fig-1b) confirms that color moieties have been removed from the original leaf. FTIR spectrum (Fig-1a,b) of original plant color leave (OPL) and MALP were recorded at the range of 4000-400 cm^{-1} OPL and MALP exhibited various peaks at 1008cm^{1-} ,1600cm^{1-} 3184cm^{1-} and 1400cm^{1-} and 512cm^{1-} respectively. It's clear from the peaks that OPL exhibit many functional group peaks as compared to MALP. The absence of peak in MALP provide the clear-cut information about the removal of color from the leaves.

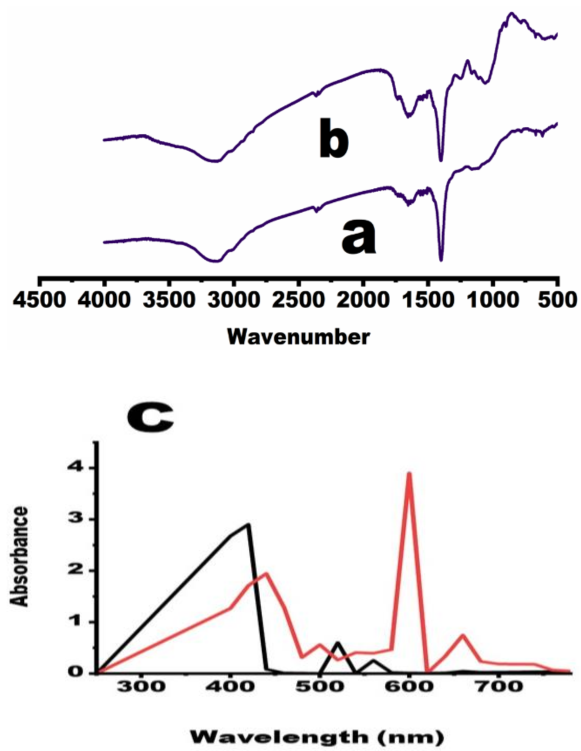

Fig. 1: (a b); FTIR and (c); UV-Visible Analysis of Purple knight original leave and Modified Leaves:

Adsorption study of sodium 4-[(4-dimethylaamino) phenyldiazenyl) benzene sulphonate (MO) solution onto MALP

The aqueous phase MO adsorption experimentation were carried out at ambident temperature in the presence of MALP by batch process using a shake with a constant shaking of 160rppm at various parameters such time, pH of solution temperature. The percent dye removal, adsorbed amount of methyl orange (MO) was determined according to following equations [42-43]

$$\%R = [\frac{Co-Ct}{Ct}]100 \qquad (1)$$

$$Qe = (Co - Ce)V/m \quad (2)$$

where C_o/C_i is the initial concentration and C_t /C_e is concertation at time t of MO, m is weight mass of adsorbent, V is the total volume of solutions. When the extent of adsorbate coverage is confined to one molecular layer, the Langmuir model is applicable. Langmuir defined chemisorption as the chemical interaction between adsorbent and adsorbate, and the equation for this is described as follows;

$$\frac{Ce}{qe} = \frac{1}{bqm} + \left(\frac{1}{qm}\right) Ce \quad (3)$$

where b =ka/kd, ka and kd, Ce, q_m, and q_e denote the adsorption and desorption constants, the equilibrium concentration, the adsorbate amount, and the adsorbent quantity per unit mass of adsorbent, respectively. The q_m and b values are calculated using the slope and intercept of this straight line of plot. To further investigate the Langmuir equation, a dimensionless separation factor can be used.

$$RL = \frac{1}{1+bCe} \, R_L \quad (4)$$

Literature attests The R_L value ranges from 0 to 1, indicating favorable adsorption, while R_L >1 indicates unfavorable adsorption, and the correlation coefficient (R^2 = 0.995-0.998) and b factor (0.904) values range indicate good adsorption onto the adsorbent surface [40]. The experimental data of present work were analyzed using the Langmuir equation illustrated in (Fig -2 a). The high value of (R^2=0.9918), R_L(1.00), and high adsorption capacity value (Table-4) in the current work indicate a good agreement of MO onto the surface of MALP.The Freundlich model is an empirical equation that is used to describe a heterogeneous system. The constants of the Freundlich equation ($qe = KC_e^{1/n}$) are denoted by K and n. The adsorbent's adsorption capacity is denoted by k, and the deviation of linearity of the adsorption is denoted by n. When the value of the constant 1/n is less than one, it indicates that the dye-fixing process on adsorbent is favorable [41]. The slope and intercept values are used to calculate K_F and n (Fig -2b).The R^2, K_F, and 1/n(0.007566) values in the current work table -4 indicate that this model fits very well and confirms that adsorption between MO and MALP is favorable. The Temkin model's linear form is described by $qe = BlnA + BlnC_e$[48]. In this formula, A represents the equilibrium binding constant and the value of B is calculated using formula RT/b. Plotting qe versus lnCe (Fig -2 c) yields a straight line, which gives the value of B(slope) and K_T (intercept). From the literature review R^2 value ranges (0.987-0.977) provide a reasonable model for the adsorption of dye onto adsorbent [42]. The current study's R^2 and KT values (table-4) confirm that adsorption between MO and MALP is favorable. Figrure- 2d) the experimental data of the present study was analyzed using the linearized form of the Brunauer-Emmett-Teller (BET) Model. According to this model, R^2 = 0.9315 indicates its follow this model when graph plotted between x/m verses concentration C_e. The linear form of Dubinin -Radusshkevich (D-R), equation $lnqe = LnQ_D - K\varepsilon^2$ used to evaluate the porosity and apparent adsorption energy.

$$\varepsilon = RTln(1+\frac{1}{Ce}) \quad (5)$$

The ε is used to calculate the value of ε at different temperature. The K and Q_D are derived from the slope and intercept of the plots ln qe and ε^2 (Fig-3a) According to the literature review, a low correlation coefficient value (R^2 = 0.784-0.823), adsorption capacity (Q_D)values indicate that the D-R did not fit satisfactory manner. The fact that (K) was less than one suggested that heterogeneity could be related to both pore structure and sorbate-adsorbent interaction [43] Table 4 in the current study shows that the Q_D obtained for methyl orange adsorption by MALP is lower than the Langmuir adsorption capacity, and the low R^2 reveals that this model does not fit very well.

Effect of content time and pH on adsorption:

From the literature survey it is confirmed the rate of uptake of dye was rapid but with the passage of time its decreased until it became constant due to attaining equilibrium after some time Because at the initial state large number of surface sites are available but with the passage of time remaining sites are difficult to occupy. The adsorption was carried out with mg/mL MO solution, 0.068 g/mL for 5-60 minutes. (Fig -4 a,b,c) present work study confirms that rate of uptake of Methyl orange onto MALP leave at different temperatures and time were rapid but with the passage of time it decreased until it became constant which indicates that equilibrium will attained. The effect of pH on the adsorption capacity of MALP were studied in the pH range 2, to 4.5, with 50/mL dye solution, having adsorbent dose 0.068g/mL at room temperature. Fig -4d) it is clear that the qe value initially increased form 0.017to 0.046 with the increase in pH and then decreased 0.0046 to 0.0033 in the pH range of 3-4.

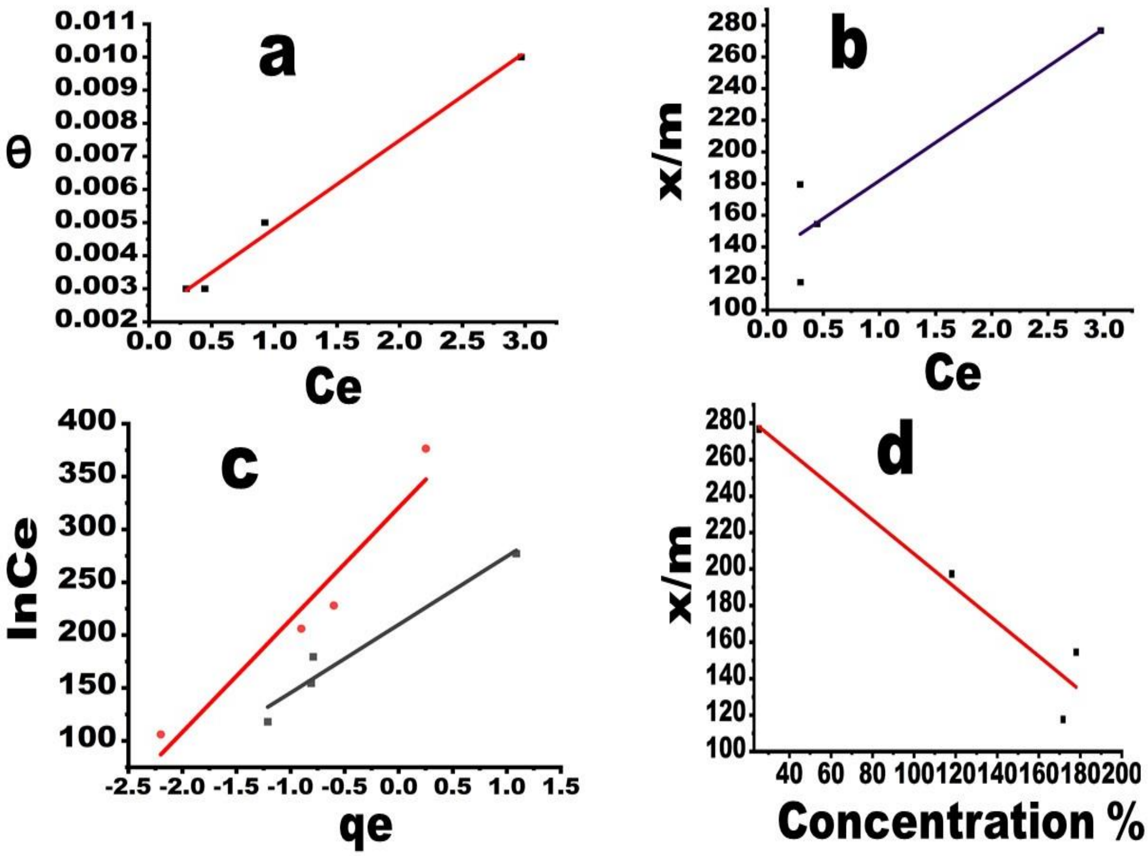

Fig. 2: a) Linearized Langmuir, b) Freundlich, c) Temkin, and d) BET adsorption models with modified purple Knight leaves powder =0.068g.

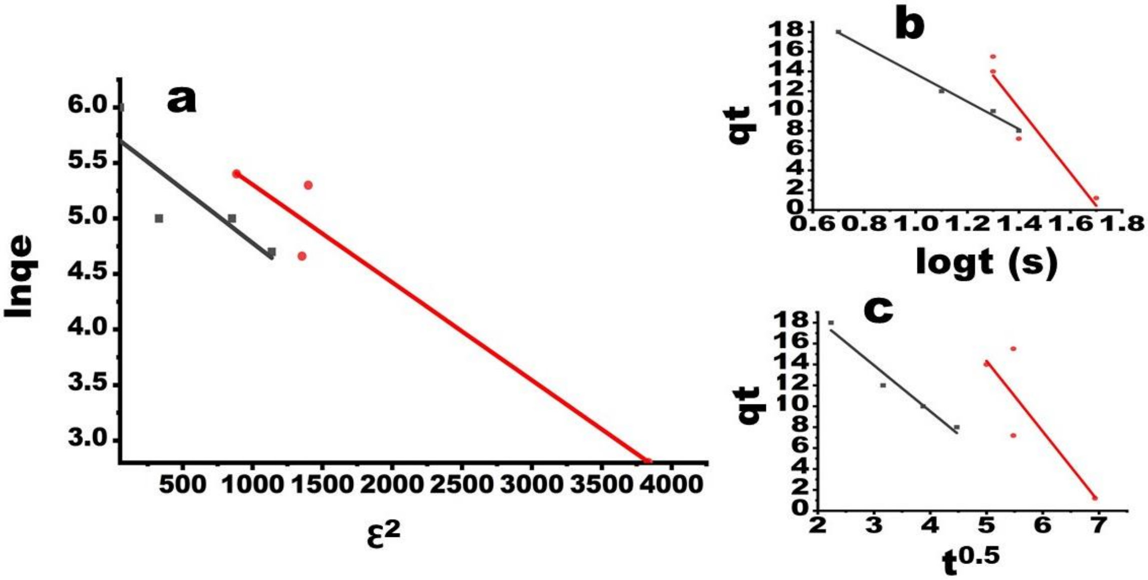

Fig. 3: a) Linearized D-R model, b) Elovich plot, and c) Intraparticle diffusion model utilizing 0.0068g modified purple Knight leaves powder.

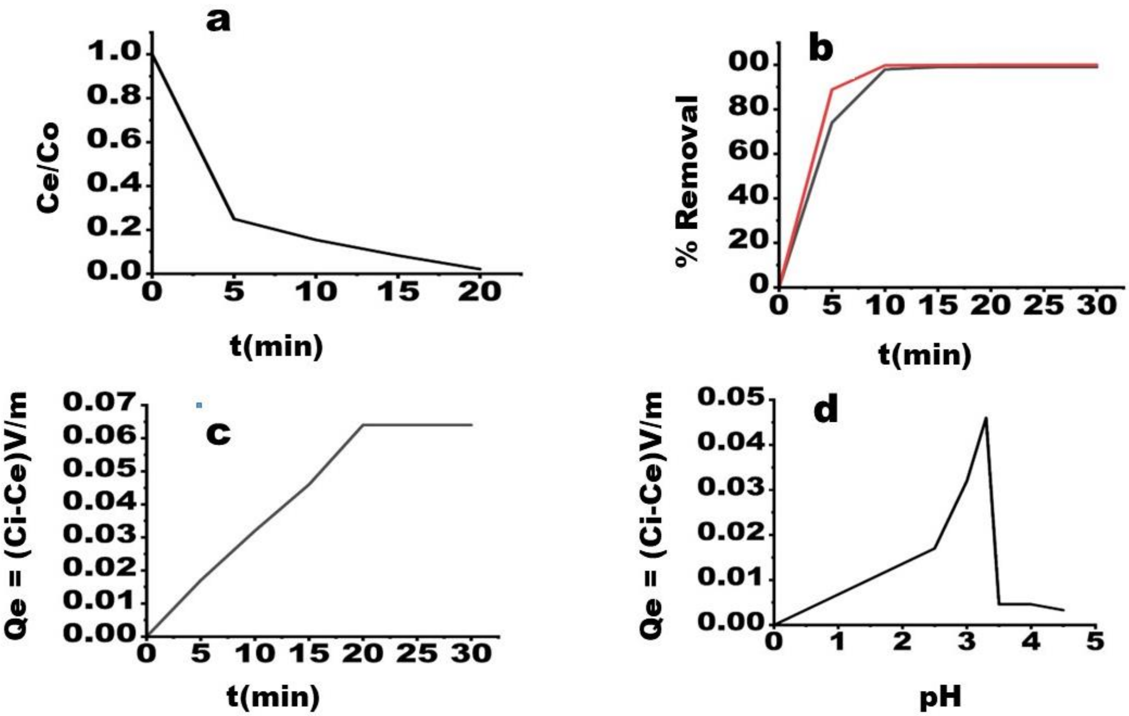

Fig 4: a) Plot of relative concentration of adsorbed Methyl Orange versus reaction time, b) Plot of percent removal of Methyl Orange versus time at 26oC and 60oC, c) Plot of quantity of Methyl Orange adsorbed onto modified Purple Knight leaves powder.

Kinetic Study of Batch Adsorption Process

Appropriate kinetics models were used to define the interactions between adsorbate and adsorbent. In order to examine the conceivable mechanism of the adsorption [44] existing literature, supports the use of non-linear / linear straight line calculations to determine the kinetic model, listed in table-3 [45, 46]. The generalized linear Elovich model is written as qt = 1/βln (αβ) + 1/βln t where α (initial adsorption rate), β (Adsorption constant) are determined from the slope and intercept respectively. According to the literature study, this model fits when the R^2 values range from 0.953 to 0.995[69]. (Fig - 3b), current study alpha and beta values calculated from slop and intercept of straight-line plot qt vs t.

The values of R^2, α, and β constants in Table -4 confirm that this model fit very well as temperature increased. The intra particle diffusion model is used to illustrate the mechanism of diffusion. According to this model the linear plot indicates the uptake process was controlled by intraparticle diffusion. The intraparticle rate diffusion constant Kip (g/mLmin$^{0.5}$) can be determined from the slope and Cip (g/mL) from the intercept of the plot of qt(mg/mL) versus $t^{0.5}$, according to the equation (Kip = to qt/$t^{0.5}$ + Cip) . The straight line obtained in this study is shown in Fig -3c at the moment. Kip, R^2, Cip, values indicate that intraparticle diffusion controls the adsorption process (table-4). Furthermore, the linear plot shows that the adsorption process is controlled by two or more steps, with the slowest rate determining step determining the kinetics of the reaction.

Table-3: Illustration of the kinetic models used in the batch adsorption study.

Kinetic Models	Linear Equations	Plot	References
Pseudo-first order PFO	$\ln(qe - qt) = lnqe - K1t/qt$	ln(q_e-q_t)vst1/q_t vs t	[47,48] [49]
Pseudo-Second order PSO	$qe = \frac{1}{k2qe2} + \frac{1}{qe}$		
Elovich	$qt = \frac{1}{\beta ln}(\alpha\beta) + \frac{1}{\beta lnt}$	q_t vs t	[50]
Intraparticle Diffusion IPD	Kip = qt/$t^{0.5}$ + Cip	q_t vs t0.5	[51]

Temperature effect and Thermodynamic Study

The temperature and the amount of adsorbed at equilibrium were investigated. (Fig-5) A plot was drawn between ln(qe/Ce) and 1/T(K^{1-}) to investigate the temperature effect and thermodynamic parameters using four different solutions of Methyl orange (0.0327g/20mL,0.0327/30mL, 0.0327g/40mL, 0.327gL/50mL) in the presence of 0.0068 grams of modified leave powder.

Table-4: Demonstrates the values of the Langmuir, Freundlich, Temkin, Dubbin Radusshkevich, BET, Elovich, Intraparticle diffusion, and Thermodynamic parameters.

T	Langmuir			Freundlich			Temkin	
K	qm mg/g	R_L	R^2	1/n	R^2	KF L/g	KT	R2 g/mLmg)$^{1/n}$
99	42.621	1.00	0.9918	0.007566	0.8617	48.022	320.65	0.987
333						209.96	0.977	

T	D- R-Model			BET-Model	Elovich		
K	K_D mol²/KJ²	Q_D g/mL	R^2	R^2	R^2	α	β
299	$-0.9x10^{-3}$	5.7513	0.7074	0.9315	0.8925	-32.907	56.367
333	$-0.1x10^{-1}$	6.186	0.947		0.9938	-13.913	27.652

T	Intraparticle Diffusion			Thermodynamic Parameters Kj/mol		
K	Cip g/mL	Kip g/mLmin$^{0.5}$	R^2	ΔH°	ΔS°	ΔG°
299	-4.3968	27.106	0.959	-4144	18.177	-9.578
333	58.0721	0.9974	0.9999	-13667	416.1	-152.23

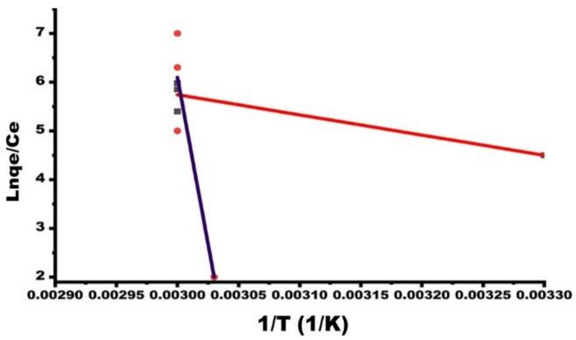

Fig. 5: Plot of ln(qe/Ce) vs 1/T (K1-) for methyl orange adsorption by modified purple Knight leaves powder (0.068g) at 26 and 60 oC utilizing various concentrations.

The intercept and slopes of the plot were used to calculate the values of ΔS° and ΔH°. At two different temperatures, the values of these two parameters were calculated using the equation ΔG = ΔH -TΔS. According to the literature review, the positive value of S° and H° confirms that the adsorption of dye by the adsorbent used in this is endothermic [52]. Literature study also reveals that If the value Ga_{ds} is ≤ -20Kj/mole and ≥ - 40Kj/mole, the process is governed by physical (via weak interaction) and chemical (via orbital interaction) The current work's negative value of ΔG (Table -4) indicates that adsorption occurs spontaneously and governed by orbital interaction. Furthermore, the present results show that from 26 to 60°C, the negative Go value confirmed physical adsorption, but as the temperature increased, chemisorption occurred, increasing the spontaneity of the methyl orange adsorption onto the modified purple Knight leave powder.

Conclusion

Purple knight Leaves powder was chemically modified and characterized in terms of functional group, and electronic spectroscopy in this current manuscript. The prepared adsorbent was used for the adsorption of aqueous methyl orange dye solution. The effects of factors, adsorption efficiency, and thermodynamic parameters were investigated. It was discovered that the optimal conditions for methyl orange adsorption onto modified leaves are concentration, pH, and temperature. Furthermore, the intraparticle diffusion model confirms that adsorption took place in stages. The Langmuir, Freundlich, Temkin, Brunauer-Emmett-Teller (BET)and Dubinin –Radusshkevich (D-R) models performed well in analyzing equilibrium data, while thermodynamic parameters confirmed that adsorption is an endothermic process. The increased adsorption capacities discovered in this study confirm that the modified leave powder, as a low-cost or no-cost biological material, will be of great interest in the purification of water and waste water.

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