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Eucalyptus bark powder as an effective adsorbent: Evaluation of adsorptive characteristics for various dyes

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ABSTRACT

Dyes are usually present in trace quantities in the treated effluents of many industries. This study investigates the potential use of Eucalyptus bark powder (EBP) as an adsorbent for adsorption of industrially important dyes namely malachite green, indigo carmine and methylene blue from wastewater. The operating variables studied are initial dye concentration, pH, temperature and contact time. It was noted that adsorption of all the dyes on Eucalyptus bark powder increases with an increase in pH and temperature. The equilibrium data are fitted to Langmuir in comparison to Freundlich isotherm equations. From these results adsorption efficiency, energy, capacity, intensity and dimensionless separation factor are also calculated. Adsorption isotherm modeling shows that the interaction of the dyes with Eucalyptus bark powder surface is localized monolayer adsorption. The adsorption of all the three dyes followed the pseudo-second order rate kinetics, Bangham's equation was also used to further check the kinetic model. On the basis of kinetic studies, various rate and thermodynamic parameters such as Gibbs free energy, enthalpy and entropy were evaluated. Influence of temperature on the removal of dye from aqueous solution shows the feasibility of adsorption and its endothermic nature. The results of the study shows that the Eucalyptus bark powder can be used as a potential adsorbent for dyes in wastewater/water.

Keywords: Waste treatment; Colorants; Biosorption; Biomass; Thermodynamics; Kinetics

1. Introduction

Discharge of wastewater/effluent containing organic pollutants into natural surface waters poses serious risk to aquatic organisms and human beings beside imparting odor to the receiving water. Dyes and pigments are widely used in textile, leather, paper, plastic, and other industries. The effluents of these industries are characterized by fluctuating pH with large load of suspended solids and COD [1]. Some dyes can cause allergic dermatitis, skin irritation, cancer and mutation in man. Recent estimates indicate that, approximately, 12% of synthetic textile dyes used each year is lost during manufacture and processing operations. Most of the used dyes are stable to photodegradation, biodegradation and oxidizing agents [2]. Removal of dyes by conventional waste treatment method is difficult since they are stable to light oxidizing agents and are resistant to aerobic digestion [3]. It is well established that for waste water treatment adsorption is a much better process than any other techniques like flocculation, froth flotation because of its economic behavior in terms of cost effectiveness [4,5]. Adsorption techniques are recommended because it removes toxic chemical without disturbing the quality of water. Recovery of toxic substances

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form the wastewater is an added advantage. Recognizing the high cost of activated carbon, many investigators have studied the feasibility of cheap, commercially available materials as its possible replacement. A number of low cost, easily available materials are being studied for the removal of different dyes from aqueous solutions at different operating conditions (Table 1), [6–22]. This laboratory tested the adsorbing ability of Eucalyptus bark powder and explored its use as potential biosorbents for removal of the hazardous dyes. For any sorbent to be feasible, it must have good adsorption capacity with regeneration ability. Eucalyptus bark powder has been so far used for removal of heavy metals i.e., Chromium [23], Mercury [24] and many other hazardous dyes and has given a good results. The dyes selected in this paper are Malachite green, Indigo carmine and Methylene blue. Malachite green belongs to the tri-phenyle methane group, it is used all over the world for dying wool, silk, cotton, leather etc. In the aquaculture and animal husbandry it also act as an antifungal and ectoparaside since 1936. It also controls diseases caused by helminthes on wide variety of fish. It has been reported to cause carcinogenesis, mutagenesis, chromosomal fractures, teratogenecity and respiratory toxicity [25–27]. The available toxicology information reveals that in the tissues of fish and mice, malachite green acts as a tumor promoter [28]. Thus Malachite green alarms the health hazards against human beings [29]. The second kind of dye is indigo carmine which is considered a highly toxic indigoid class of dye, its touch can cause skin and eye irritations to human being. It can also cause permanent injury to cornea and conjunctiva. The consumption of the dye Methylene blue can also prove fatal, as it is carcinogenic in nature and can lead to acute toxicity. The present study is aimed towards environmentally compatible adsorbent for removal of these dyes from wastewater. The present investigation also deals with the preparation of Eucalyptus bark powder which is a waste/byproduct in agricultural industry. The developed Eucalyptus bark powder is utilized for the remediation of malachite green, indigo carmine and methylene blue from water/wastewater.

2. Materials and methods

2.1. Materials

2.1.1. Preparation of adsorbate

All reagents and chemicals used in the study were of AR grade. Stock solutions of the test reagent were made

Table 1
Some low cost materials studied for dye(s) removal from aqueous solutions.

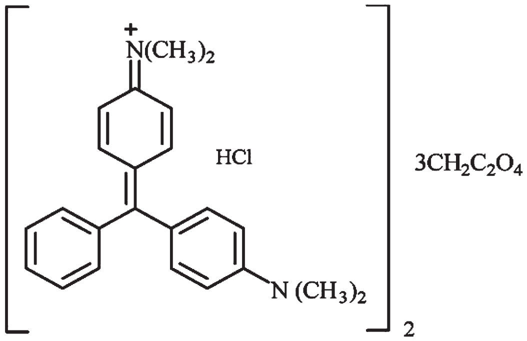
Adsorbents	Dye	References
Removal of Malachite green		
1. Silk cotton hull, coconut tree sawdust	Malachite green	[6]
2. Parthenium hysterophorus	Malachite green	[7]
3. Rice husk	Malachite green	[8]
4. Indian Rosewood	Malachite green	[9]
5. Prosopis cineraria	Malachite green	[11]
6. De-oiled soya	Malachite green	[10]
7. Hen feathers	Malachite green	[12]
8. Eucalyptus bark	Malachite green	This study powder
Removal of Indigo carmine		
1. Bottom ash	Indigo carmine	[14]
2. De-oiled soya	Indigo carmine	[14]
3. Rice husk ash	Indigo carmine	[13]
4. Eucalyptus bark	Indigo carmine	This study powder
Removal of Methylene blue		
1. Bamboo dust, coconut shell, groundnut shell, rice husk	Methylene blue	[15]
2. Silk cotton hull, coconut tree sawdust, sago waste, maize cob	Methylene blue	[6]
3. Parthenium hysterophorus	Methylene blue	[7]
4. Coir pith	Methylene blue	[16]
5. Banana and orange peels	Methylene blue	[17]
6. Giant duckweed	Methylene blue	[18]
7. Rice husk	Methylene blue	[19]
8. Fuller's earth	Methylene blue	[20]
9. Neem leaf powder	Methylene blue	[21]
10. Mango seed kernal	Methylene blue	[22]
11. Eucalyptus bark	Methylene blue	This study powder

by dissolving the dye in doubly distilled water of appropriate pH. The pH of the test solution was adjusted by using reagent grade dilute sulphuric acid (0.1 N) and sodium hydroxide (0.1 N). Further solutions of different concentrations were made by using same stock solutions. The dyes selected for the studies, along with their structures are given below.

Malachite Green (C I No. 42000)

Chemical formula = $C_{50}H_{52}N_4O_8$, MW = 927.03, λ_{max} = 617 nm.

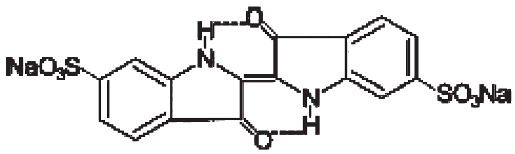
IUPAC name = *N*-[4-(4-dimethylaminophenyl)phenyl-methylene]-2,5-cyclohexadien-1-Ylidene-*N*-methyloxalate.



Indigo Carmine (C I No. 73015)

Chemical formula = $C_{16}H_8N_2O_8$ Na_2 S_2, MW = 466.36, λ_{max} = 610 nm.

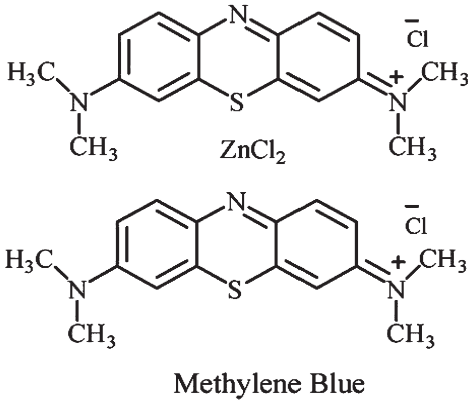
IUPAC name = 3.3′-dioxo- 2,2′-bis-indolyden-5.5′-disulfonic acid disodium salt.



Methylene Blue (C I No. 61734)

Chemical formula = $C_{16}H_{18}N_3SCl$, MW = 775.98, λ_{max} = 665 nm.

IUPAC name = 3,7 bis (Dimethylamine phenazathionium chloride tetramethylthionine Chloride).



Methylene Blue

2.1.2. Preparation of adsorbent

Eucalyptus bark was collected from local furniture shops. Collected bark was dried, crushed and washed thoroughly with deionized water to remove impurities. It was air dried in hot air oven for 3–4 hrs at a temperature about 101–105°C for 24 hrs. These dried barks were then grinded in a local mixer grinder to make powder out of it. The powder was then sieved through a 150–220 mesh size for adsorption studies. Finally, the product was stored in a vacuum desiccators until required. The developed powder is designated as EBP (Eucalyptus bark powder). The powder having 150–220 mesh size was used in both the sorption and kinetic studies unless stated. Various parameters for Eucalyptus bark powder are summarized in (Table 2).

2.1.3. I.R. Analysis of the adsorbent

FT-IR band assignment indicated the presence of carbonyl, carboxyl, lactones, olefinic and aromatic structures. The 1800–1540 cm^{-1} is associated with C═O stretching mode in carbonyls, carboxylic acid and lactones and C═C bonds in olefinic and aromatic structures whereas the 1440–1000 cm^{-1} band was assigned to the C—O and O—H bending modes. The assignment of a specific wave number to a given functional group was not possible because the absorption bands of various functional groups overlap and shift, depending on their molecular structure and environment.

2.2. Equipments

The pH measurement was made by using a pH meter (model 744, Metrohm). Absorbance measurements were made on UV–visible spectrophotometer model GBC Cintra 40. The spectrophotometer response time was 0.1 s and the instrument had a resolution of 0.1 nm. Absorbance values were recorded at the wavelength for maximum absorbance i.e. 617 nm, 610 nm and 665 nm as mentioned above. The concentration of respective compound was measured with a 1-cm path-length cell, with

Table 2
Characteristics of Eucalyptus bark powder.

Parameters	Values
Ash content (%)	13.09%
Bulk density(mg/m^3)	0.582
pH_{ZPC}	6.6
Volatile matter (%)	86.91%
C (%)	39.81
H (%)	4.37
N (%)	0.33

an accuracy of +0.004. Scanning electron microscopy (SEM) measurement of Eucalyptus bark powder was made using model (SC 7640,U.K) (Fig. 1). SEM was used to investigate the surface topography of the Eucalyptus bark powder. Sample was set in epoxy and were placed in the sample chamber and evacuated to high vacuum. The sample is bombarded with a finely focused electron beam. A three-dimensional topographic image (SEM-micrographs) is formed by collecting the secondary electrons generated by the primary beam. Surface area of the Eucalyptus bark powder was determined using methylene blue method [30].

2.3. Sorption procedure

Sorption studies were performed by the batch technique to obtain rate and equilibrium data. The batch technique was selected because of its simplicity. Batch sorption studies were performed at different temperatures, concentrations and adsorbent doses to obtain equilibrium isotherms for the treatment of malachite green, indigo carmine and methylene blue bearing wastewater. For isotherm studies, a series of 100 ml conical flasks were employed. Each conical flask was filled with 50 ml of each dye (malachite green, indigo carmine and methylene blue) solution of varying concentrations (10^{-6} M to 10^{-4} M) separately and adjusted to the desired pH and temperature. A known amount of adsorbent was added to each conical flasks, and the flasks were agitated intermittently for the desired period of time. The concentration range was chosen on the basis of a good deal of preliminary investigations, which demonstrated that equilibrium was established within 150–180 min (Fig. 2). Equilibration for longer time, that is between 190–420 min, gave practically the same uptake results. Therefore, a contact period of 150 min was selected for malachite green, 180 min for methylene blue and 120 min for indigo carmine. After this the solution was filtered and analyzed for the concentration of malachite green, indigo carmine and methylene blue remaining in the solution by using spectrophotometer at the corresponding λ_{max}. The effect of pH was observed by studying the adsorption of malachite green, indigo carmine and methylene blue over a broad pH range of 2–8. The sorption studies were also carried out at different temperatures i.e., 283, 298, 313 K to delineate the effect of temperature and to evaluate the sorption thermodynamic parameters. Adsorption of malachite green, indigo carmine and methylene blue was also studied at different doses and concentrations of adsorbents. The concentration of dyes retained in the adsorbent phase were calculated by using Eq. (1)

$$q_e = (C_o - C_e)V/W \tag{1}$$

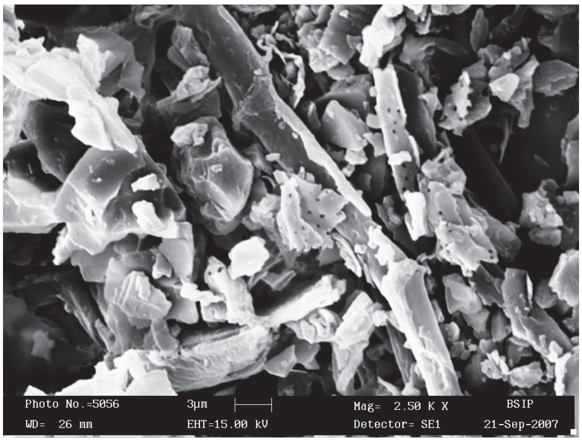


Fig. 1. Scanning electron micrograph (SEM) of Eucalyptus bark powder.

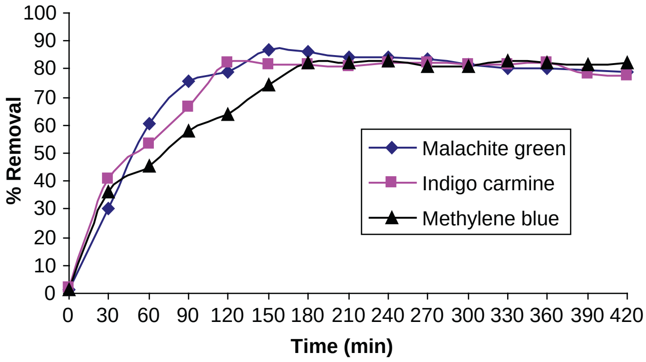


Fig. 2. Attainment of time equilibrium for malachite green, indigo carmine and methylene blue over Eucalyptus bark powder.

where q_e is the amount (mol.g^{-1}) of dye adsorbed, C_o and C_e are the initial and equilibrium concentrations (mg.l^{-1}) of dye in solution, V is the volume (l) of adsorbate and W is the weight (g) of the adsorbent.

3. Results and discussions

3.1. Adsorption kinetics study

Successful application of the adsorption technique demands development of cheap nontoxic, readily available adsorbents of known kinetic parameters and sorption characteristics. Foreknowledge of optimal conditions would enable a better design and modeling of the process. Thus the effect of some major parameters, viz., contact time, amount of adsorbent and concentration of adsorbate were studied using the batch technique. The extent of adsorption of all the three dyes are found to increase with temperature. The rate of removal of all the three dyes increasing along with the increase temperature indicates the endothermic nature of the process resembling with the results of thermodynamic analysis.

The adsorption rate data for the studied adsorbates onto the adsorbents were analyzed using two kinetic models viz., pseudo-first order equation and pseudo-second order equation were tested. pseudo first-order Lagergren equation [31].

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t \quad (2)$$

where q_e and q_t are the amounts of dye adsorbed at equilibrium at time t (mol.g^{-1}), respectively, and k_1 is the rate constant of pseudo first-order sorption (l.min^{-1}), pseudo second-order equation [32] is expressed as follows:

$$t/q_t = (1/k_2 q_e^2 t + 1/q_e)t \quad (3)$$

where q_e is the amount of dyes sorbed at equilibrium (mol.g^{-1}), k_2 is the equilibrium rate constant of pseudo second-order sorption Both the models were studied at different temperatures to find out the effect of temperatures on rate equation parameters. It was observed that pseudo-first order constant (k_1) as well as pseudo-second order equation parameter (k_2, v_0 and q_e) generally increase with increase in temperature. Variation of half life (t 50) with initial adsorbate concentration validates the adsorption reaction to be of the second-order (Fig. 3) rather than first order one. The q_e values were calculated using the pseudo-first-order and pseudo-second-order rate equation (Table 3) and it was observed that the theoretical q_e values calculated using the second-order-rate-equation agrees more accurately with the second-order-equation in comparison to pseudo-first–order equation.

This suggests that each dye adsorption system using Eucalyptus bark powder follows the pseudo second-order kinetic which provides a better correlation of data.

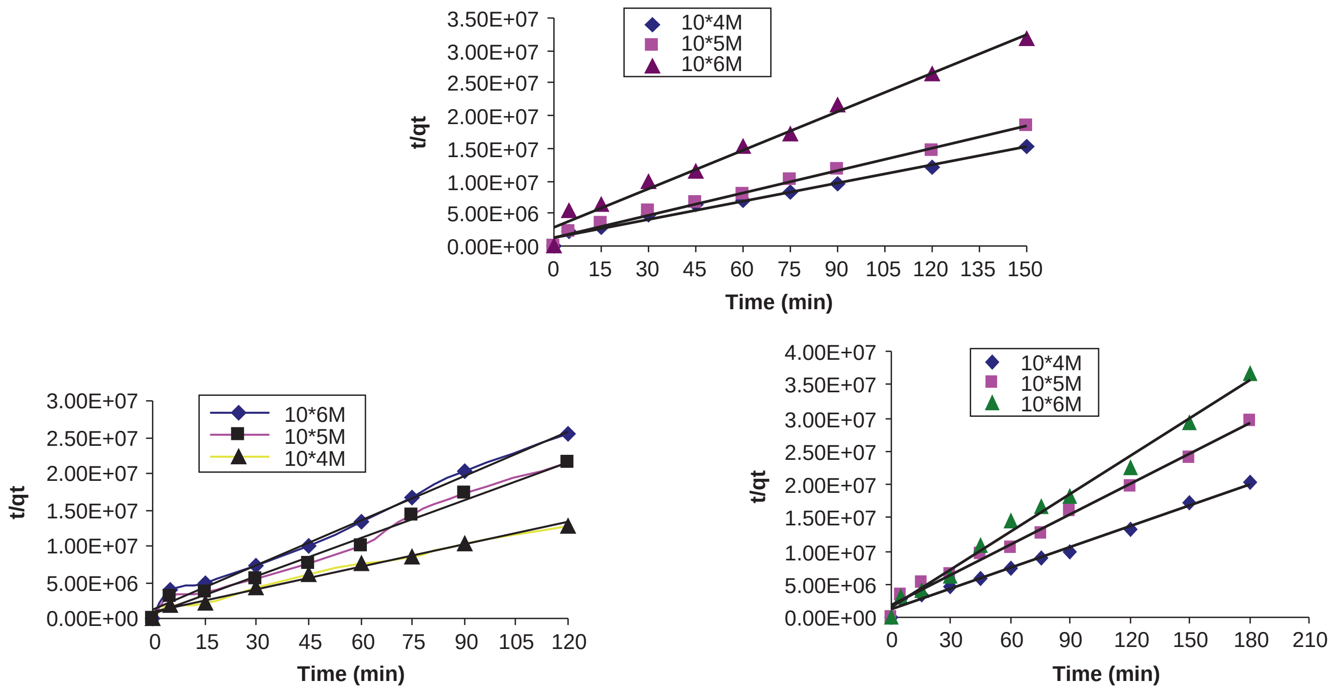


Fig. 3. (a,b,c) Pseudo-second order reaction (t/qt) for removal of (a) malachite green, (b) indigo carmine and (c) methylene blue at different initial concentrations over Eucalyptus bark powder.

Table 3
Comparison of kinetic parameters for the adsorption of malachite green, indigo carmine and methylene blue onto Eucalyptus bark powder at various temperatures.

Adsorbate	q_e,exp (× 10^4 mol.g^{-1})			q_e,cal-1 (× 10^4 mol.g^{-1})			q_e,cal-2 (× 10^4 mol.g^{-1})		
	10°C	25°C	40°C	10°C	25°C	40°C	10°C	25°C	40°C
Malachite green	2.91	3.05	3.14	2.61	2.78	2.89	2.95	3.16	3.17
Indigo carmine	2.15	3.36	3.52	1.68	2.29	1.41	2.20	3.33	3.51
Methylene blue	1.84	1.96	2.05	2.14	2.69	2.63	1.95	2.02	2.11

3.1.1. Effect of the amount of adsorbent and the initial concentration of the adsorbate

To investigate the effect of adsorbent mass on amount of adsorption, a series of experiments were carried out keeping the agitation time constant and varying both the amount of adsorbent and the adsorbate concentration at constant temperature. The percentage of dye removal increased from 2.81% to 81% for malachite green, 3.5% to 90% for indigo carmine and 3% to 82% for methylene blue. The results as a whole indicate two distinct trends: the amount adsorbed, q_e (mol.g^{-1}), increased with an increase in the dye concentration and decreased with an increase in the amount of the adsorbent. The latter trend may be due to the effect of adsorbent mass on porosity of the adsorbent suspension. In general, the trends might have been influenced by changes in a number of physical properties of the solid-liquid suspensions including their viscosity.

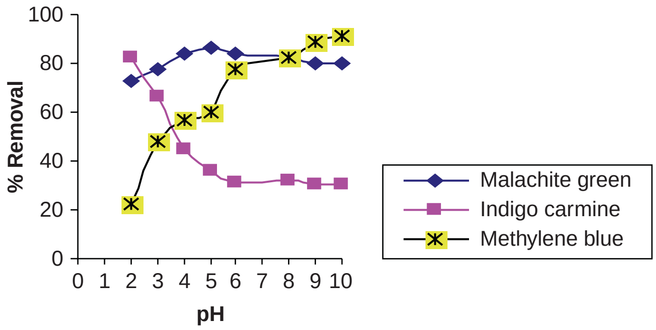


Fig. 4. Plot of pH vs. % removal of malachite green, indigo carmine and methylene blue over Eucalyptus bark powder.

3.1.2. Temperature effect

The influence of effect of temperature on malachite green, Indigo carmine and methylene blue adsorption is shown in (Fig. 5). The effect of temperature on the adsorption rate was studied by carrying out a series of experiments at 10°C, 25°C and 40°C. The adsorption of malachite green increases from 51% to 93%, Indigo carmine increased from 45% to 90% and 47% to 89% for methylene blue respectively. This suggests that the adsorption process is endothermic in nature for all the three types of dyes. Increasing temperature may also produce a swelling effect within the internal structure of the bark powder enabling more dye molecules diffusion into Eucalyptus bark powder**,** this is due to the possibility of an increase in the porosity and in the total pore volume of the adsorbent with the increase of temperature. Further, it is also believed that the possibility of increase of the number of active sites for the adsorption with the increase of temperature. This may also be a result of an increase in the mobility of the dye molecule with the rise of temperature. [33].

3.2. Adsorption isotherm

Adsorption isotherms were determined for various dye-adsorbent systems. The distribution of dyes between the adsorbent and the dye solution at equilibrium is important in establishing the capacity of the adsorbent for the dye.The analysis and design of sorption process requires the relevant adsorption equilibria, which is the most important piece of information in understanding an adsorption process. Sorption equilibria provide fundamental physiochemical data for evaluating the applicability of sorption process as a unit operation. In surface adsorption studies, the relationship between

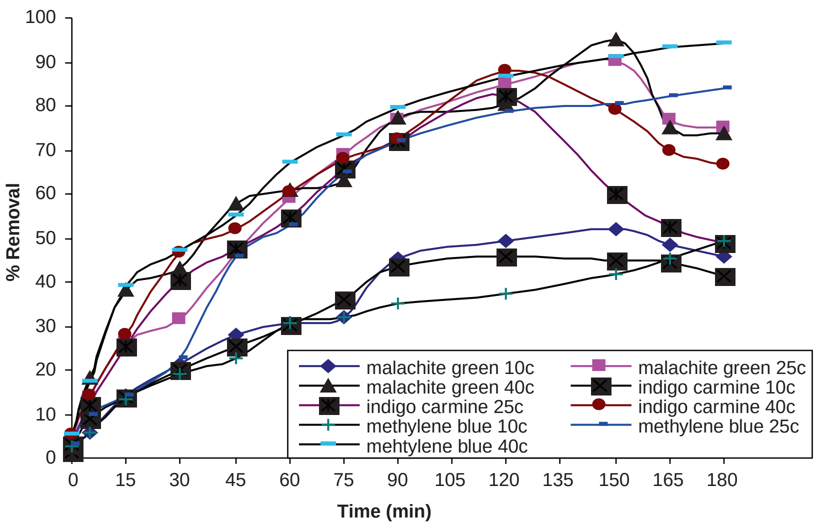


Fig. 5. Effect of temperature on the removal of malachite green, indigo carmine and methylene blue at optimum pH; adsorbent amount = 1.0 g/L; initial concentration = 1 × 10^{-5} M.

the solute concentration and the species uptake can be described in terms of either a Freundlich-type [34] and Langmuir-type [35] isotherm equations.

3.2.1. Langmuir isotherm

The Langmuir adsorption isotherm sheds no light on the mechanistic aspects of adsorption, it provides information on uptake capabilities and also reflects the usual equilibrium process behaviors. It assumed that the forces that are exerted by chemically unsaturated surface atoms do no extend further than the diameter of any sorbed molecule resulting the sorption to a mono-layer. The Langmuir equation can be written as Eq. 4.

$$C_e/q_e = (1/Q^0\,b) + (1/Q^0)\,C_e \tag{4}$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mol.g^{-1}), C_e is the equilibrium concentration of solute in the bulk solution (mol.$^{-1}$), Q^0 is the monolayer adsorption capacity (mol.g^{-1}) and b is the constant related to the free energy or net enthalpy of adsorption. The values of Q^0 and b were calculated from the slope and intercept of the linear plot, C_e/q_e versus C_e with R^2 ranging from 0.98–0.99 for malachite green, indigo carmine and methylene blue over Eucalyptus bark powder, respectively, gives an accurate description of Langmuir equation (Fig. 6). The fitting results are presented in Table 4. The adsorption capacities, Q^0 were found to be 4.58×10^4, 5.87×10^4 and 4.87×10^4

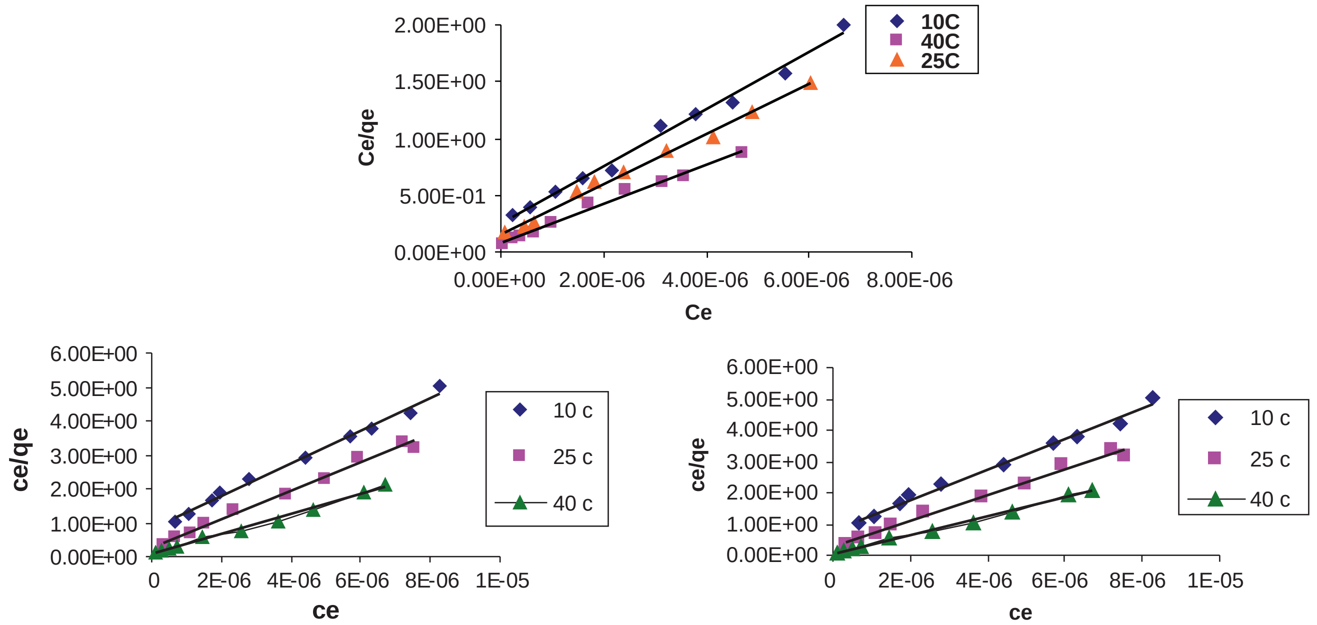


Fig. 6. (a,b,c) Langmuir isotherm constants for the adsorption of (a) malachite green, (b)indigo carmine and (c) methylene blue over Eucalyptus bark powder.

Table 4
Langmuir and freundlich isotherm constants for the adsorption of malachite green, indigo carmine and methylene blue over Eucalyptus bark powder.

Langmuir constants	10°C			25°C			40°C		
Adsorbate	Q^0 ($\times 10^4$ mol.g^{-1})	b ($\times 10^{-3}$ l.mol^{-1})	R^2	Q^0 ($\times 10^4$ mol.g^{-1})	b ($\times 10^{-3}$ l.mol^{-1})	R^2	Q^0 ($\times 10^4$ mol.g^{-1})	b ($\times 10^{-3}$ l.mol^{-1})	R^2
Malachite green	3.22	4.13	0.98	3.66	5.47	0.98	4.58	5.55	0.98
Indigo carmine	4.17	2.85	0.99	5.65	4.62	0.99	5.87	5.01	0.99
Methylene blue	3.89	3.14	0.98	4.44	4.22	0.98	4.87	4.96	0.96
Freundlich constants	K_F($\times 10^3$ mol.g^{-1})			1/n			R^2		
Adsorbate	10°	25°	40°	10°	25°	40°	10°	25°	40°
Malachite green	3.67	3.98	2.69	0.15	0.18	0.14	0.74	0.69	0.92
Indigo carmine	12.41	21.23	19.91	0.55	0.67	0.76	0.92	0.89	0.90
Methylene blue	2.14	1.54	1.33	0.18	0.41	0.65	0.89	0.89	0.89

for malachite green, indigo carmine and methylene blue over Eucalyptus bark powder. The essential characteristics of Langmuir equation can be expressed in terms of a dimensionless separation factor R_L [36].

$$R_L = 1/1 + b\,C_0 \tag{5}$$

where C_0 is the initial dye concentration (mol.l^{-1}) and R_L values indicate the shape of the isotherm. The R_L values were found between 0 and 1 for all the three dyes confirm the on going adsorption process are favorable (fig not shown). The adsorption isotherm assumes that intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer of adsorbate at the outer surface of the adsorbent. It also assumes that adsorption takes place at specific sites within the adsorbent. It is believed that once the adsorbate occupies a site, no further adsorption take place at that site.

3.2.2. Freundlich isotherm

The Freundlich model does not indicate a finite uptake capacity of the sorbent and thus can only reasonably be applied in the low to intermediate concentration range. The Freundlich equation can be written as Eq. 6.

$$\log q_e = \log K_F + 1/n \log C_e. \tag{6}$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mol.g^{-1}), C_e is the equilibrium concentration of solute in the bulk solution (mol.l^{-1}), K_F is the constant indicative of the relative adsorption capacity of the adsorbent (mol.g^{-1}) and $1/n$ is a constant indicative of the intensity of the adsorption. The magnitude of the exponent n gives an indication on the favorability of adsorption. It is generally stated values of n in the range 2–10 represent good, 1-2 moderately difficult, and less than 1 poor adsorption characteristics [37]. Freundlich isotherms for the adsorption of malachite green, Indigo carmine and methylene blue on Eucalyptus bark powder at different temperatures are presented in (Fig. 7). The linear plots of log q_e versus log C_e for Freundlich isotherms and C_e/q_e versus C_e for Langmuir isotherms shows that adsorption of malachite green, Indigo carmine and methylene blue fitted Langmuir model the slightly better than the Freundlich model.

3.2.3. Sorption thermodynamics

For designing sorption column or batch sorption systems, the designer should be able to understand the following: what changes can be expected to occur and how fast will they take place. The fastness of the reaction can be calculated from the knowledge of kinetic studies. But the change in reaction that can be expected during the process require the brief idea of thermodynamic parameters. The concept of thermodynamic assumes that in an

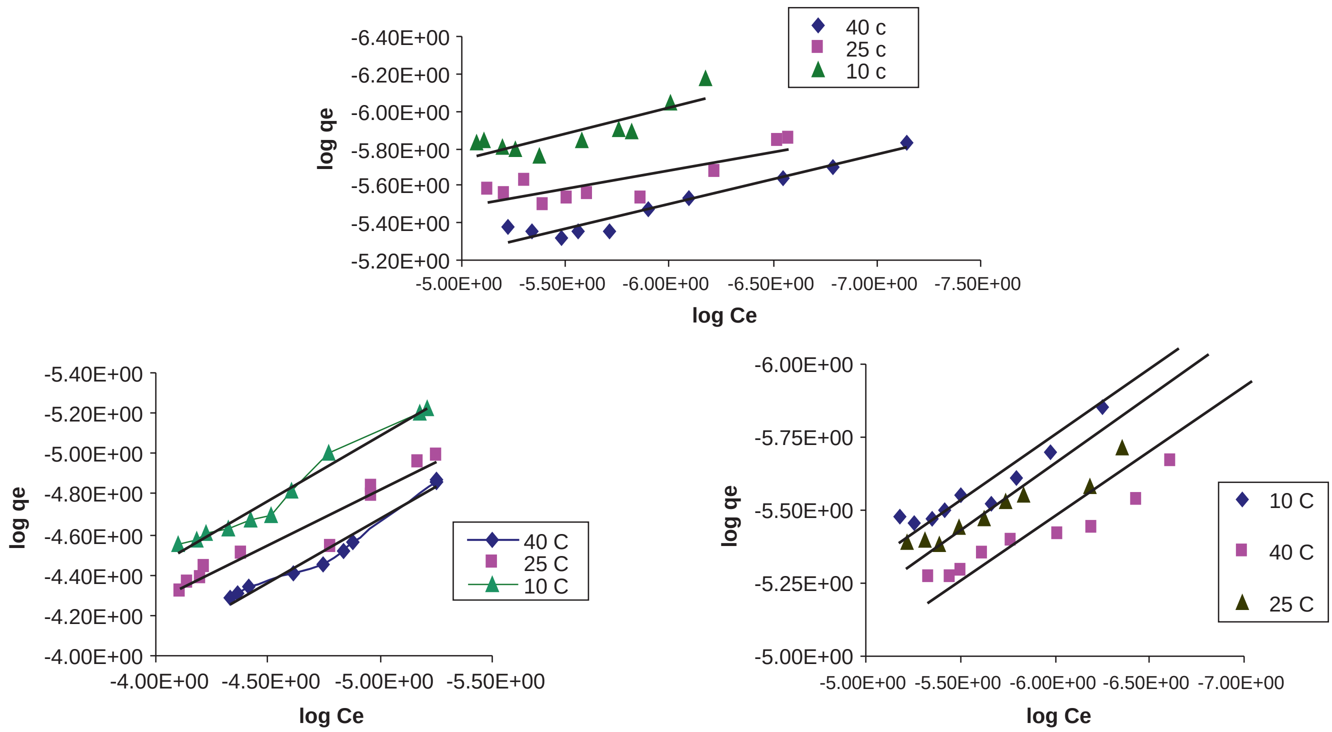


Fig. 7. (a,b,c) Freundlich isotherm constants for the adsorption of (a) malachite green, (b) indigo carmine and (c) methylene blue over Eucalyptus bark powder.

isolated system where energy cannot be gained or lost, the entropy change is the driving force. The thermodynamic parameters that must be considered to determine the process are standard enthalpy of sorption ($\mathbf{H}^0$), standard free energy change ($\mathbf{G}^0$) and standard entropy change ($\mathbf{S}^0$). The important thermodynamic function ΔH^0 is very useful whenever there is a differential change occurs in the system. Enthalpy is an additive property that is its value is additive. The negative value of ΔH^0 indicates the exothermic process and positive value indicates the endothermic process. The other important thermodynamical parameter is the change in entropy ΔS^0. The parameter ΔS^0 is used to identify the spontaneity in the sorption process.The value of ΔH^0 and ΔS^0 were computed using the equation as follows:

$$\Delta G^0 = -RT \ln k \tag{7}$$

$$\Delta H^0 = R\,(T_2\,T_1/T_2 - T_1) \ln K_2/K_1 \tag{8}$$

$$\Delta S^0 = \Delta H^0 - \Delta G^0/T \tag{9}$$

where k is the Langmuir constant same as b at different temperatures. The values obtained from thermodynamic analysis are given in Table 5. Positive values of ΔH^0 and ΔS^0 (for malachite green, Indigo carmine and methylene blue over Eucalyptus bark powder) indicate the endothermic nature of the process. The negative values of ΔG^0 indicate the feasibility and spontaneous nature of adsorption. The similar results were obtained by [14,21].

3.2.4. Effect of pH

The adsorption of dyes (malachite green, Indigo carmine and methylene blue) on Eucalyptus bark powder over a pH range of 2–10 were studied and shown in (Fig. 4).The adsorption of methylene blue, a basic dye increases with increasing pH. This can be explained on the basis of zeta potential of Eucalyptus bark powder and found to be 6.6. Thus it seems that for pH values above zeta potential of Eucalyptus bark powder, negative charge density on the surface increases. The charge developed in the acidic medium favour association of the anionic dyes due to which maximum adsorption of malachite green and indigo carmine was observed in this range i.e., (pH 5 for malachite green and pH 2 for indigo carmine). However, for pH values above the zeta potential of the adsorbent (Eucalyptus bark powder), as the adsorbent slowly becomes negatively charged, favors the adsorption of cationic dye. Also methylene blue dye molecules becomes protonated in the acid medium with deprotonation likely taking place at higher pH. Consequently, the positive charge density would be found more on the dye molecule at pH less than the zeta potential on adsorbent and this account for the higher uptake of dye onto negatively charged surface of adsorbent.

Table 5
Thermodynamic parameters of the adsorption.

	−ΔG			ΔH	ΔS
Adsorbate	10°C	25°C	40°C		
Malachite green	18.62	20.40	21.45	20.21	0.14
Indigo carmine	19.66	21.45	24.36	25.25	0.16
Methylene blue	21.58	15.28	26.25	18.05	0.15

−ΔG = (KJ/mol), ΔH = (KJ/mol), ΔS = (KJ/mol/k^{-1}).

3.2.5. Intra-particle diffusion study

An empirically found functional relationship, common to the adsorption process, is that uptake varies almost proportionally with $t^{1/2}$, the Weber–Morris plot [38], rather than with the contact time t. An intraparticle diffusion model of is shown as:

$$q_t = k_{int}\, t^{1/2} + C \tag{10}$$

where q_t is the amount of dye adsorbed (mol/g) at time t, C is the intercept.

According to Eq. 10 a plot of q_t versus $t^{1/2}$ should be a straight line with a slope k_{int} and intercept C when adsorption mechanism follows the inter- particle diffusion process. The values of intercept give an idea about the boundary layer thickness, i.e., the larger intercept, the greater is the boundary layer effect. k_{int} is the intra-particle diffusion rate constant (mol.g^{-1} min$^{1/2}$). The plot may present multilinearity, indicating that a few steps take place. (Fig. 8 a–c) represent the plot of mass of dye adsorbed per unit mass of adsorbent, q_t versus $t^{1/2}$ is presented for malachite green, Indigo carmine and methylene blue. The plots of q_t versus $t^{½}$ are found to be straight line with regression co-efficient ranging from (0.96–0.99) for malachite green, (0.98–0.99) for indigo carmine and (0.97–0.98) for methylene blue. The linearity of the plots demonstrated that intra-particle diffusion played a significant role [39] in the uptake of the dye by Eucalyptus bark powder. This also confirms that adsorption of the dye on the adsorbent was a multi-step process, involving adsorption on the external surface and diffusion into the interior. All the steps slow down as the system approaches equilibrium. Since the plot goes through the origin, thus it can be said that the intra-particle diffusion is the sole rate limiting step in this process.

3.3. Bangham's equation

Kinetic data can further be used to check by using Bangham's equation

$$\log \log (C_0/C_0 - q_t m) = \log (k_0 m/2.303\, V) + \log (t) \tag{11}$$

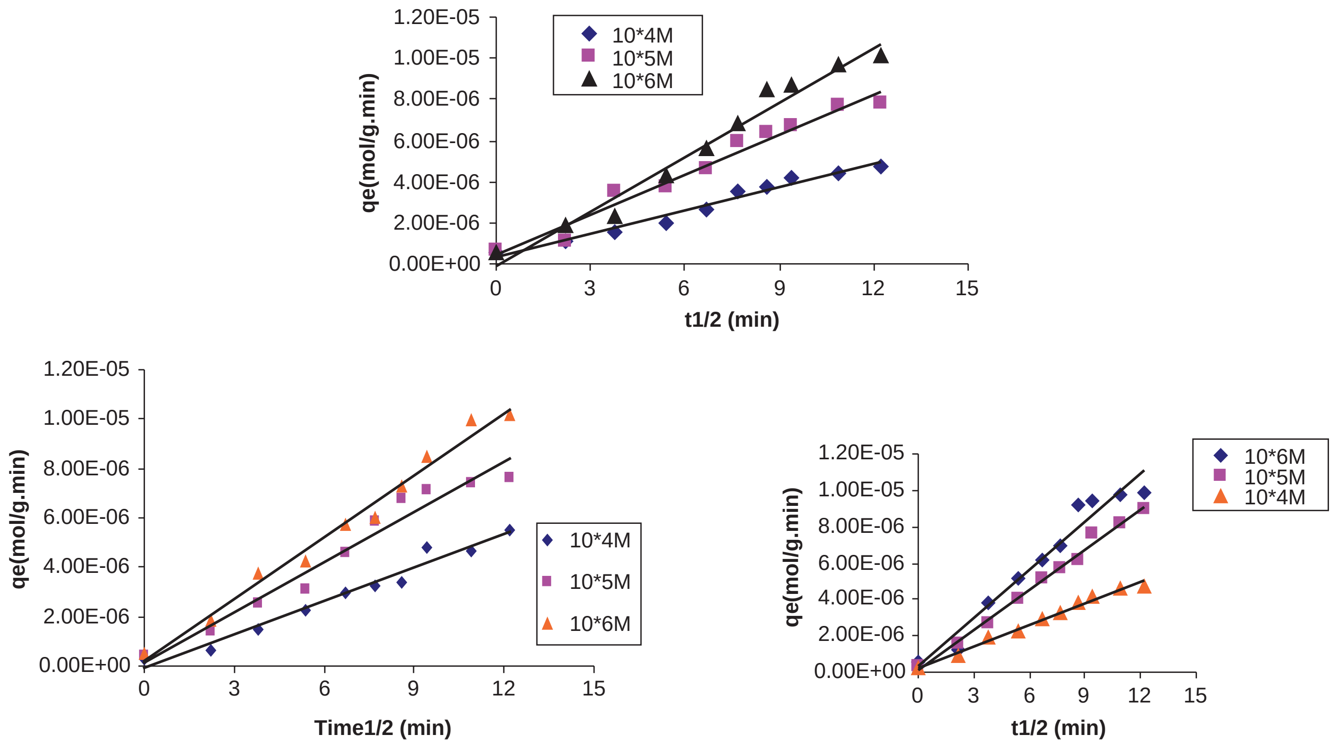


Fig. 8. (a,b,c) Intra particle diffusion for removal of (a) malachite green, (b) indigo carmine and (c) methylene blue over Eucalyptus bark powder.

Table 6
Bangham's constants for adsorption of malachite green, indigo carmine and methylene blue at three different adsorbate concentrations.

Adsorbates	2 g.l^{-1}			1 g.l^{-1}			0.5 g.l^{-1}		
	Kb (ml/g/l)	a	R^2	Kb (ml/g/l)	a	R^2	Kb (ml/g/l)	a	R^2
Malachite green	2.51	0.85	0.98	2.84	0.54	0.99	2.01	0.92	0.99
Indigo carmine	3.11	0.64	0.96	2.99	0.46	0.99	2.51	3.51	0.89
Methylene blue	2.62	0.46	0.97	2.88	0.54	0.96	2.14	0.61	0.95

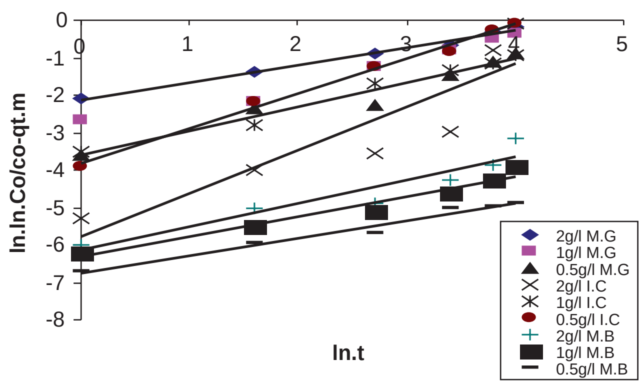


Fig. 9. Bangham's plot for removal of malachite green, indigo carmine and methylene blue over Eucalyptus bark powder, at different concentrations; optimum pH; Temperature = 25°C; dose = 1 g/l.

where C_0 is the initial concentration of adsorbate in solution (mg.l^{-1}), V is the volume of the solution (ml), m is the weight of adsorbent per liter of solution (g.l^{-1}) q_t is the amount of adsorbate retained at time t, and K_0 are constants. The values are summarized in Table 6. The logarithmic plot (Fig. 9), according to above equation yielded perfect linear curves for adsorption of malachite green, indigo carmine and methylene blue over Eucalyptus bark powder at three different adsorbate concentrations, showing that the diffusion of adsorbate into pores of the adsorbent is not the only rate controlling step [40].

4. Conclusion

The results of this work suggests that the recycling of an agricultural waste byproduct as adsorbent for the treatment of dyeing industry wastewater.

(i) Eucalyptus bark powder is a promising adsorbent for removal of dyes (Malachite green, Indigo carmine and Methylene blue) from water.
(ii) The experimental data produced perfect fit with the Langmuir isotherm. Suggest the monolayer coverage of the dyes onto Eucalyptus bark powder with adsorption capacity as 4.58×10^4 mol.g^{-1}, 5.87×10^4 mol.g^{-1} and 4.87×10^4 mol.g^{-1} for malachite green, indigo carmine and methylene blue respectively.
(iii) The kinetics of the adsorption of dyes, (Malachite green, Indigo carmine and Methylene blue) onto EBP to pseudo second order chemical reaction kinetics.
(iv) This pseudo second-order kinetics is further supported by Bangham's equation.
(v) The adsorption of all the three dyes increased with decrease in initial concentration of the dye molecules.
(vi) The rate of adsorption of (Malachite green, Indigo carmine and Methylene blue) onto increased with increasing temperature. Thus suggesting the reaction to be spontaneous and endothermic in nature.

Eucalyptus bark powder act as a good adsorbent for removal of colour from industrial and other effluents. However, as with all other bio-resources, the processes are likely to be very complicated and a detailed characterization of the surface will be necessary to develop more insight into the mode of action.

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Nomenclature

λ_{max} – wavelength for maximum absorbance
q_e – amount of dye adsorbed (mol.g^{-1})
C_o – the initial concentration of the solute in the bulk solution (mol.l^{-1})
C_e – the equilibrium concentration of the solute in the bulk solution (mol.l^{-1})
V – the volume of adsorbate (l)
W – the weight of the adsorbent (g)
Q^0 – the monolayer adsorption capacity (mol.g^{-1})
b – Langmuir constant related to the free energy of adsorption (l.mol^{-1})
K_F – Freundlich constant indicative of the relative adsorption capacity of the adsorbent (mol.g^{-1})
$1/n$ – Freundlich constant, indicative of the intensity of the adsorption.
k_1 – the first-order rate constant (min^{-1})
k_2 – the pseudo-second-order rate constant. (g.mol^{-1} min^{-1}),
v_0 – the initial sorption rate (mol.g^{-1}min^{-1})
k_i – the intra-particle diffusion rate constant (mol.g$^{-1.}$ min$^{-0.5}$).
ΔG – Gibbs free energy (kJ.mol^{-1})
ΔH – Enthalpy (kJ.mol^{-1})
ΔS – Entropy (kJ.mol^{-1}k^{-1})
R_L – the parameter to indicate the shape of isotherm
K_E – the Elovich equilibrium constant (l.mol^{-1})
q_m – the Elovich maximum adsorption capacity (mol.g^{-1})
r – coefficient of correlation
R^2 – the correlation coefficient
C_0 – the initial concentration of adsorbate in solution (mg.l^{-1})
V – the volume of the solution (ml)
m – the weight of adsorbent per liter of solution (g.l^{-1})
q_t – the amount of adsorbate retained
t – time (min)
K_b – Bangham's constant
a – Bangham's constant

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